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Ultraviolet spectra and ferroine reaction of bipyridines and pyridyl substituted s-triazines

Edward Bracy Buchanan Jr.

Iowa State University

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ULTRAVIOLET SPECTRA AND FERROINE REACTION
OF BIPYRIDINES AND PYRIDYL SUBSTITUTED
s-TRIAZINES

by

Edward Bracy Buchanan Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

Ames, Iowa

1959

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INTRODUCTION

Analytical chemists have made a great deal of use of the organic compounds of the bipyridine and tripyridine type for the determination of iron by colorimetric methods. In recent years considerable attention has been focused upon the nature of the bonding between iron(II) and these ligands in the hope that a better understanding of the structural and spacial configurations of the ligand would lead them to other more sensitive and specific reagents.

The work now to be described introduces a new series of compounds useful for the colorimetric determination of iron. This series, the pyridyl substituted s-triazines, contains the same active functional group through which bi- and tri-pyridine and the phenanthrolines as well, exert their action in forming chelate ring compounds with iron(II). This functional group, $-N=C-C=N-$, is present in monopyridyl-s-triazine because of the particular location of the 2-pyridyl group. Two such functional groups are present in 2,4-bis(2-pyridyl)-s-triazine and three in 2,4,6-tris(2-pyridyl)-s-triazine. The question then arises: does only one of these functional groups participate in union with iron(II), or do two or three? If the latter, then conceivably polymerization may occur. If the former, what is the nature of the iron derivative, its composition and stereochemical configuration?

The primary purpose of this work is an attempt to correlate the properties of the members of this new series with analogous members of the bi- and tripyridine systems and to determine if any of the compounds are suitable as analytical reagents.

The approach to the problem has been twofold. First, the combining ratio of the various triazines and iron(II) was determined. Second, a comparison of the ultraviolet absorption spectrum of both the free reagent and the iron(II) derivatives of the various pyridyl substituted s-triazines and the analogous bi- and tripyridines was made to determine the similarities between the electronic transitions taking place. It was hoped that such a comparison might reveal the spatial configuration of the ligand and at the same time give some clue as to the process by which the functional group becomes activated and thus capable of uniting with the ferrous ion.

Inasmuch as the ultraviolet and visible portions of the spectrum are produced by electronic transformations within the molecule and as these transformations often result from properties of the molecule as a whole rather than arising from a particular portion of the molecule, their interpretation is useful in the determination of the spatial configuration of the molecule. However, the interpretation of the spectrum

of molecules as complex as the polypyridyls must of necessity be empirical. Although certain success has been obtained with the more rigorous quantum-mechanical calculations using simple molecules, the number of parameters involved in the polypyridyl system is too great and the resultant problem too complex for an exact solution at this time. Therefore, it was necessary to return to a simpler analogous system for which the spectra had been already interpreted, and build up from this a series of reasonable postulates which would account for the spectra of the more complicated systems. To this end, the polyphenyl series was taken as the foundation, and a set of transitions postulated to account for the spectra of the progressively more complicated systems: the phenylpyridyls, the polypyridyls, and the pyridyl-s-triazines. This interpretation of the various spectra then made possible an assignment the spacial configurations of the ligands and their iron(II) derivatives.

HISTORICAL

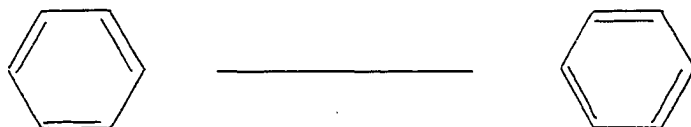
The Ultraviolet Absorption Spectra

In general three distinct types of absorption bands in the ultraviolet are discerned, each being caused by an electronic transformation of a different origin. These bands are differentiated by the magnitude of their molar absorptivity.

The designation of these various types of bands and their limits of molar absorptivity are (1):

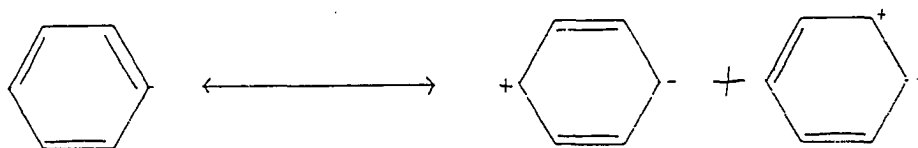
Designation	Molar absorptivity
R bands	100 or less
B bands	250 to 3000
K bands	10,000 or more

R (Radical) bands take their origin from electronic transformations within a particular radical. They are as indicated above very weak in intensity. B (Benzenoid) bands are thought to be due to a series of forbidden transformations of the type generally shown by the Kekule formula, thus:



Finally K (Konjugiert) bands are due to the electronic transformations which are transmitted through a conjugated chain of alternate double and single bonds; these are the most in-

tense of the absorption bands. When this conjugation is limited to a single benzene ring the designation is often changed to E and the band is referred to as an E band. Benzene exhibits a pair of E bands and a B band, and can therefore, be used to show the type of transformation producing each of the bands. The pair of E bands are the result of transformations of the type (2):



In 1940 Gillam and Hey (3) published the results of a rather complete study of the polyphenyls. They observed that the E band of benzene was replaced by a K band at approximately the same wavelength when two benzene nuclei were conjugated as in biphenyl. However, this change was accompanied by an enormous increase in the intensity of the absorption. The nature of the bond linking the two benzene nuclei has attracted a considerable amount of attention. Chemically it is generally considered to be a single bond; however, X-ray data show it to be considerably shorter than the usual 1.54 Å of the single carbon-carbon bond. It is generally assigned a value of 1.48 Å. This shorter value indicates that there is present a considerable amount of resonance interaction between the nuclei; the para quinoid structure is the one generally postulated. Such a structure accounts for the large increase

in the molar absorptivity of biphenyl over that of benzene.

Gillam and Hey also showed that when a third phenyl group is introduced, the resultant molecule has an absorption spectrum which falls into either one of two classes. If the benzene nuclei are attached so as to permit conjugation over the length of the molecule, both the molar absorptivity and the wavelength of the absorption maximum increase. However, if the attachment is meta to the other group then conjugation cannot take place and only the molar absorptivity of the compound increases, and the wavelength of the maximum of the absorption peak remains relatively constant. Conjugation over the length of the molecule can take place only in the para substituted compounds, whereas in the meta substituted compound this conjugation is limited to two rings. While no studies have been made on the ortho substituted triphenyl series it is believed that such an arrangement would lead only to a benzenoid band of low intensity, as the two attached phenyl groups would offer steric hinderance to a planar molecule. Figure 1 shows the two types of changes to be expected.

In 1941 Gillam, Hey and Lambert (4) published the spectra of various phenylpyridyls and bipyridyls. These spectra, 2-phenylpyridine, 3-phenylpyridine and 4-phenylpyridine, are recorded in Figure 2. The spectra of 2,2'-bipyridine and

Figure 1. Absorption spectra of polyphenyl compounds

Para system:

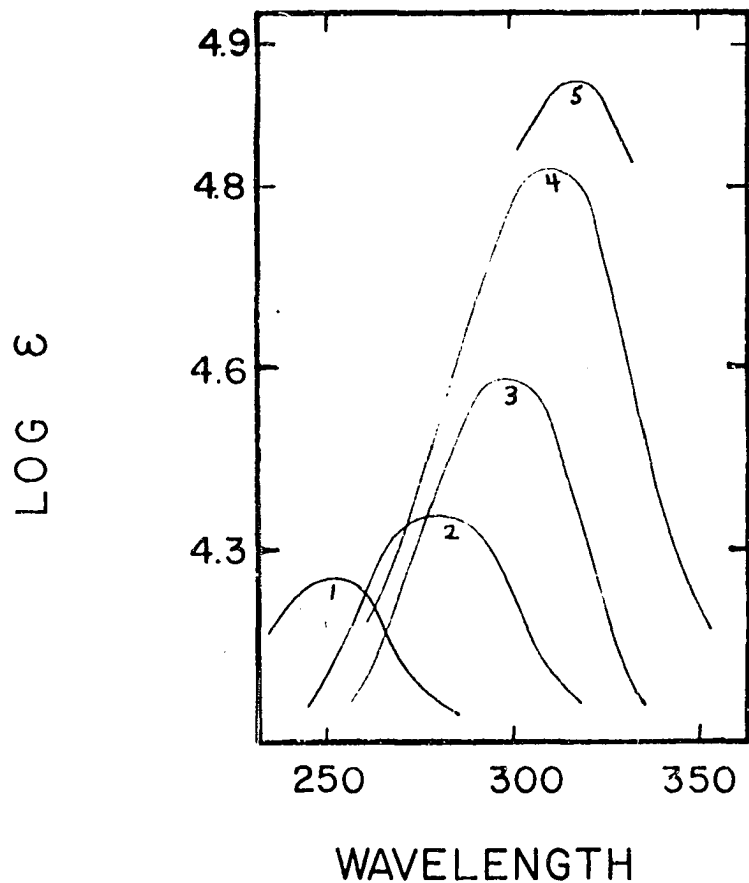
- 1 biphenyl
- 2 terphenyl
- 3 quatraphenyl
- 4 quinquiphenyl
- 5 sexiphenyl

Meta system:

- 1 biphenyl
- 2 terphenyl
- 3 noniphenyl
- 4 duodecipheryl
- 5 quindecipheryl

Taken from Gillam (5)

PARA SYSTEM



META SYSTEM

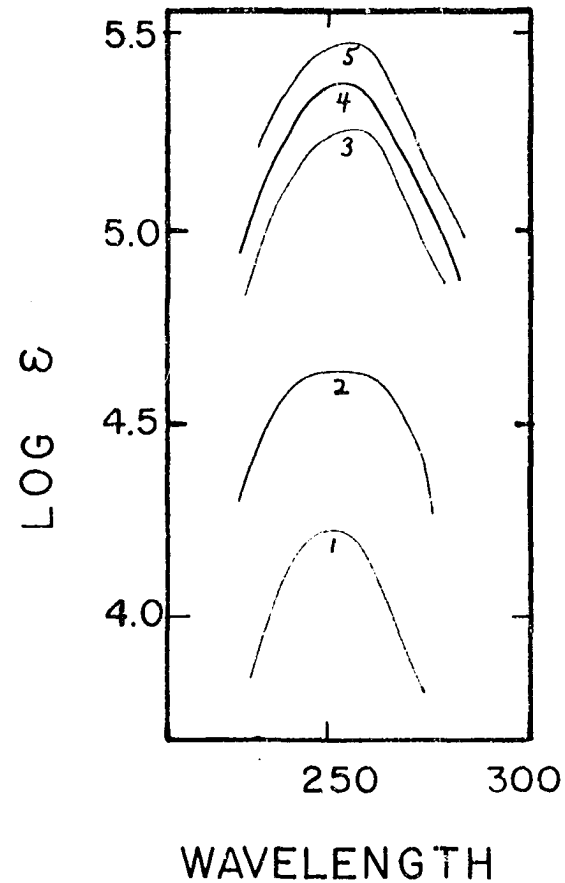


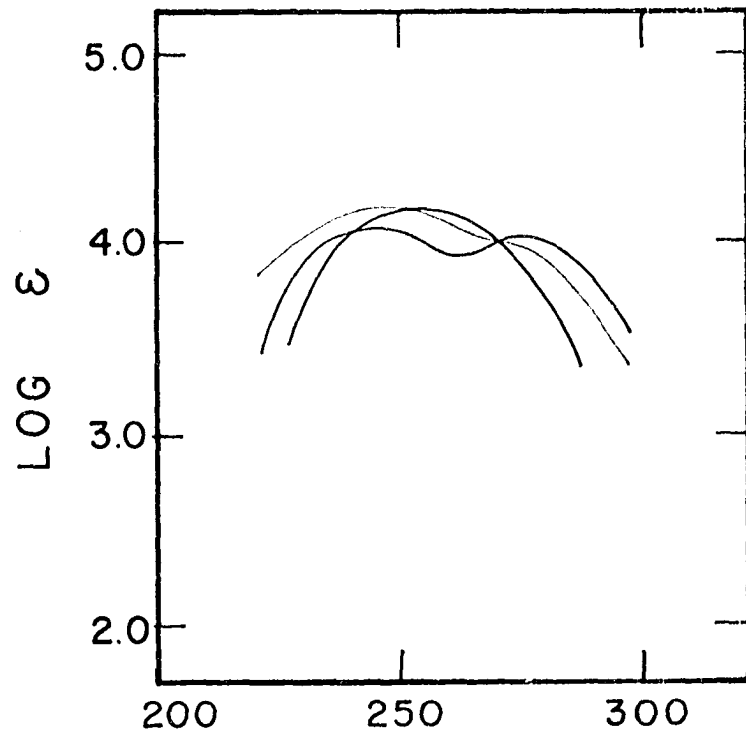
Figure 2. Absorption spectra of
phenylpyridines
2-phenylpyridine —
3-phenylpyridine —
4-phenylpyridine —

Taken from Friedel and
Orchin (6)

Figure 3. Absorption spectra of bi-
pyridine
2,2'-bipyridine —
3,3'-bipyridine —
4,4'-bipyridine —

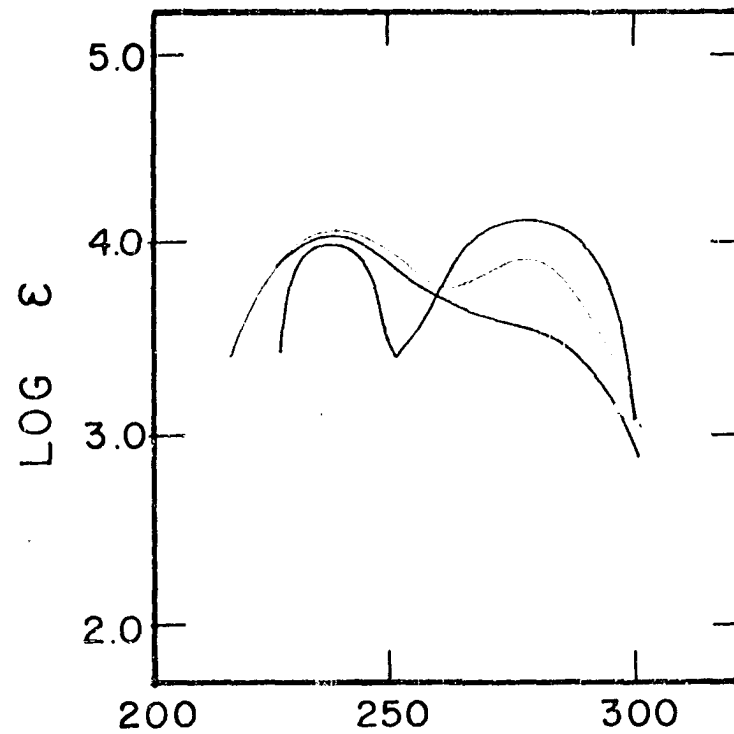
Taken from Friedel and
Orchin (6)

FIGURE 2



WAVELENGTH

FIGURE 3



WAVELENGTH

4,4'-bipyridine together with the spectrum of 3,3'-bipyridine as reported by Anneliese (7) are reproduced in Figure 3.

Brown and Mihm (8) have shown that in the case of the alkyl substitution of pyridine it is the position of the substituent and not the size of the group that causes the change in the absorption spectrum. An ortho or meta-alkyl substituent causes the B band of pyridine to undergo a bathochromic shift; whereas, a para-alkyl substituent produces a hypsochromic shift. Brown has also studied the effect of the methyl substituent on the acid dissociation constant, pK_2 , of pyridine and has found that in general an alkyl substituent increases the basicity of the compound over that of the parent. The strongest effect is observed when the substituent is located in the para position; the effect of the ortho substituent is just slightly less. A meta substituent exerts a considerably smaller influence upon the basicity than the other two positions. The pK_a values given for the methyl pyridines are:

Compound	pK_a
pyridine	5.17
2-methylpyridine	5.97
3-methylpyridine	5.68
4-methylpyridine	6.02

The Ferroine Reaction

In 1898 Blau (9) reported that 2,2'-bipyridine, 2,2'-bipiperidine and 1,10-phenanthroline form stable red compounds with iron(II). This reaction, termed the ferroine reaction, results in highly colored cations, a chelate ring being formed by the iron atom and the $-N=C-C=N-$ group. Inasmuch as a similar arrangement is present in ethylenediamine and 8-aminoquinoline but these compounds do not give the ferroine reaction, it was considered that the aromatic character of the heterocyclic nitrogen was essential for the activation of the ligand (10). In 1951 Krumholz concluded that the color produced as a result of the reaction was due to a transition which involved the entire dipyridyl molecule (11).

In 1953 Krumholz (12) concluded that dipiperidine was oxidized or dehydrogenated first to give the compound 3,4,5,6,3',4',5',6'-octahydro-2,2'-dipyridine and that this compound was responsible for the ferroine reaction observed earlier with dipiperidine. Inasmuch as the nitrogen atoms in this diimine are not contained in a heterocyclic aromatic nucleus he concluded that the original postulate that aromaticity was essential was erroneous. To test this theory he attempted to prepare the compounds biacetyl-bis-N-methylimine and glyoxal-bis-N-methylimine. The compounds themselves could

not be prepared but a mixture of the reactants, biacetyl and methylamine, when added to a solution containing iron(II) did produce a red color. The resulting compound was isolated as the iodide salt and upon analysis was found to be tris-(biacetyl-bis-N-methylimine)iron(II) iodide. Thus, it became apparent that a cyclic structure is not essential for the ferroine reaction. His work also suggests that some movement of electrons from the iron to the functional group occurs.

Continuing the work of Krumholz, Busch and Bailar (13) studied the spectra and magnetic susceptibility of the ferroine type compounds. They also prepared the structural link between the diimines, of Krumholz and the bipyridines of Blau, namely pyridinalmethylimine. Their work corroborates that of Krumholz. They further suggested that the color produced in these compounds is the result of resonance involving six iron(II) nitrogen bonds involving d^2sp^3 hybridized sigma bonds and π bonding between the unhybridized d -electron pairs of the iron(II) and the π electron cloud of the ligand. Using a valence bond picture such an arrangement would appear:



Studies of the effect of substituent groups on the parent ligand's ability to enter into the ferroine reaction have

been conducted by many workers (14, 15, 16, 17, 18, 19, 20). In the case of 1,10-phenanthroline it is now possible to predict the wavelength of maximum absorption of the ferrous compound as well as the formal reduction potential with a fair degree of accuracy given the substituent groups and the position of the substitution (21). This state of refinement has not been reached in the case of the bi- and tripyridines, probably because rotation is possible about the 2,2' bond between the pyridine groups which introduces a further factor. The effects of substitution in certain positions are well known, thus substitution in the 3,3'-positions prevents the pyridine rings from becoming coplanar and the ferroine reaction becomes difficult (22). Substitution in the 6,6'-positions prevents the approach of three of the ligands to the iron atom and the ferroine reaction cannot take place. Substitution in the 2,9 positions in 1,10-phenanthroline has the same effect. Although these compounds will not give the ferroine reaction they are capable of reacting with the cuprous atom (cuproine reaction) (23).

EXPERIMENTAL WORK

Recording of Spectra

The spectrum of an aqueous solution of the free base and the iron(II) complexes were determined with a Model 12 Cary spectrophotometer. In the visible portions of the spectrum 5 cm. cells were used, whereas the ultraviolet portions of the spectrum were recorded using 1 cm. cells. In all cases the comparison cell was filled with distilled water.

2,2'-bipyridine

A 1×10^{-3} molar solution of 2,2'-bipyridine was prepared by dissolving 0.0781 g. of the free base (obtained from the G. Frederick Smith Chemical Co.) in a few ml. of dilute hydrochloric acid. The resultant solution was then diluted to 500 ml. with distilled water.

A volume of 5 ml. of the above solution was introduced into each of a pair of 100 ml. volumetric flasks. To one of the pair 4 ml. of a 4×10^{-4} molar solution of iron(III) chloride was added. Then to each of the flasks was added 5 ml. of a 5 percent solution of hydroxylammonium chloride and 5 ml. of a 5 percent solution of sodium acetate. The solution was then diluted to the mark and mixed. The absorption spectrum of both the iron(II) compound and the free reagent were then recorded through the ultraviolet range, and

the spectrum of the iron(II) compound was recorded through the visible range. These spectra are reproduced in Figures 4 and 5.

2,2',2''-tripyridine

The commercial material (G. Frederick Smith Chemical Co.) was purified by two successive recrystallizations from a slightly alkaline aqueous solution. A small quantity of decolorizing charcoal was added to the first recrystallization. The free base was dried in a vacuum over anhydrous magnesium perchlorate. A 1×10^{-3} molar solution of the free base was prepared by dissolving 0.1166 g. of the purified material in a small quantity of distilled water containing a few drops of hydrochloric acid. The resultant solution was then diluted to 500 ml.

A volume of 5 ml. of this stock solution was introduced into each of a pair of 100 ml. volumetric flasks. To one was added 4 ml. of a 4×10^{-4} M solution of iron(III) chloride. Then to each was added in succession 5 ml. of the 5 percent hydroxylammonium chloride solution and 5 ml. of 5 percent sodium acetate solution. The solutions were then diluted to the mark and mixed. The absorption spectrum of both the iron(II) derivative and the free reagent were then recorded through the ultraviolet range. The spectrum of the iron(II)

Figure 4. The ultraviolet spectra of bipyridine and its iron(II) derivative

- 2,2'-bipyridine
- tris(2,2'-bipyridine)iron(II) chloride

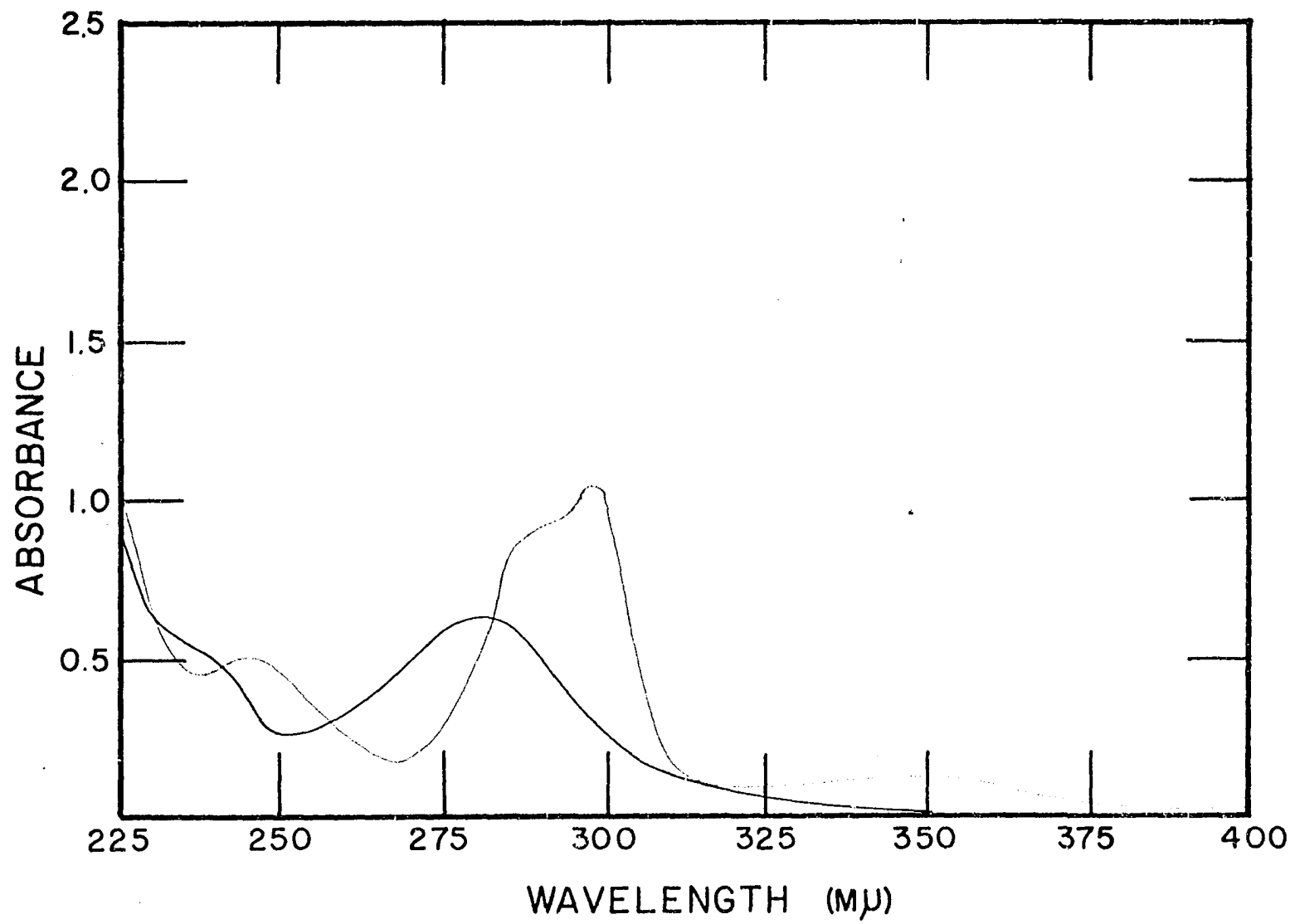
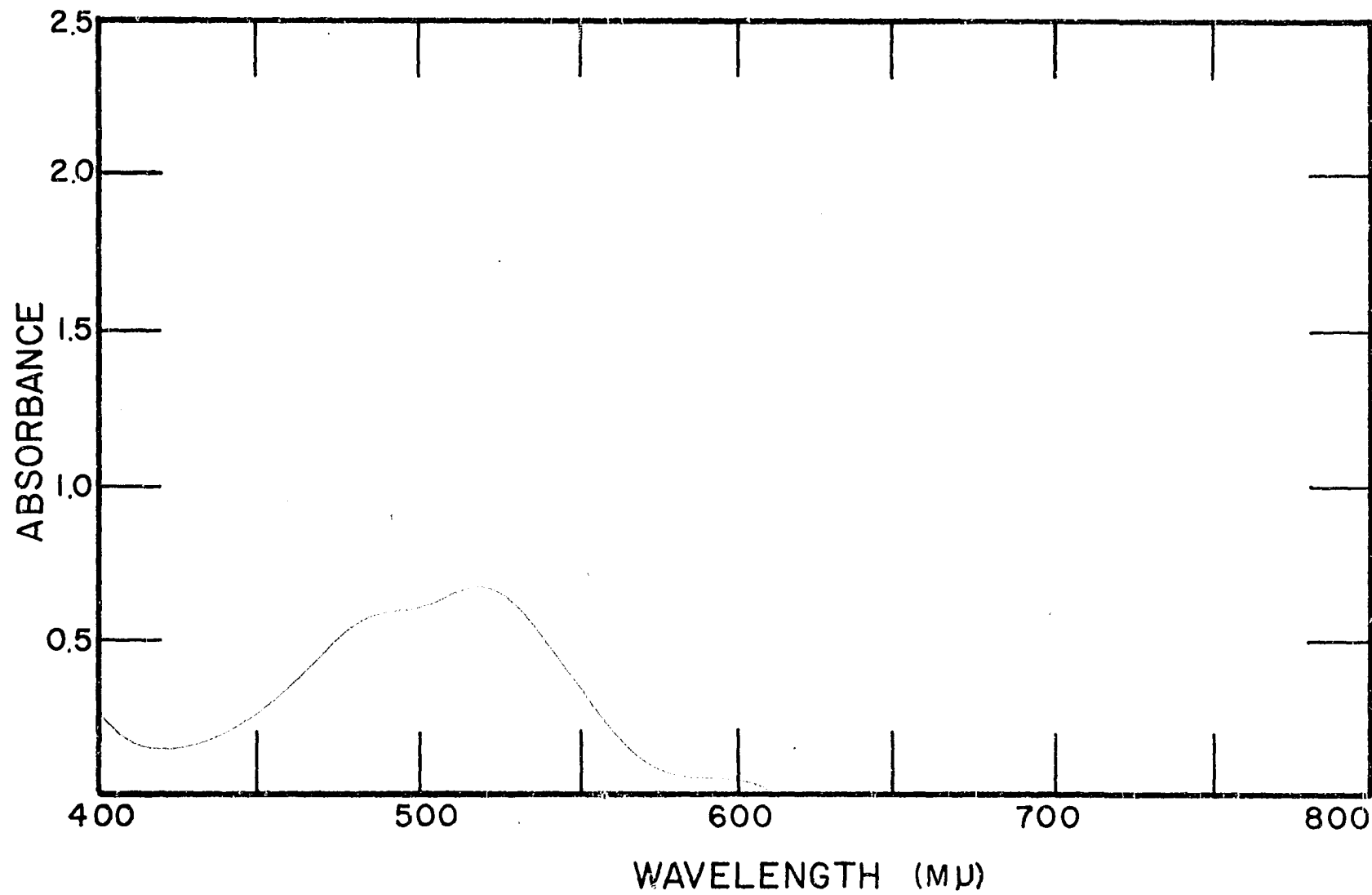


Figure 5. The visible spectrum of tris(2,2'-bipyridine)iron(II) chloride



derivative was also recorded through the visible region. These spectra are reproduced in Figures 6 and 7.

3,3'-dimethyl-2,2' bipyridine

The material obtained from the G. Frederick Smith Chemical Co. was purified by treating the compound with a quantity of iron(II) and extracting the resultant aqueous solution with diethylether to remove a yellow oil. The iron(II) compound was then broken up by the addition of strong base and the solution again extracted with ether, which isolated the free base. The material so recovered was dried in a vacuum over anhydrous magnesium perchlorate. The material was a viscous, colorless liquid. A 1×10^{-3} molar solution was prepared by dissolving 0.0461 g. of the free base in 250 ml. of water.

A volume of 5.00 ml. of this stock solution was then introduced into each of two volumetric flasks. To one of the pair 4.00 ml. of a 4×10^{-4} molar solution of iron(III) chloride was added. Then to each of the flasks was added 5 ml. of 5 percent hydroxylammonium chloride solution followed by 5 ml. of 5 percent sodium acetate solution. The solutions were then diluted to the mark and mixed. The absorption spectrum of both the iron derivative and the free reagent were then recorded through the ultraviolet range. A second

Figure 6. The ultraviolet spectrum of 2,2',2''-tripyridine and its iron(II) derivative

- 2,2',2''-tripyridine
- bis(2,2',2''-tripyridyl)iron(II) chloride

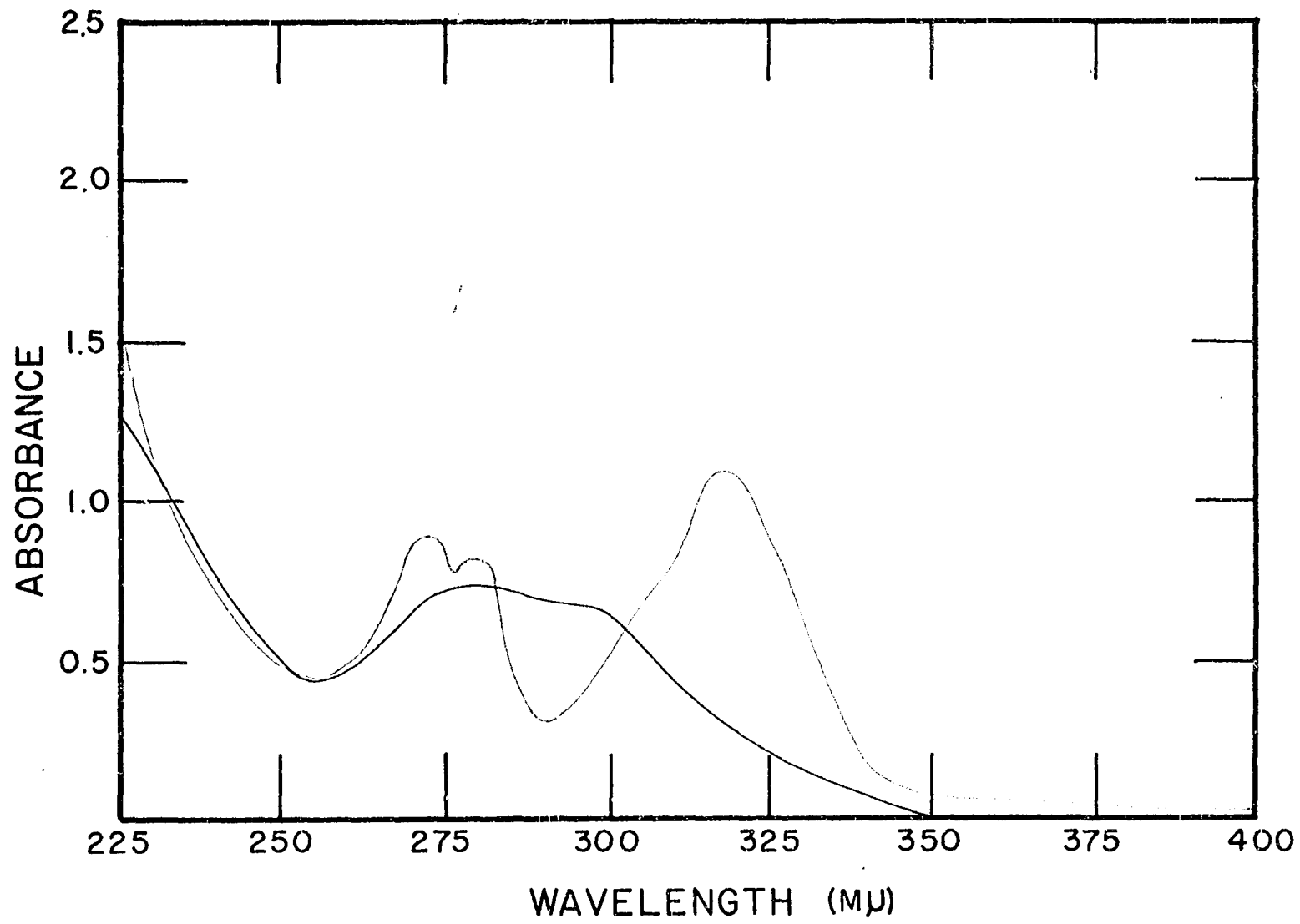
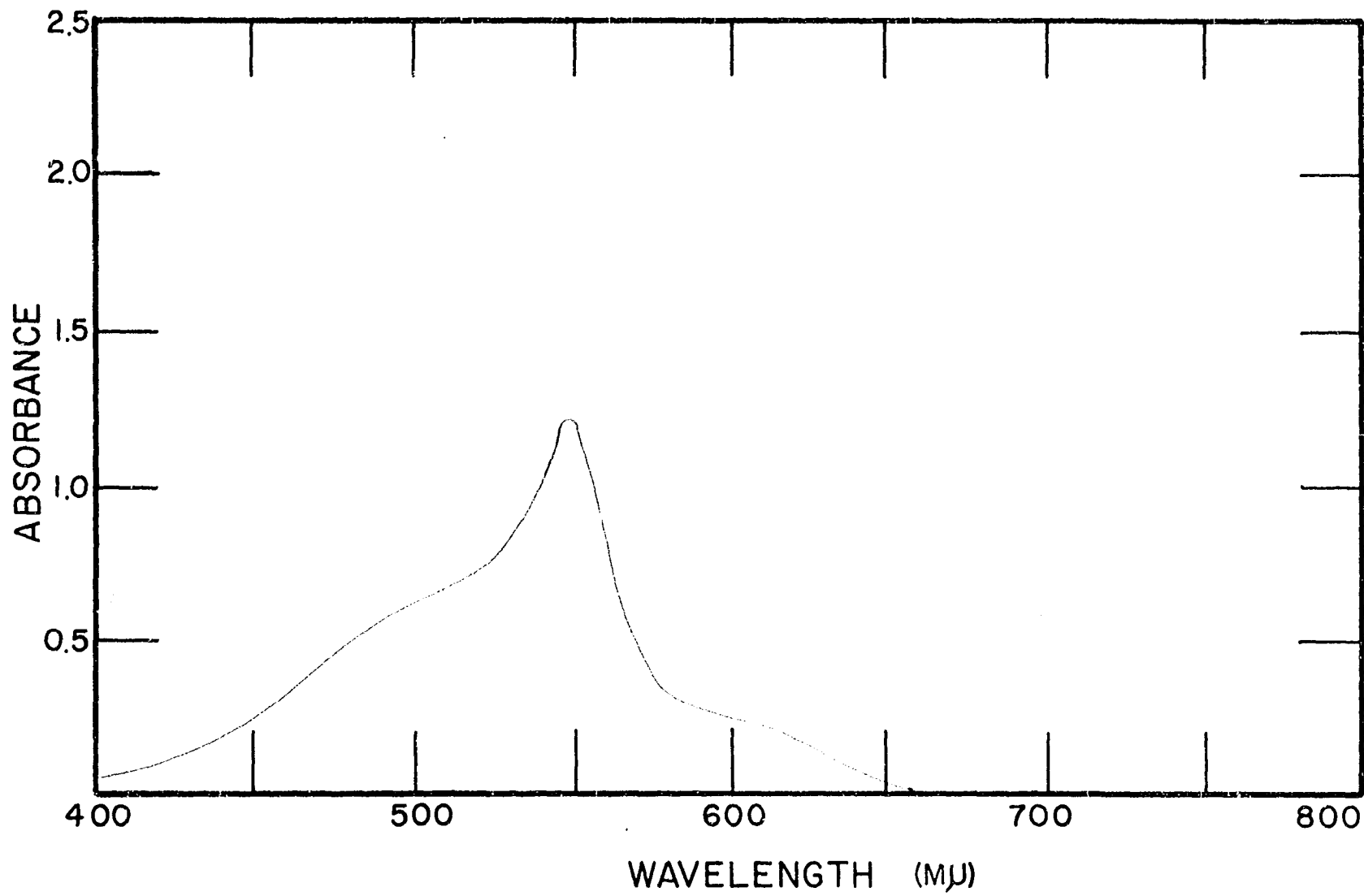


Figure 7. The visible spectrum of bis(2,2',2''-tripyriddy)iron(II) chloride



more concentrated solution (4.5×10^{-5} molar) of the iron derivative was prepared and the absorption spectrum in the visible region recorded. These spectra are reproduced as Figures 8 and 9.

4,4'-dimethyl-2,2'-bipyridine

A 1×10^{-3} molar stock solution of 4,4'-dimethyl-2,2'-bipyridine was prepared by dissolving 0.0922 g. of the free base, M.P. $170 - 173^{\circ}$ C, (obtained from the G. Frederick Smith Chemical Co.) in a few ml. of dilute hydrochloric acid. The resultant solution was then diluted to 500 ml. with distilled water.

A volume of 5 ml. of the above solution was introduced into each of a pair of 100 ml. volumetric flasks. To one of the pair 4 ml. of a 4×10^{-4} molar solution of iron(III) chloride was added. Then to each of the flasks was added 5 ml. of a 5 percent solution of hydroxylammonium chloride and 5 ml. of a 5 percent solution of sodium acetate. The solution was then diluted to the mark and mixed. The absorption spectrum of both the iron(II) compound and the free reagent were then recorded through the ultraviolet range, and the spectrum of the iron(II) compound was recorded through the visible range. These spectra are reproduced in Figures 10 and 11.

Figure 8. The ultraviolet absorption spectrum of 3,3'-dimethyl-2,2'-bipyridine and its iron(II) derivative

- 3,3'-dimethyl-2,2'-bipyridine
- tris(3,3'-dimethyl-2,2'-bipyridyl)iron(II) chloride

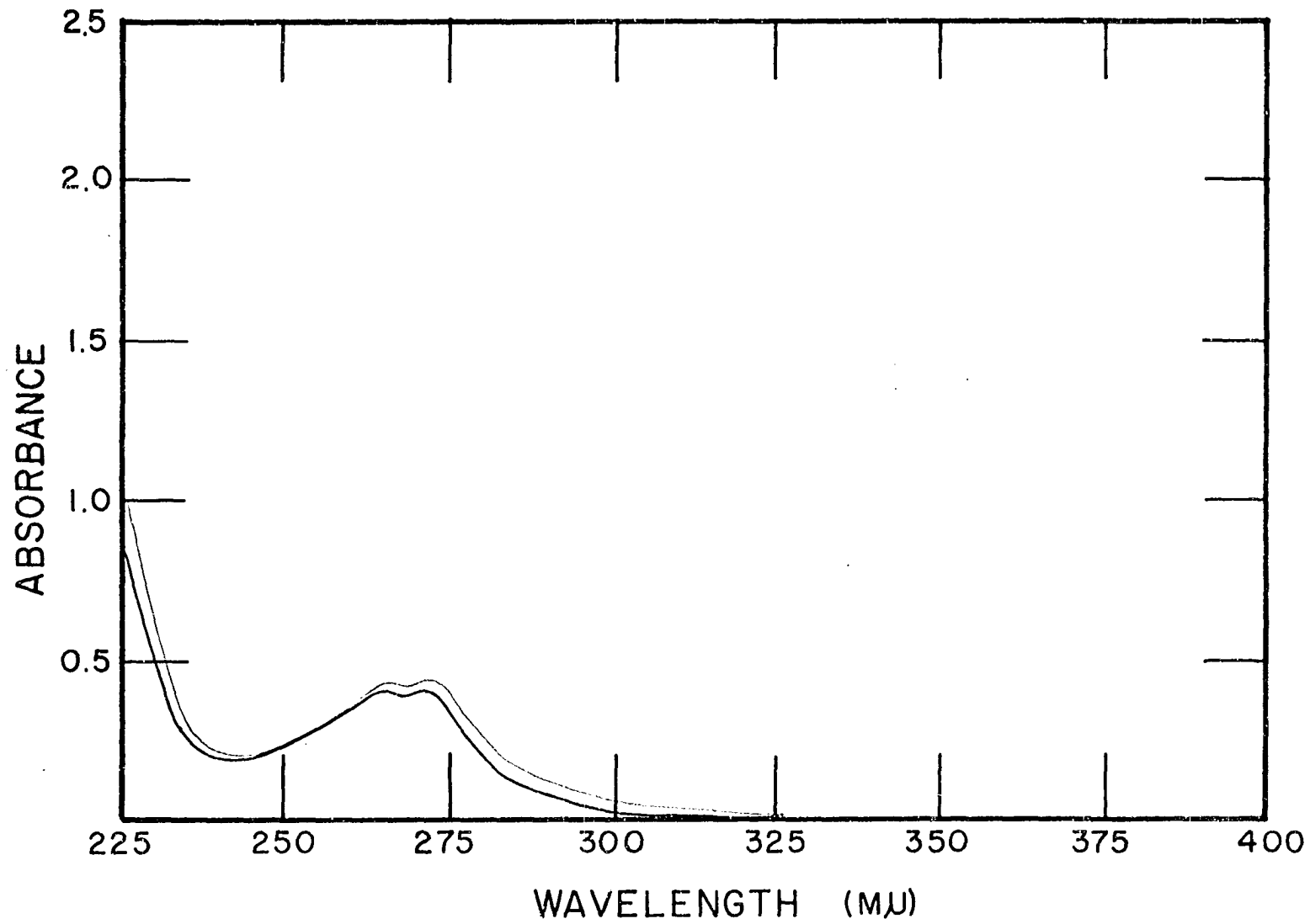


Figure 9. The visible spectrum of tris(3,3'-dimethyl-2,2'-bipyridyl)-iron(II) chloride

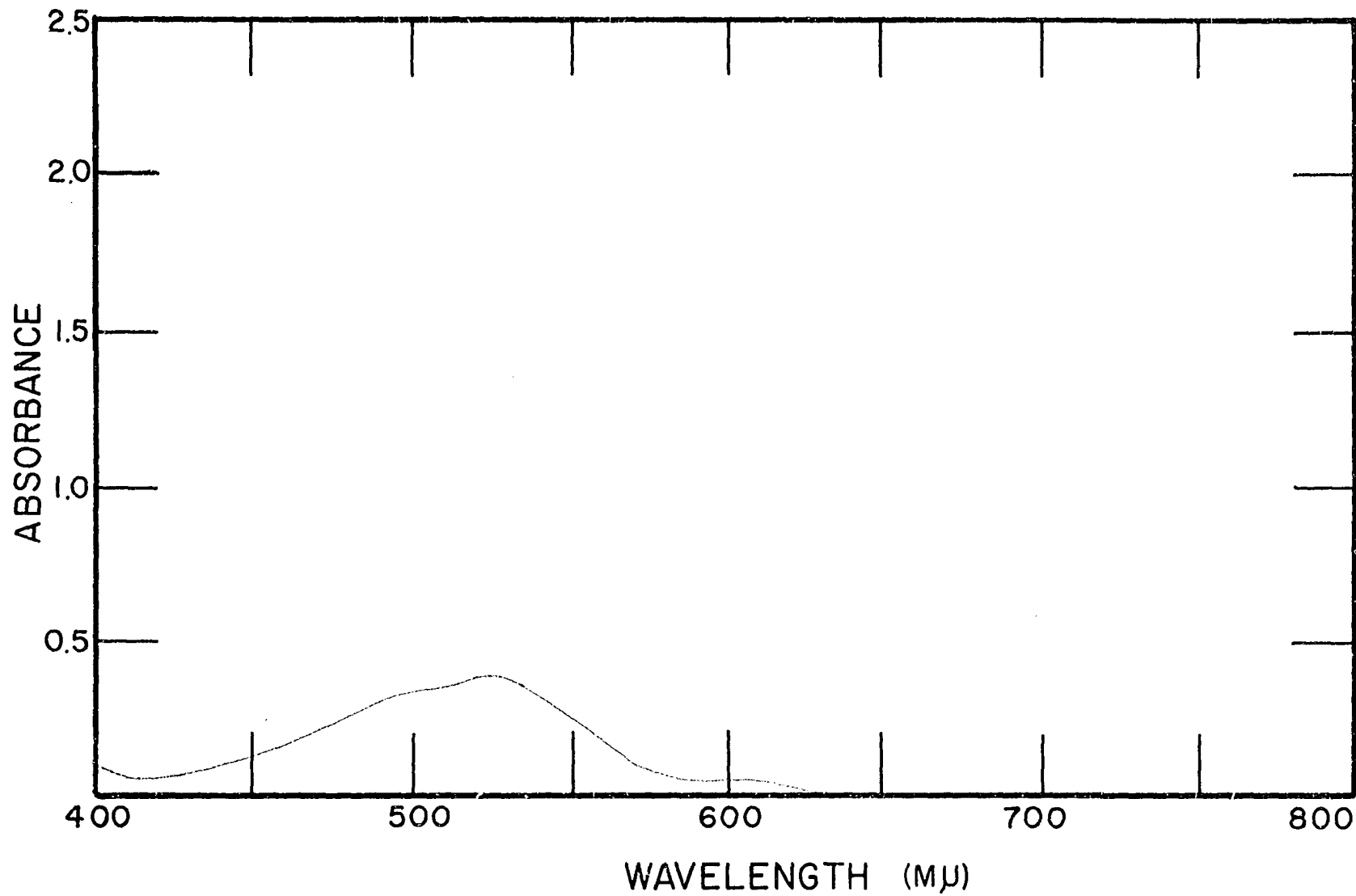


Figure 10. The ultraviolet absorption spectrum of 4,4'-dimethyl-2,2'-bipyridine and its iron(II) derivative

- -4,4'-dimethyl-2,2'-bipyridine
- -tris(4,4'-dimethyl-2,2'-bipyridyl)iron(II) chloride

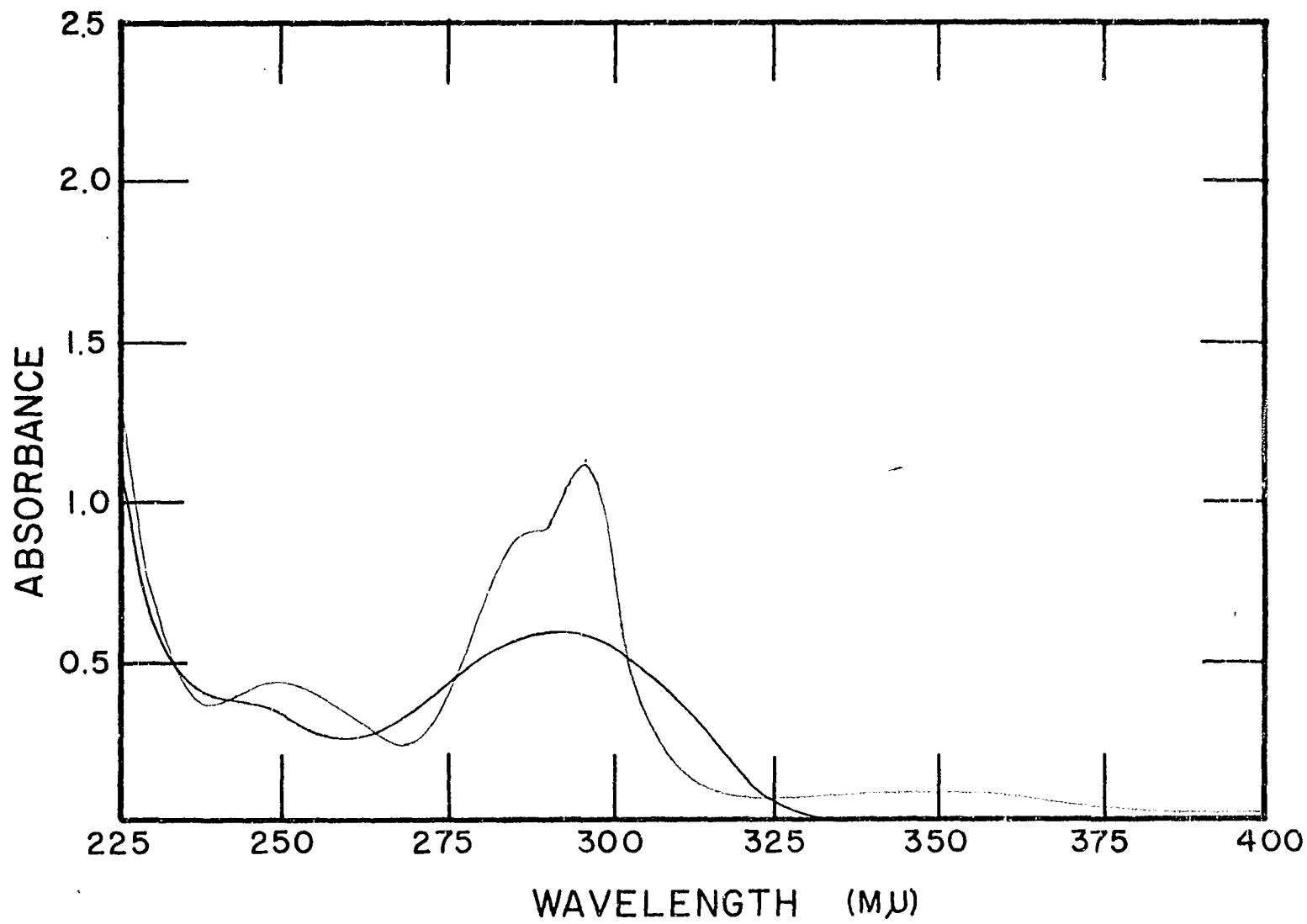
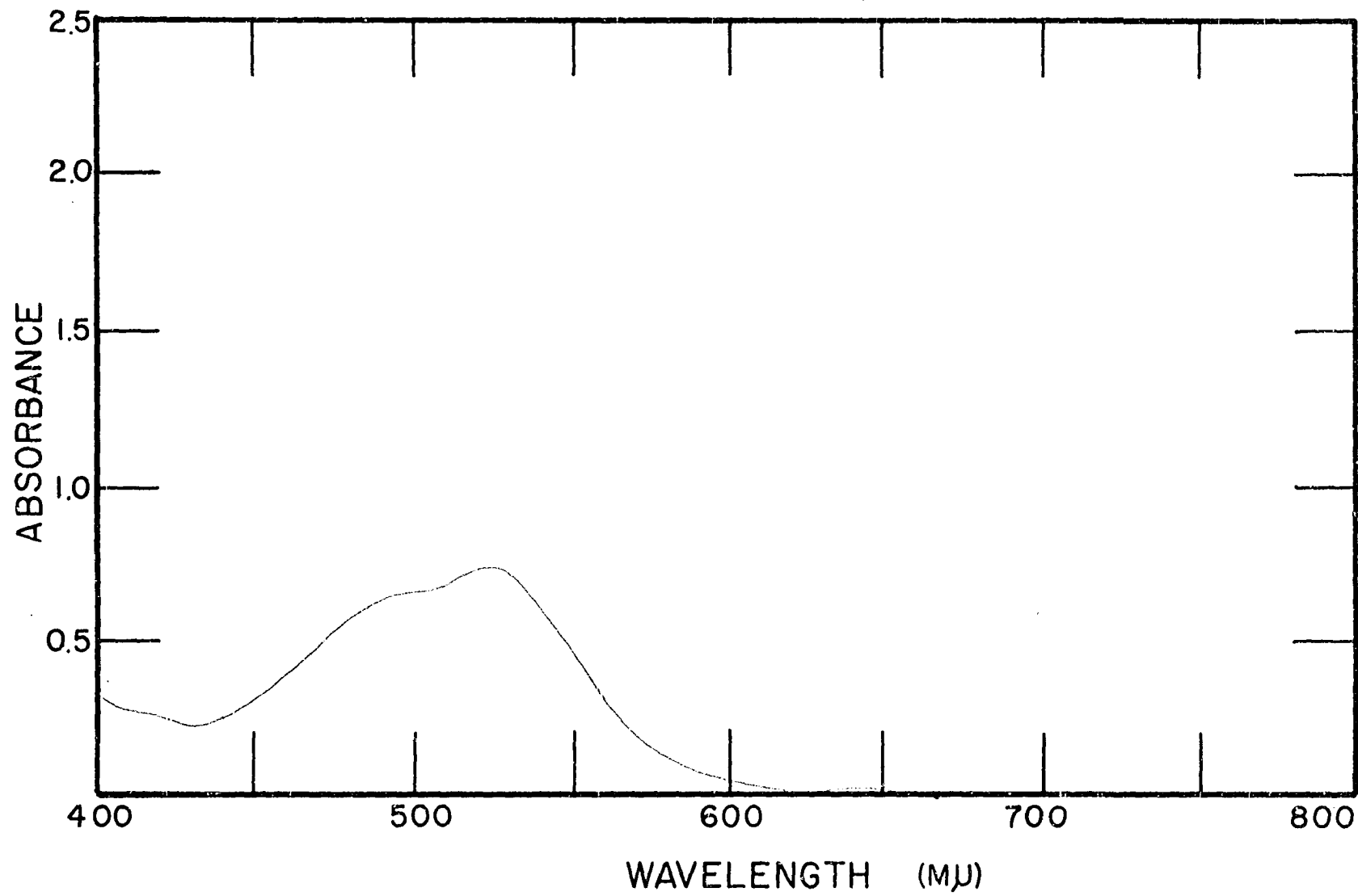


Figure 11. The visible absorption spectrum of tris(4,4'-dimethyl-2,2'-bipyridyl) iron(II) chloride



5,5'-dimethyl-2,2'-bipyridine

The material, obtained from the G. Frederick Smith Chemical Co., was purified by treating the compound with a quantity of iron(II) and extracting the resultant aqueous solution with ether. This process removes a yellow material. The complex was then broken by the addition of strong alkali and the suspension was again extracted with ether which isolated the free base. Upon evaporation of the ether a white material was obtained. The material so recovered was dried in a vacuum over anhydrous magnesium perchlorate. This material had a melting point of 118 - 119° C. A 1×10^{-3} molar solution was prepared by dissolving 0.9922 g. of the reagent in a small quantity of dilute hydrochloric acid and diluting the resultant solution to 500 ml.

A volume of 5 ml. of the above solution was introduced into each of a pair of 100 ml. volumetric flasks. To one of the pair 4 ml. of a 4×10^{-4} molar solution of iron(III) chloride was added. Then to each of the flasks was added 5 ml. of a 5 percent solution of sodium acetate. The solution was then diluted to the mark and mixed. The absorption spectrum of both the iron(II) compound and the free reagent were then recorded through the ultraviolet range, and the spectrum of the iron(II) compound was recorded through the visible range. These spectra are reproduced in Figures 12 and 13.

6,6'-dimethyl-2,2'-bipyridine

A 1×10^{-3} molar stock solution of 6,6'-dimethyl-2,2'-bipyridine was prepared by dissolving 0.0922 g. of the free base, M.P. $155 - 157^{\circ}$ C, (obtained from the G. Frederick Smith Chemical Co.) in a few ml. of dilute hydrochloric acid. The resultant solution was then diluted to 500 ml. with distilled water.

A volume of 5 ml. of the above solution was introduced into each of a pair of 100 ml. volumetric flasks. To one of the pair 4 ml. of a 4×10^{-4} molar solution of iron(III) chloride was added. Then to each of the flasks was added 5 ml. of a 5 percent solution of sodium acetate. The solution was then diluted to the mark and mixed. The absorption spectrum of both the free reagent and the solution containing both the free reagent and iron were recorded through the ultra-violet region. As there was no complex formed there was no absorption to record in the visible region. The ultraviolet absorption spectra are reproduced in Figure 14.

Triamino-s-triazine

A 1×10^{-3} molar stock solution of triamino-s-triazine was prepared by dissolving 0.0631 g. of the free base (obtained from American Cyanimide Co.) in a few ml. of dilute hydrochloric acid. The resultant solution was diluted to 500 ml. with distilled water.

Figure 12. The ultraviolet spectrum of 5,5'-dimethyl-2,2'-bipyridine and its iron(II) derivative

- -5,5'-dimethyl-2,2'-bipyridine
- -tris(5,5'-dimethyl-2,2'-bipyridyl)iron(II) chloride

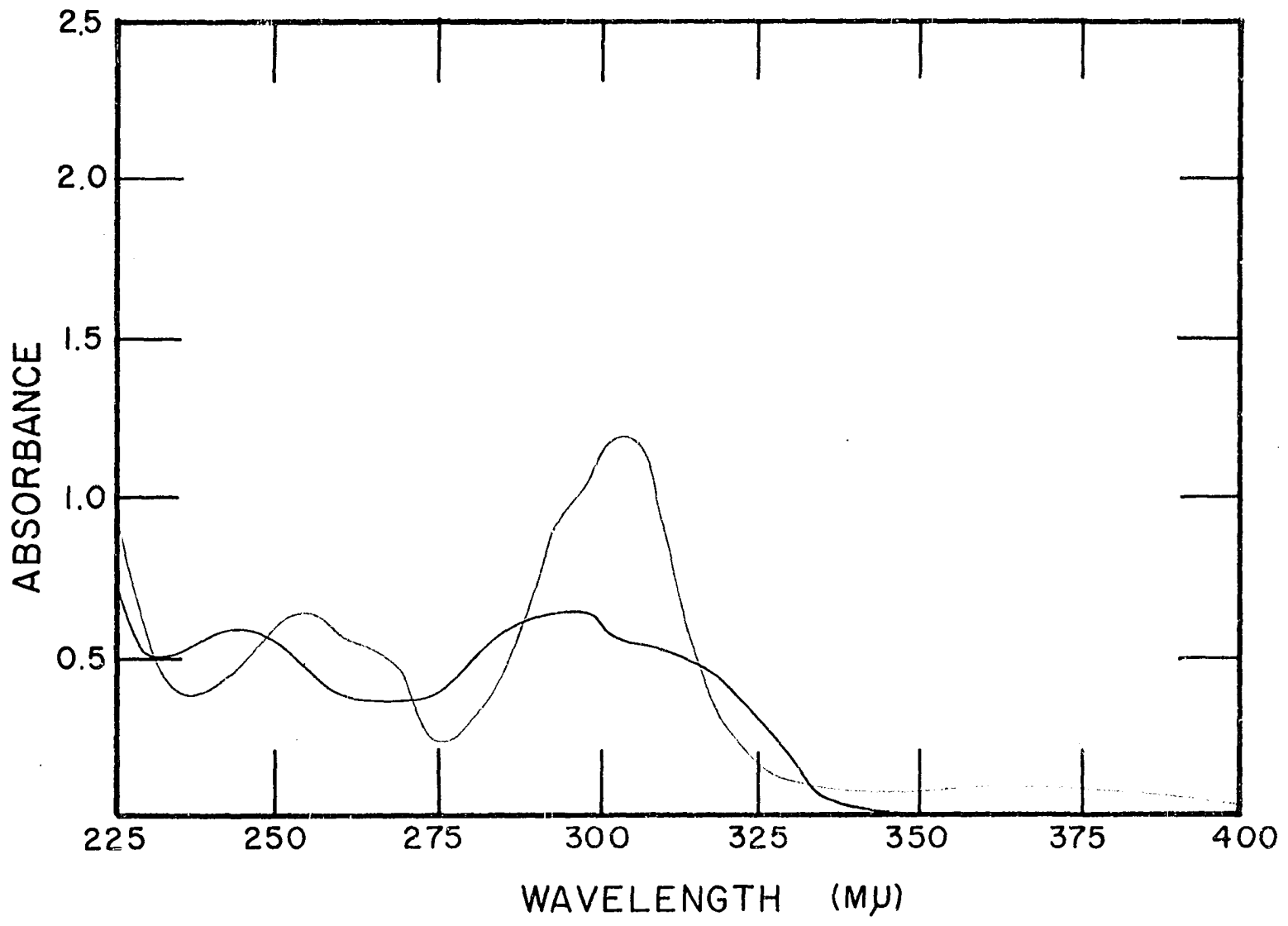


Figure 13. The visible spectrum of tris(5,5'-dimethyl-2,2'-bipyridyl)iron(II) chloride

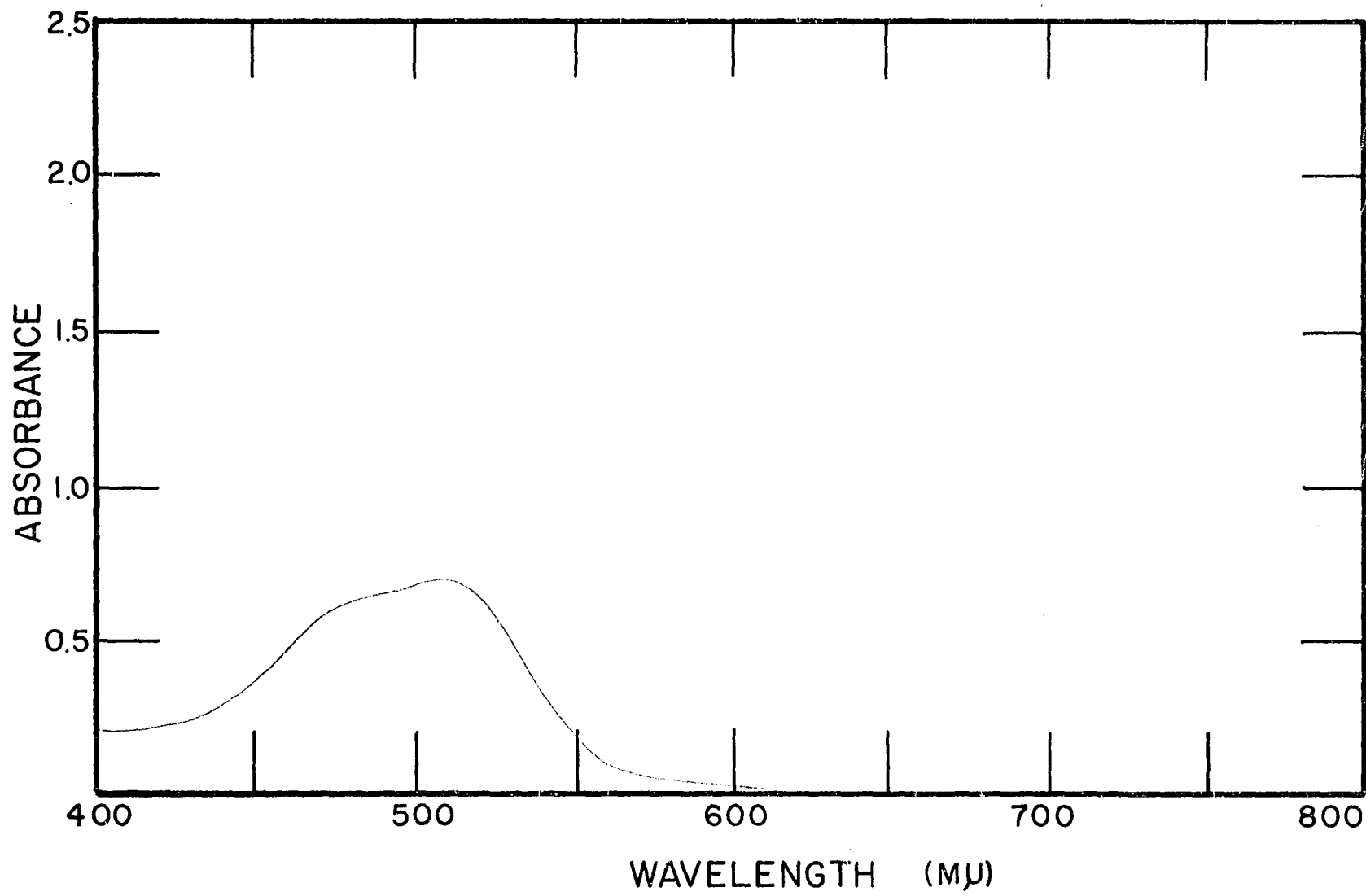
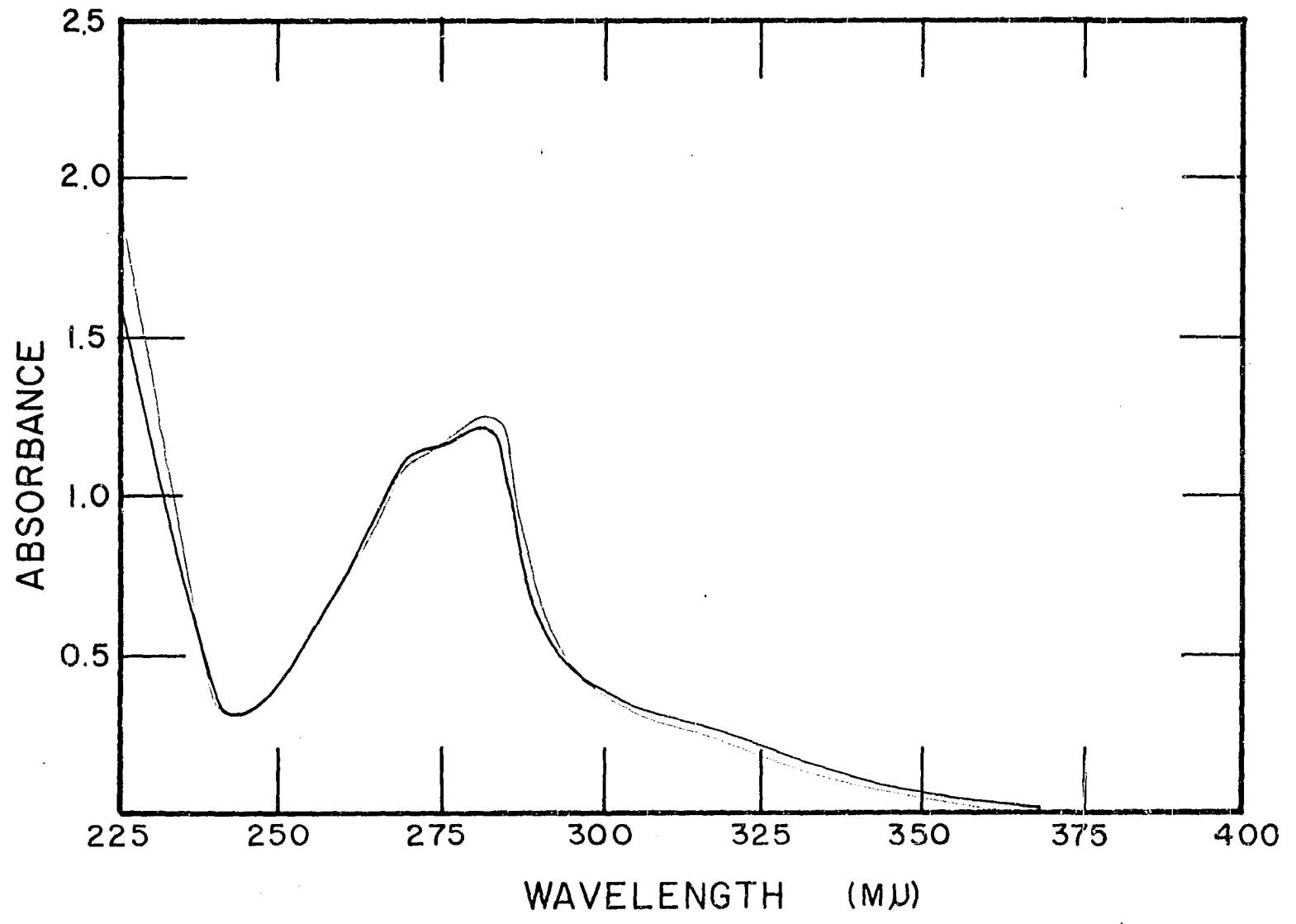


Figure 14. The ultraviolet absorption spectrum of 6,6'-dimethyl-2,2'-bipyridine;
alone and in the presence of iron(II) chloride

- 6,6'-dimethyl-2,2'-bipyridine
- 6,6'-dimethyl-2,2'-bipyridine in the presence of iron(II) chloride



A volume of 5 ml. of this stock solution was introduced into each of a pair of 100 ml. volumetric flasks. To one was added 4 ml. of a 4×10^{-4} molar solution of iron(III) chloride. Then to each was added in succession 5 ml. of the 5 percent hydroxylammonium chloride solution and 5 ml. of 5 percent sodium acetate solution. The solutions were then diluted to the mark and mixed. The absorption spectrum of both the free reagent and that of the reagent and iron were recorded through the ultraviolet region. As there is no complex formed there is no absorption in the visible region. The spectrum of this reagent is reproduced in Figure 15.

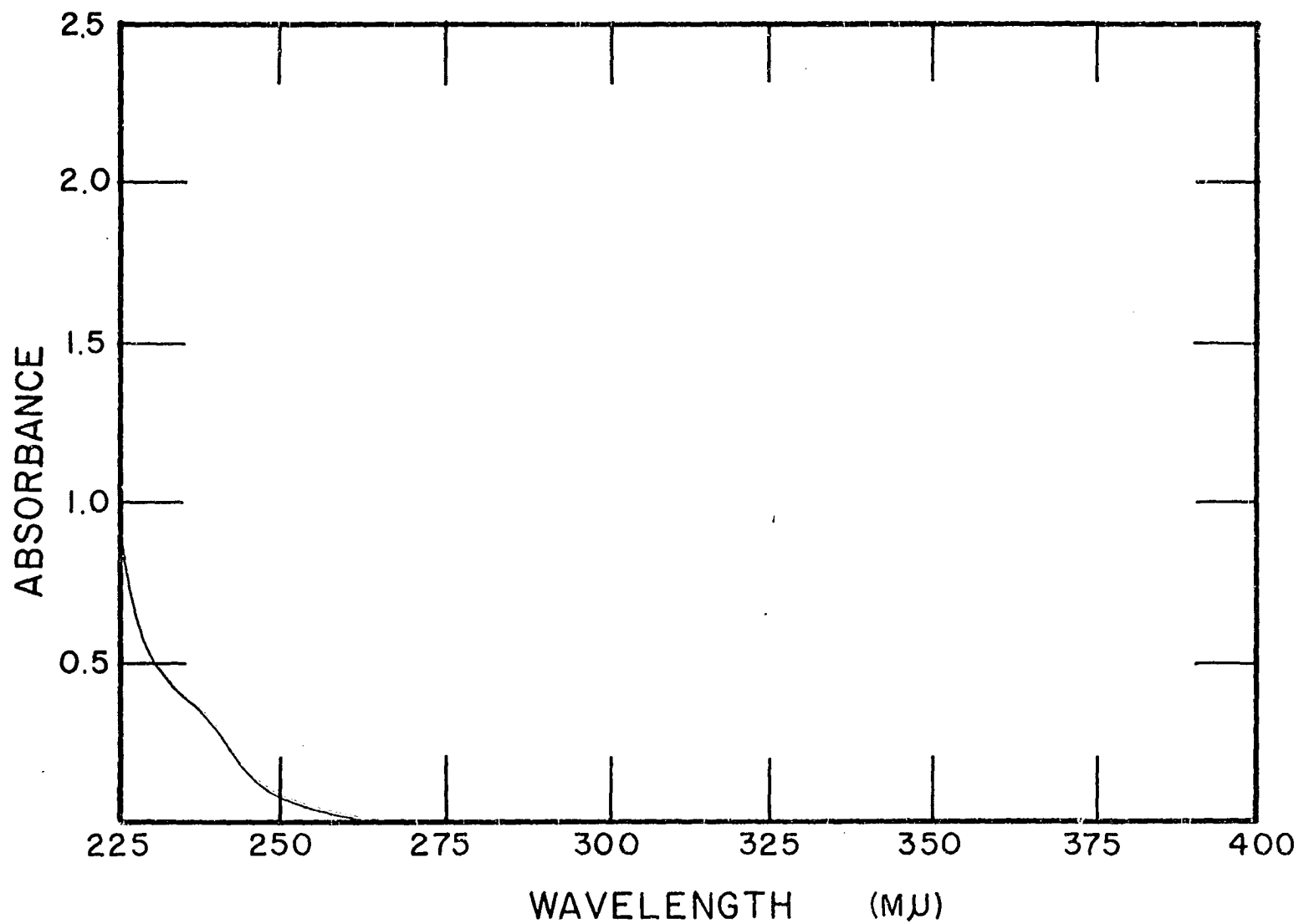
4,6-diamino-2(2'-pyridyl)-s-triazine

A 1×10^{-3} molar solution of 4,6-diamino-2(2'-pyridyl)-s-triazine was prepared by dissolving 0.0941 g. of the free base (obtained from Prof. F. Case, Temple University) in a few ml. of dilute hydrochloric acid. The resultant solution was then diluted to 500 ml. with distilled water.

A volume of 5.00 ml. of this stock solution was then introduced into each of two volumetric flasks. To one of the pair 4.00 ml. of a 4×10^{-4} molar solution of iron(III) chloride was added. Then to each of the flasks was added 5 ml. of 5 percent hydroxylammonium chloride solution followed by 5 ml. of 5 percent sodium acetate solution. The solutions

Figure 15. The ultraviolet absorption spectrum of triamino-s-triazine;
alone and in the presence of iron(II) chloride

- -triamino-s-triazine
- -triamino-s-triazine in the presence of iron(II) chloride



were then diluted to the mark and mixed. The absorption spectrum of both the iron derivative and the free reagent were then recorded through the ultraviolet range. A second more concentrated solution of the iron derivative was prepared and the absorption spectrum in the visible region recorded in order to obtain a better indication of the wavelength of the absorption maximum. These spectra are reproduced in Figures 16 and 17.

2-amino-4,6-bis(2'-pyridyl)-s-triazine

A 1×10^{-3} molar solution of 2-amino-4,6-bis(2'-pyridyl)-s-triazine was prepared by dissolving 0.1251 g. of the free base (obtained from Prof. F. Case, Temple University) in a few ml. of dilute hydrochloric acid. The resultant solution was diluted to 500 ml.

A volume of 5.00 ml. of this stock solution was then introduced into each of two volumetric flasks. To one of the pair 5.00 ml. of a 4×10^{-4} molar solution of iron(III) chloride was added. Then to each of the flasks was added 5 ml. of 5 percent hydroxylammonium chloride solution followed by 5 ml. of 5 percent sodium acetate solution. The solutions were then diluted to the mark and mixed. The absorption spectrum of both the iron derivative and the free reagent were then recorded through the ultraviolet range and the spectrum

Figure 16. The ultraviolet absorption spectrum of 4,6-diamino-2(2'-pyridyl)-
-s-triazine and its iron(II) derivative
— -4,6-diamino-2(2'-pyridyl)-s-triazine
— -tris(4,6-diamino-2(2'-pyridyl)-s-triazine)iron(II) chloride

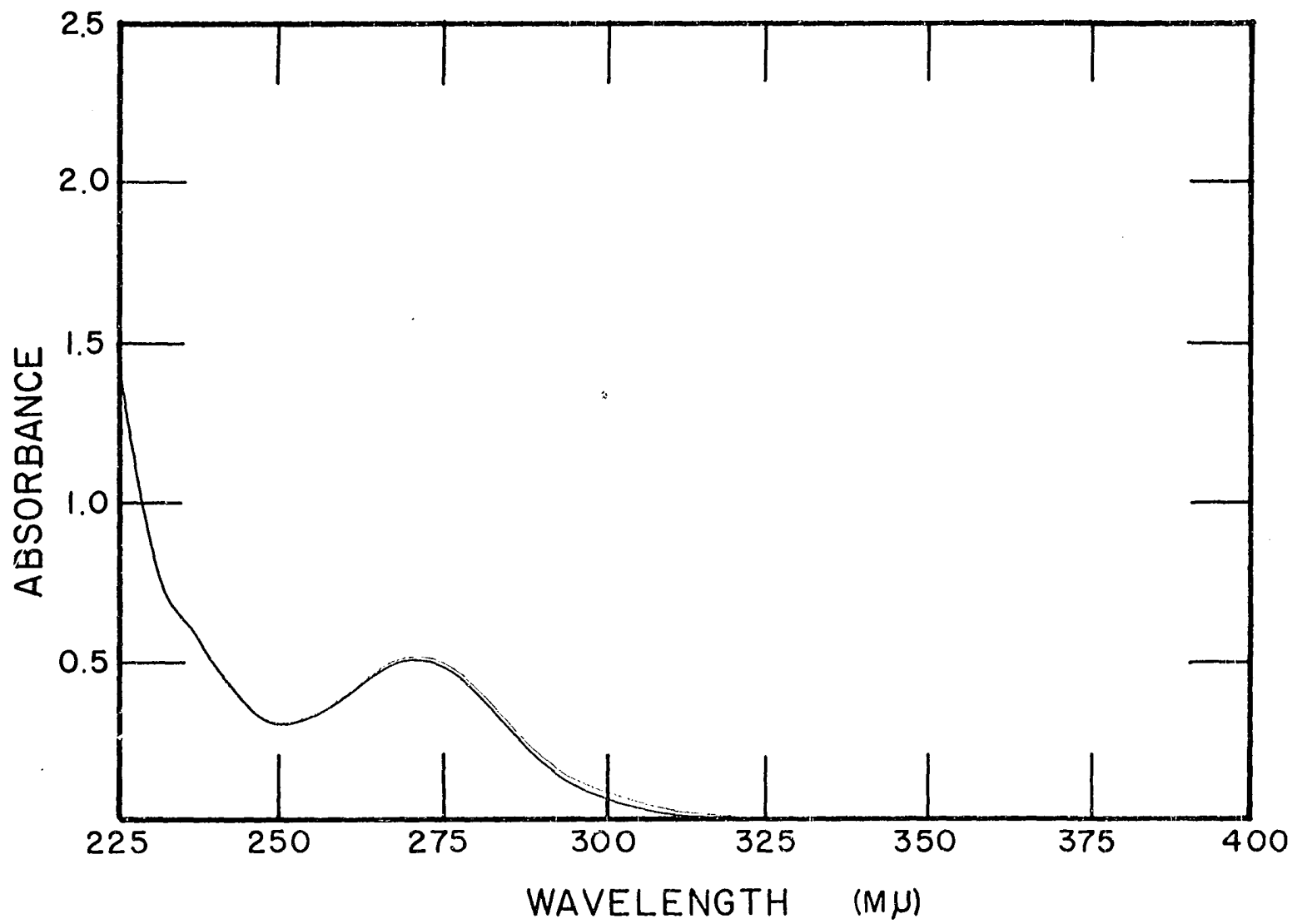
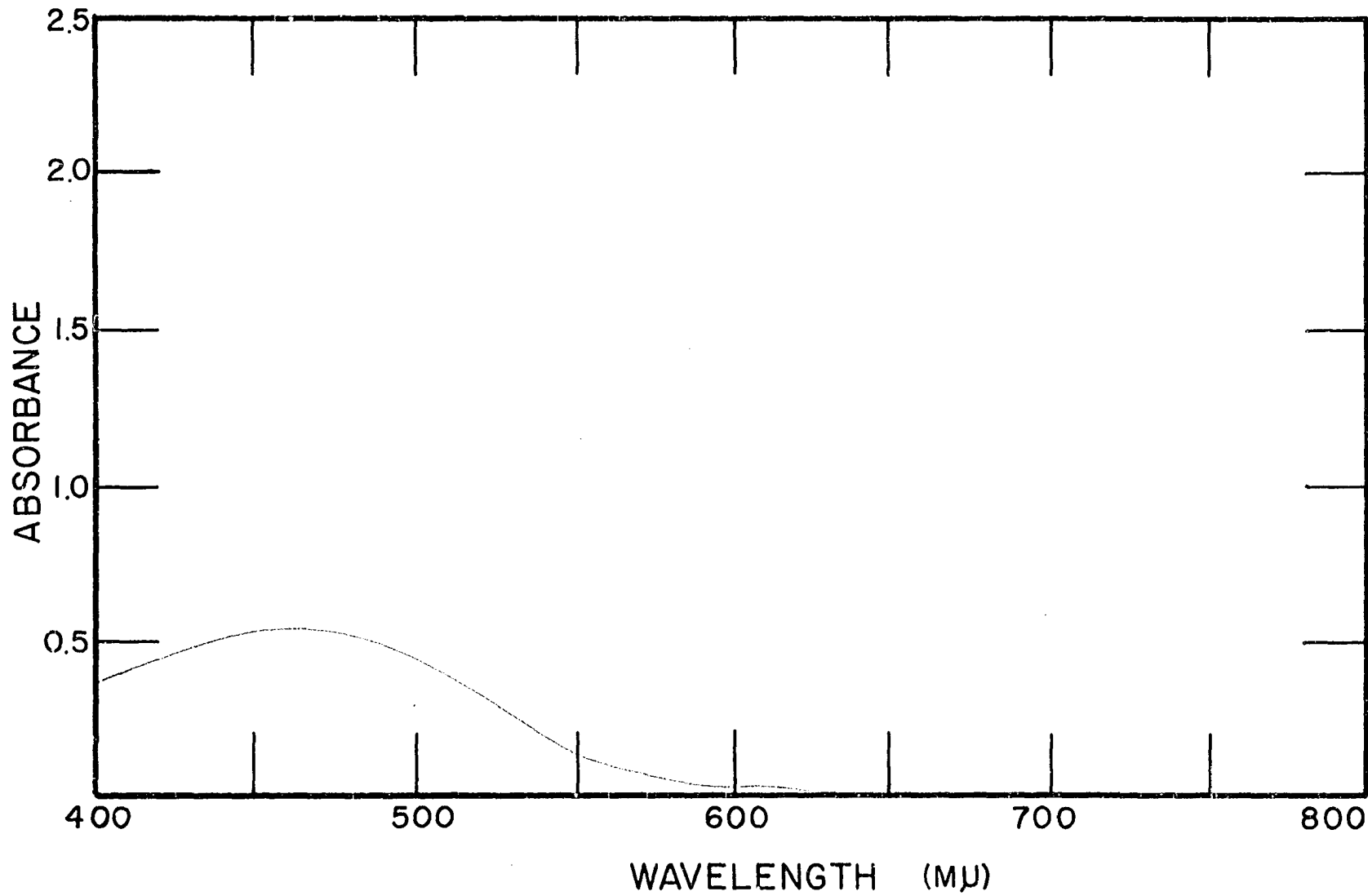


Figure 17. The visible absorption spectrum of tris(4,6-diamino-2(2'-pyridyl)-
-s-triazine)iron(II) chloride



of the iron(II) compound was recorded through the visible range. These spectra are reproduced in Figures 18 and 19.

2,4,6-tris(2'-pyridyl)-s-triazine

A 1×10^{-3} molar solution of 2,4,6-tris(2'-pyridyl)-s-triazine was prepared by dissolving 0.1562 g. of the free base (obtained from Prof. F. Case, Temple University) in a few ml. of dilute hydrochloric acid. The resultant solution was then diluted to 500 ml. with distilled water.

A volume of 5 ml. of the above solution was introduced into each of a pair of 100 ml. volumetric flasks. To one of the pair 5 ml. of a 4×10^{-4} molar solution of iron(III) chloride was added. Then to each of the flasks was added 5 ml. of a 5 percent solution of hydroxylammonium chloride and 5 ml. of a 5 percent solution of sodium acetate. The solution was then diluted to the mark and mixed. The absorption spectrum of both the iron(II) compound and the free reagent were then recorded through the ultraviolet range, and the spectrum of the iron(II) compound was recorded through the visible range. These spectra are reproduced in Figures 20 and 21.

The Effect of Acidity upon the Spectra
of the Reagents and upon the Formation
of the Complexes

Inasmuch as a new series of reagents for iron has been introduced, it was considered desirable to study the effect

Figure 18. The ultraviolet absorption spectrum of 2-amino-4,6-bis(2'-pyridyl)-
-s-triazine and its iron(II) derivative
-- -2-amino-4,6-bis(2'-pyridyl)-s-triazine
— -bis(2-amino-4,6-bis(2'-pyridyl)-s-triazine)iron(II) chloride

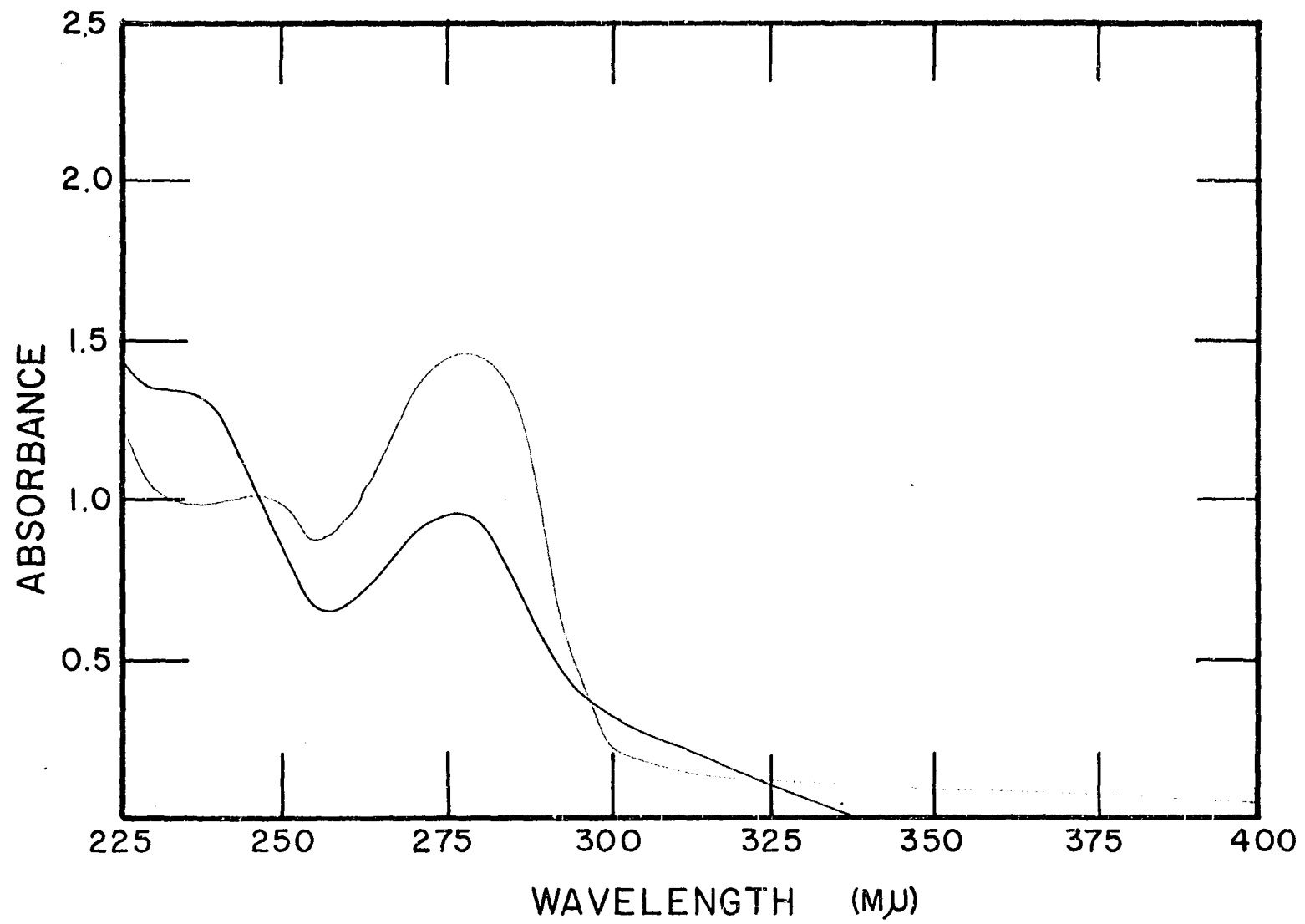


Figure 19. The visible absorption spectrum of bis(2-amino-4,6-bis(2'-pyridyl)-
-s-triazine(iron(II) chloride

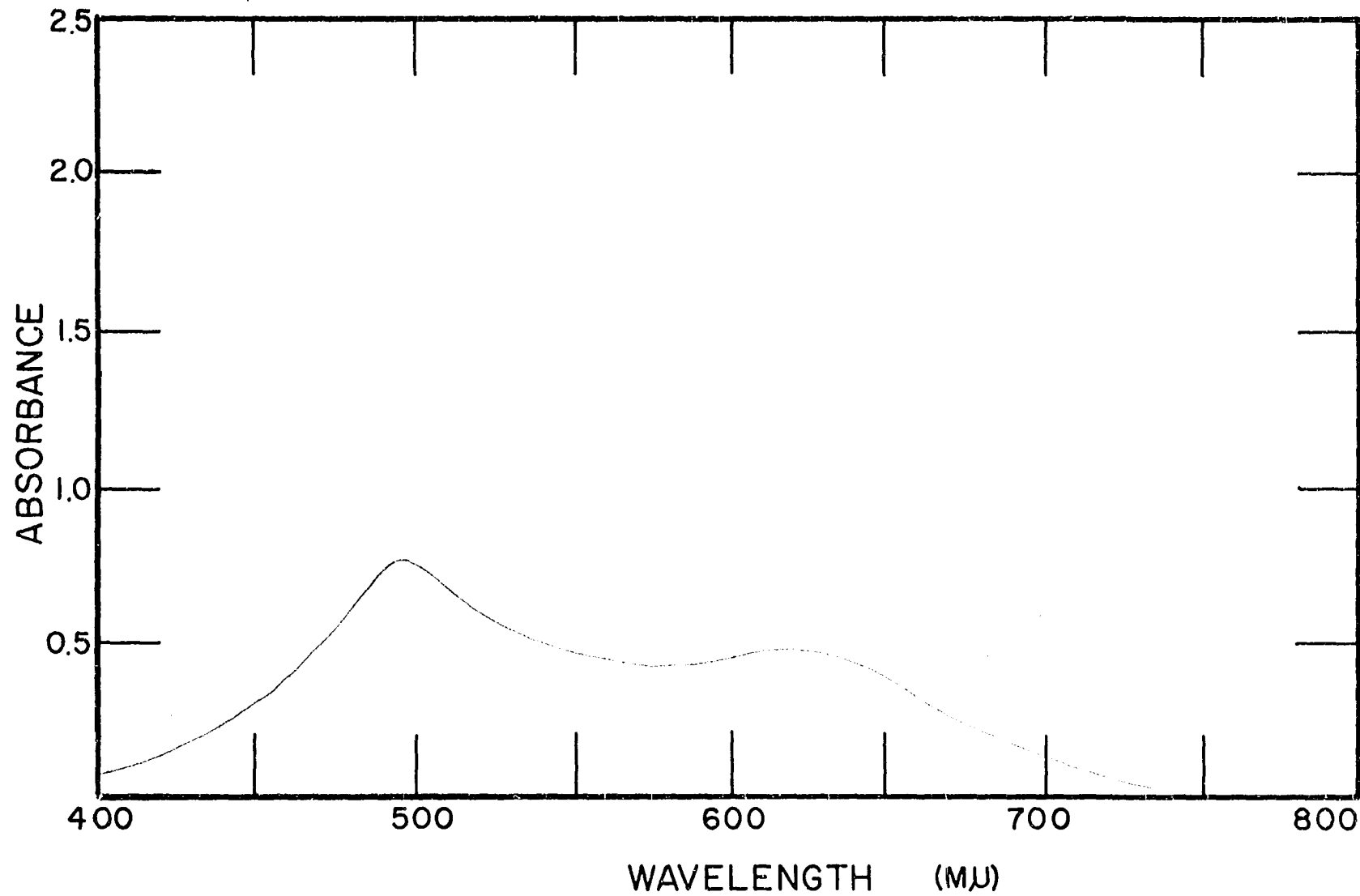


Figure 20. The ultraviolet spectrum of 2,4,6-tris(2'-pyridyl)-s-triazine and its iron(II) derivative

- 2,4,6-tris(2'-pyridyl)-s-triazine
- bis(2,4,6-tris(2'-pyridyl)-s-triazine)iron(II) chloride

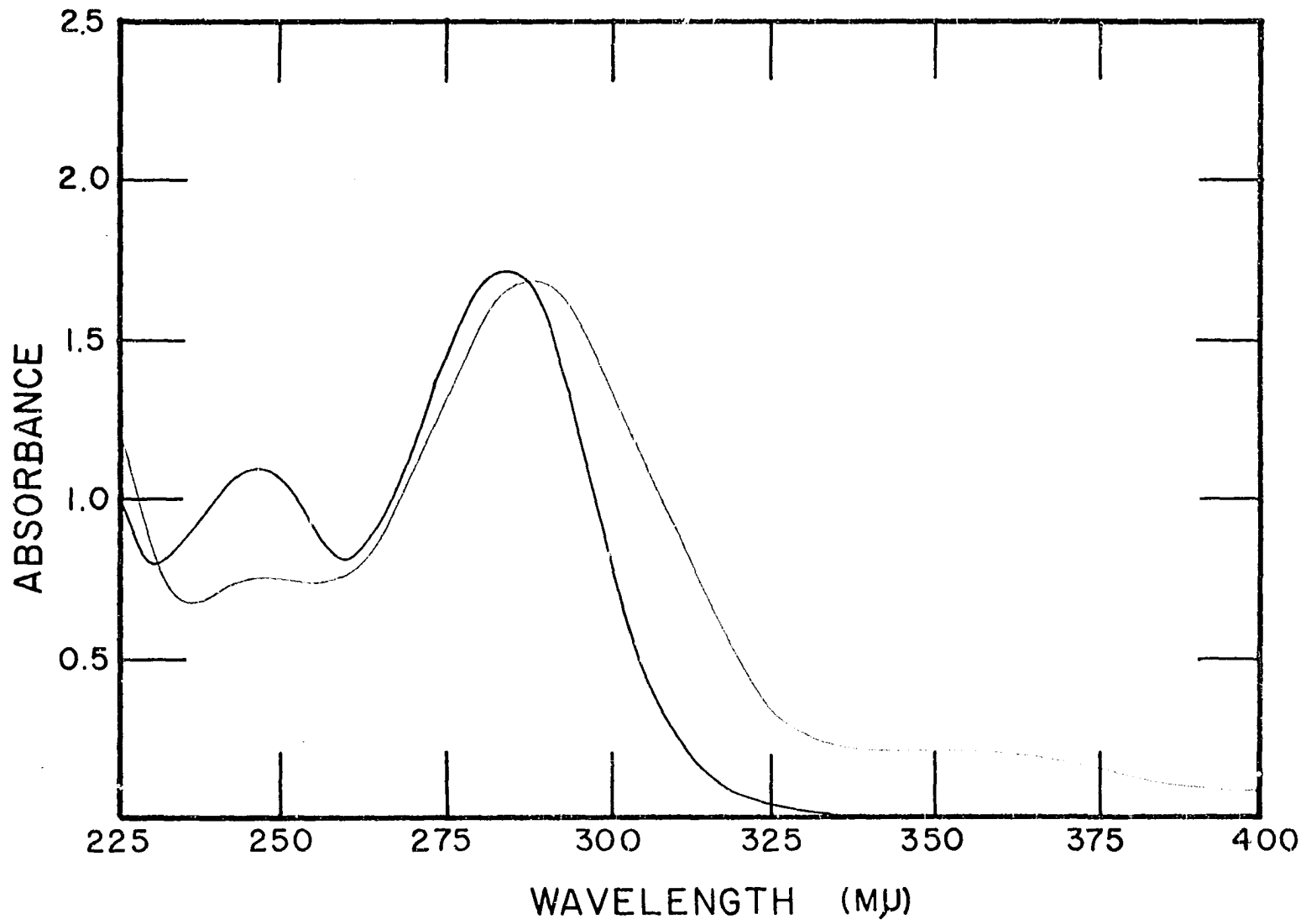
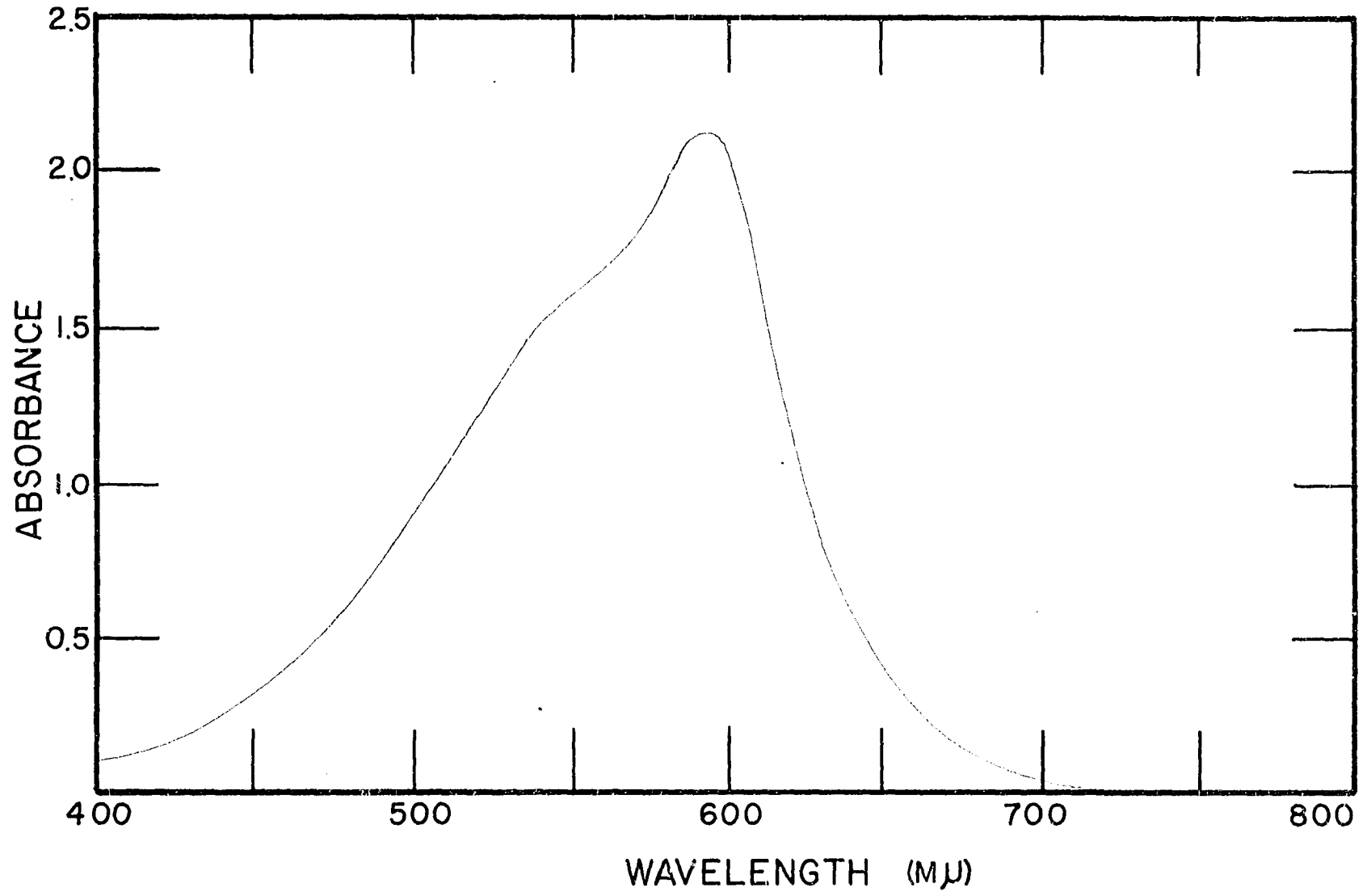


Figure 21. The visible spectrum of bis(2,4,6-tris(2'-pyridyl)-s-triazine)iron(II) chloride



of acidity upon the absorption spectra of these reagents as well as upon the stability of the complexes. This series of reagents contain a basic nitrogen which should be capable of attaching a proton. Thus one would expect a variation in the absorption spectrum which would be a function of the pH of the solution.

In order to determine the extent of this variation a 5×10^{-5} molar solution of the reagent was prepared by introducing 5 ml. of a 1×10^{-3} molar stock solution of the reagent into a 100 ml. volumetric flask. A volume of 5 ml. of a hydroxylammonium chloride solution (5%) was added and the solution diluted to a volume of approximately 90 ml. The pH of the solution was then adjusted to the desired value by means of hydrochloric acid or ammonium hydroxide. The pH of the solution was determined by means of a Beckman Model H-2 pH meter just prior to scanning the spectrum. The change in the spectrum was observed for each pH unit from a pH of 2 to a pH of 9. The observed variations are shown in Figure 22 for triamino-s-triazine; in Figure 23 for 2-pyridyl-4,6-diamino-s-triazine; in Figure 24 for 2-amino-4,6-dipyridyl-s-triazine; and Figure 25 for tripyridyl-s-triazine. Comparison of the spectra of the reagents in acid solution with that of the iron complex of these reagents indicates that the proton has the same effect on the ultraviolet spectrum as iron(II). However, the ability of iron(II) to produce an absorption band in the

Figure 22. The ultraviolet absorption spectrum of triamino-s-triazine in solutions of varying acidity

pH	1-3	—
pH	4	—
pH	5	—
pH	6	—

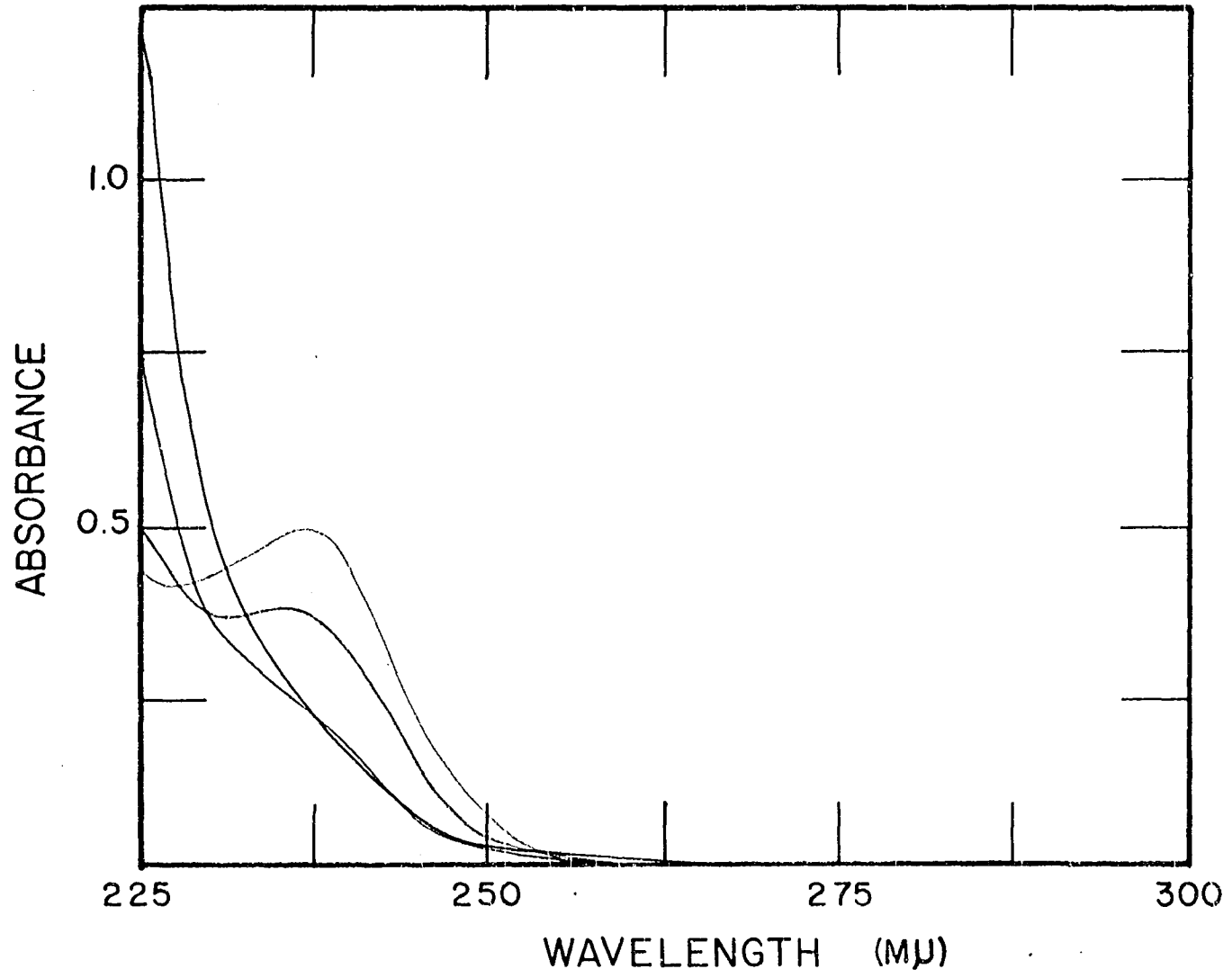


Figure 23. The ultraviolet absorption spectrum of 2-pyridyl-4,5-diamino-s-triazine in solution of varying acidity

pH	2	-----
pH	3	=====
pH	4	=====
pH	5-9	=====

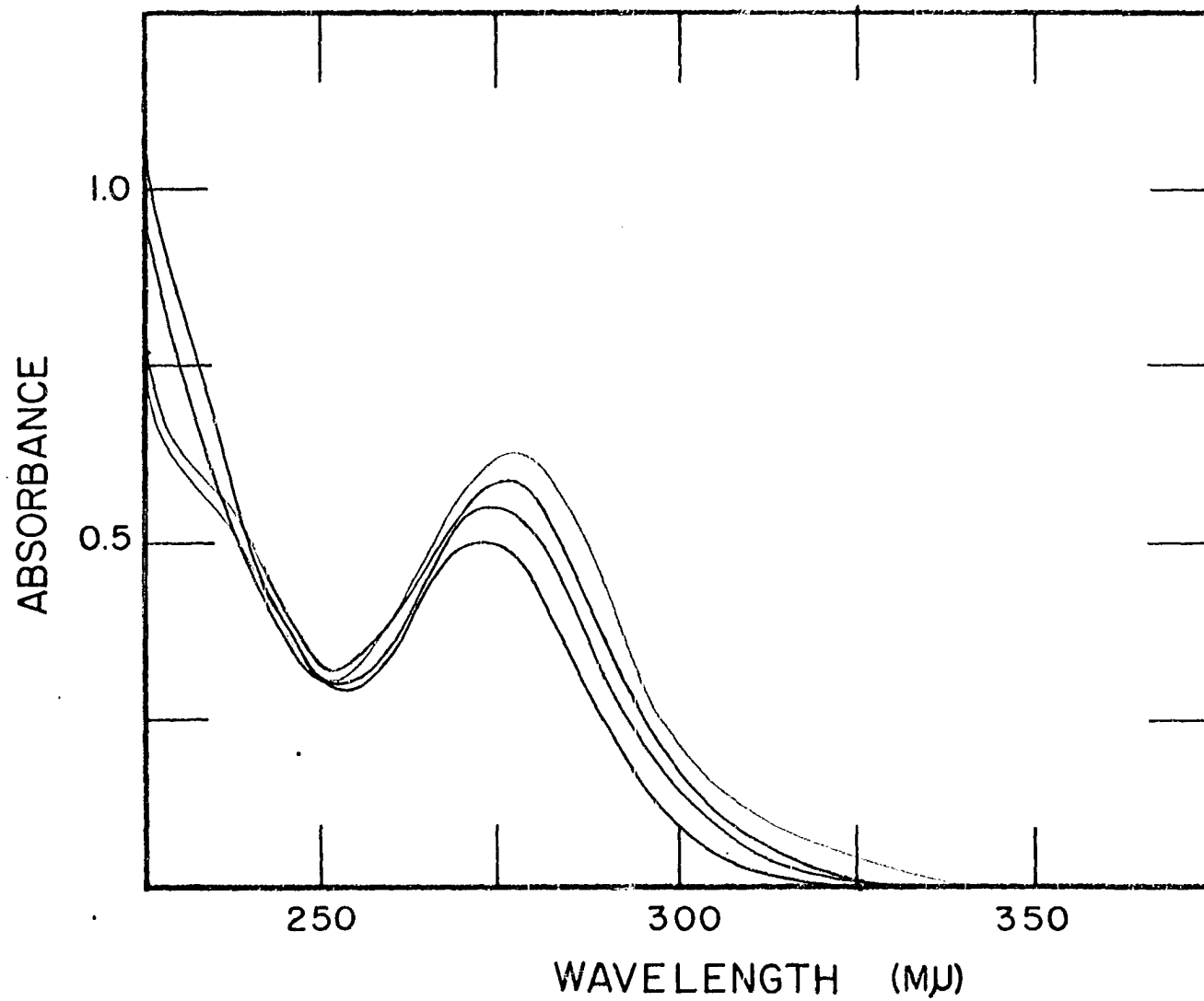


Figure 24. The ultraviolet absorption spectrum of 2-amino-4,6-dipyridyl-s-triazine in solutions of varying acidity

pH	2	_____
pH	3	_____
pH	4	_____
pH	5 - 9	_____

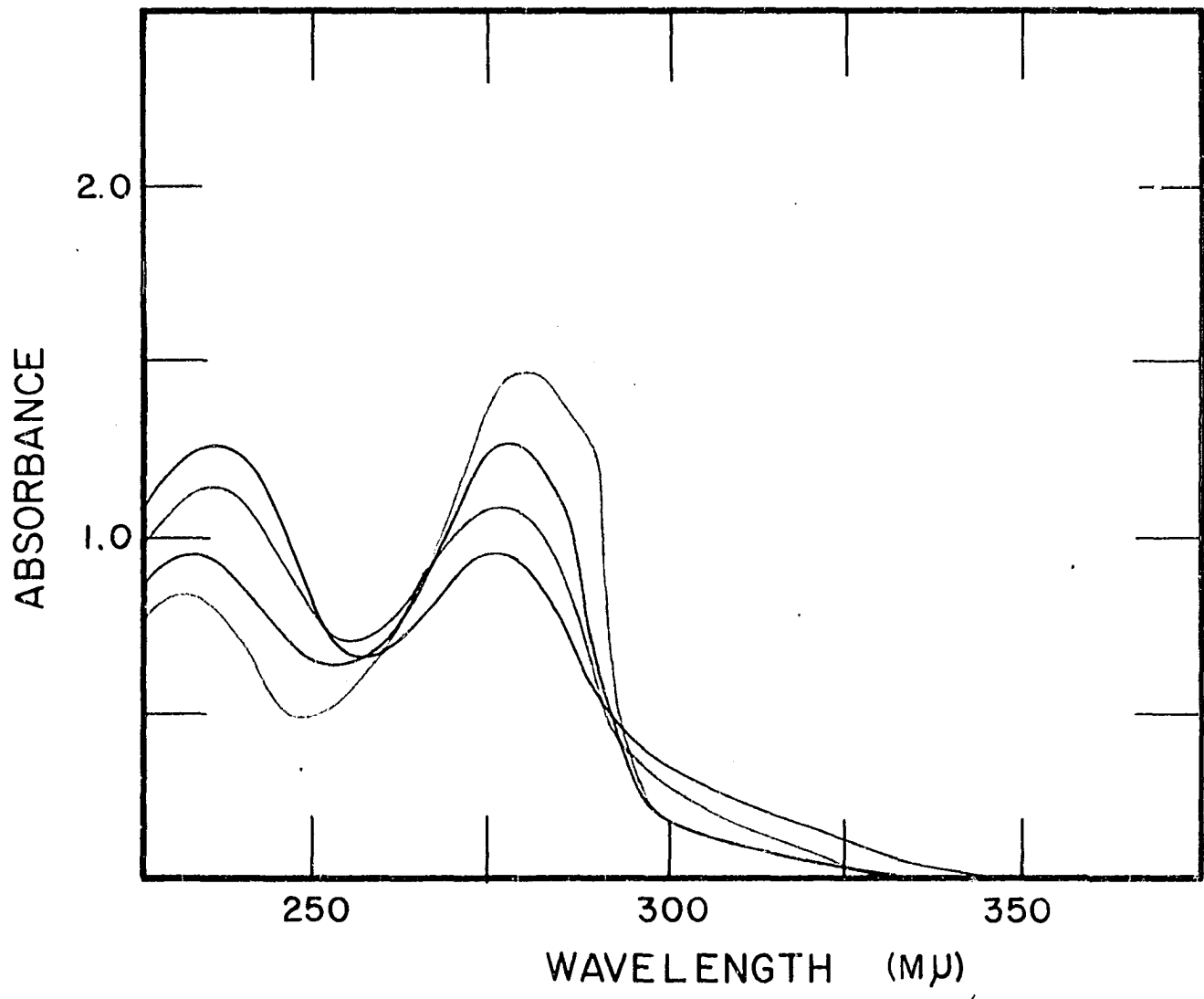
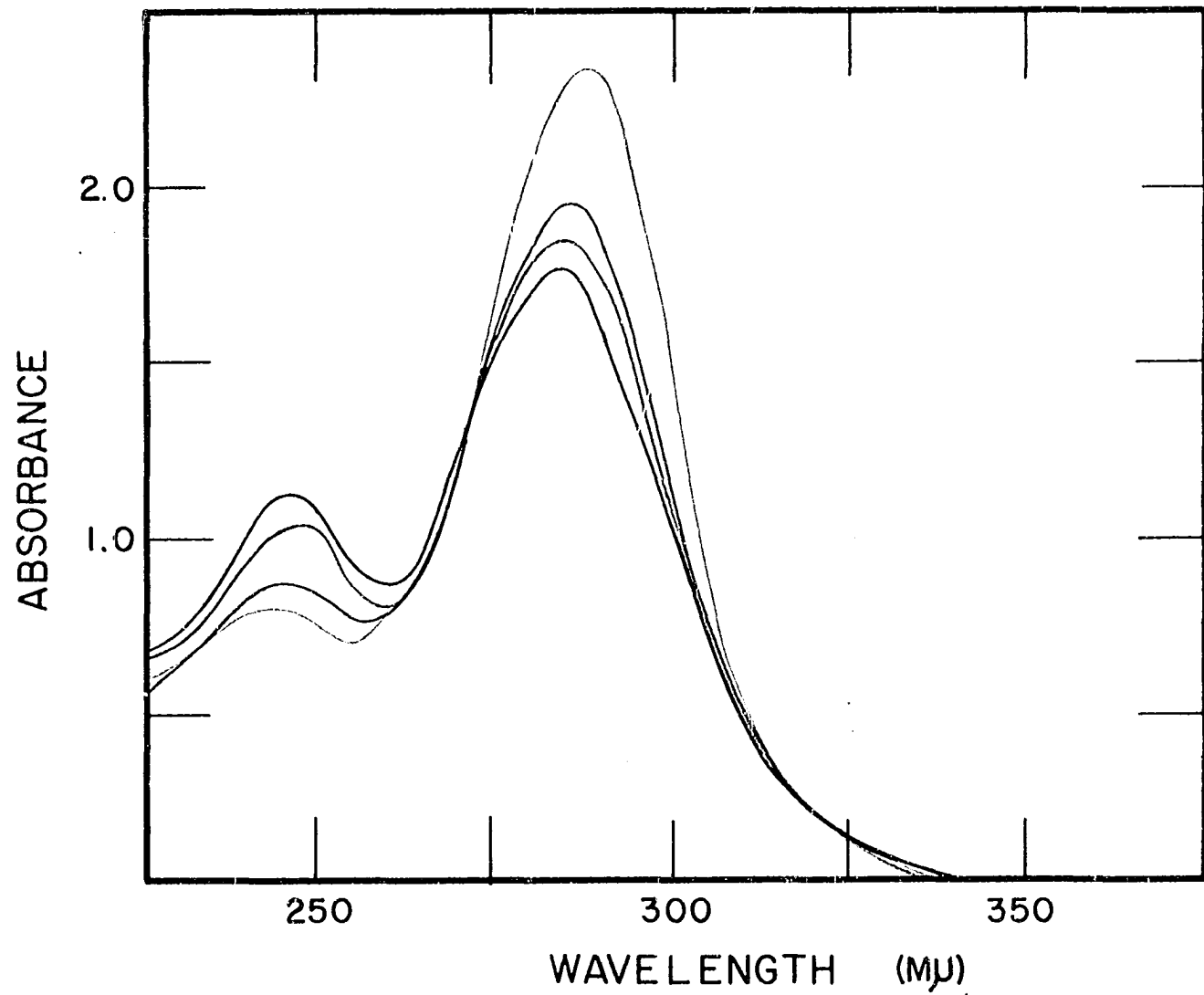


Figure 25. The ultraviolet absorption spectrum of tripyridyl-s-triazine in solutions of varying acidity

pH	2	----
pH	3	----
pH	4	----
pH	5-9	----



visible is unique. And the acidity, so long as it is maintained within certain limits, is without effect on this visible absorption.

In order to form the complex between iron and the 2-pyridyl-4,6-diamino-s-triazine the pH of the solution must be adjusted to a value very close to 6. In the case of the dipyridyl and tripyridyl substituted triazines the range of stability is much larger. These complexes being stable within the pH range of 4 to 9 with the best results occurring at a pH of 6.

The Metal Derivatives of Pyridyl Substituted Triazines

2-pyridyl-4,6-diamino-s-triazine

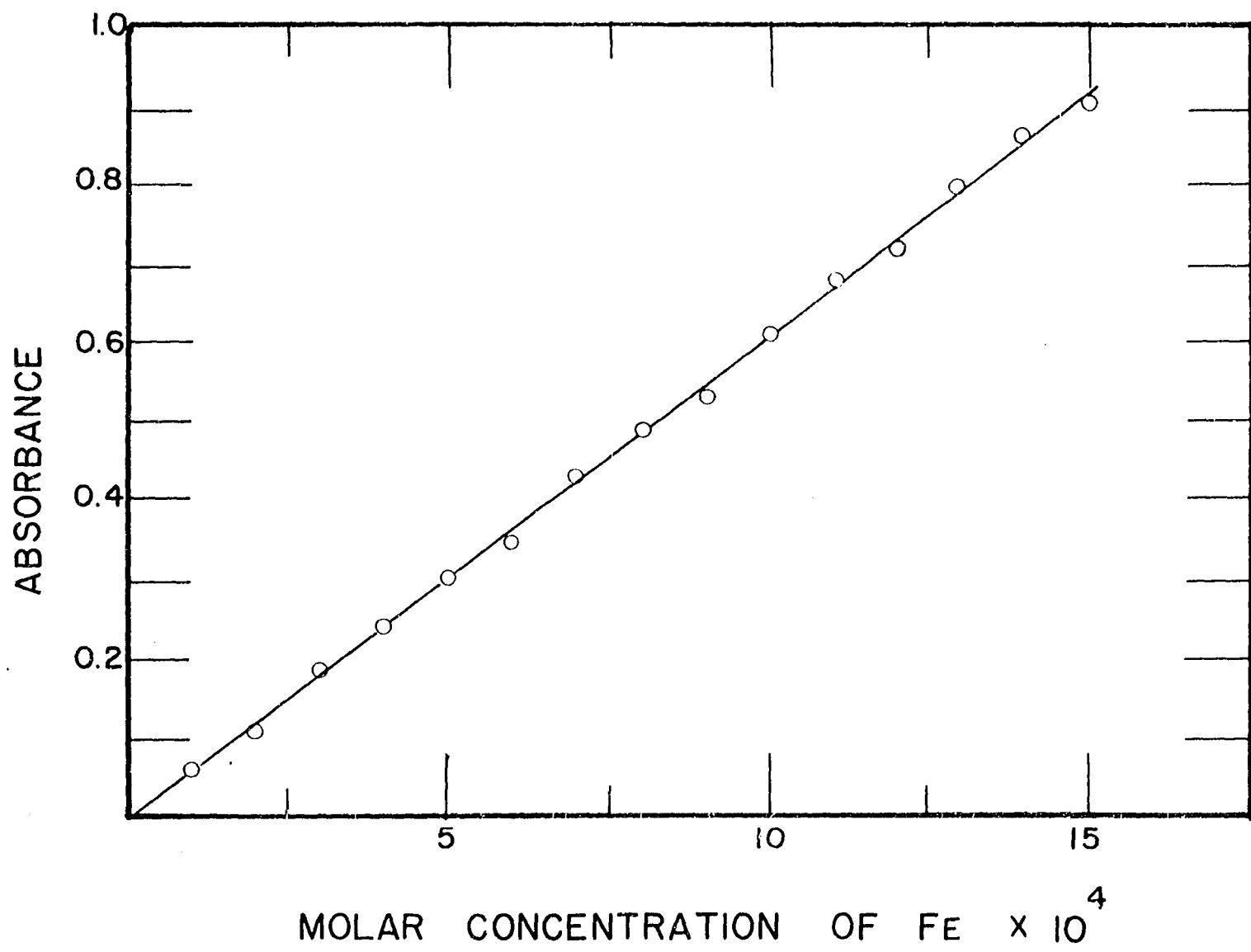
In order to determine the molar absorptivity and the applicability of Beer's Law to this complex stock solutions of iron(III) chloride and the reagent were prepared in the following manner. A solution which was approximately 0.1 molar in the free base was prepared by dissolving 2 g. of the free base in a little dilute hydrochloric acid and diluting the resultant solution to 100 ml. A 0.01 molar stock solution of iron(III) chloride was prepared by dissolving 0.5585 g. of electrolytic iron in hydrochloric acid and diluting the resultant solution to 1 l.

Quantities of between 1 and 15 ml. of this stock solution of iron(III) chloride were introduced into 100 ml. volumetric flasks. These solutions were then treated successively with the following reagents: a volume of 5 ml. of hydroxylammonium chloride solution (5%); 10 ml. of the reagent stock solution and finally 5 ml. of sodium acetate solution (5%). The contents of the flasks were then diluted to the mark and mixed. The absorbance of the solutions were then measured immediately against distilled water using a Beckman Model B spectrophotometer and 2 cm. cells. The need for haste in the measurements was caused by the tendency of the complex to precipitate from solution. A definite turbidity in the more concentrated solutions could be detected after a half hour. The results of this determination are reproduced in Figure 26.

The combining ratio of the ligand with iron(II) was determined by the method of continuous variations. For this purpose stock solutions of both the free reagent and iron(III) chloride were prepared with a molar concentration of 1×10^{-2} .

Quantities of the iron(III) chloride solution varying between 1 and 10 mls. were introduced into a series of 25 ml. volumetric flasks. A volume of 5 ml. of hydroxylammonium chloride solution (5%) was added to each of the flasks. Sufficient amounts of the reagent were added to bring the total of

Figure 26. Beer's law plot for tris-(2'-pyridyl)-4,6-diamino-s-triazine)-iron(II)
Wave length: 454 mu; cell length 2 cm.



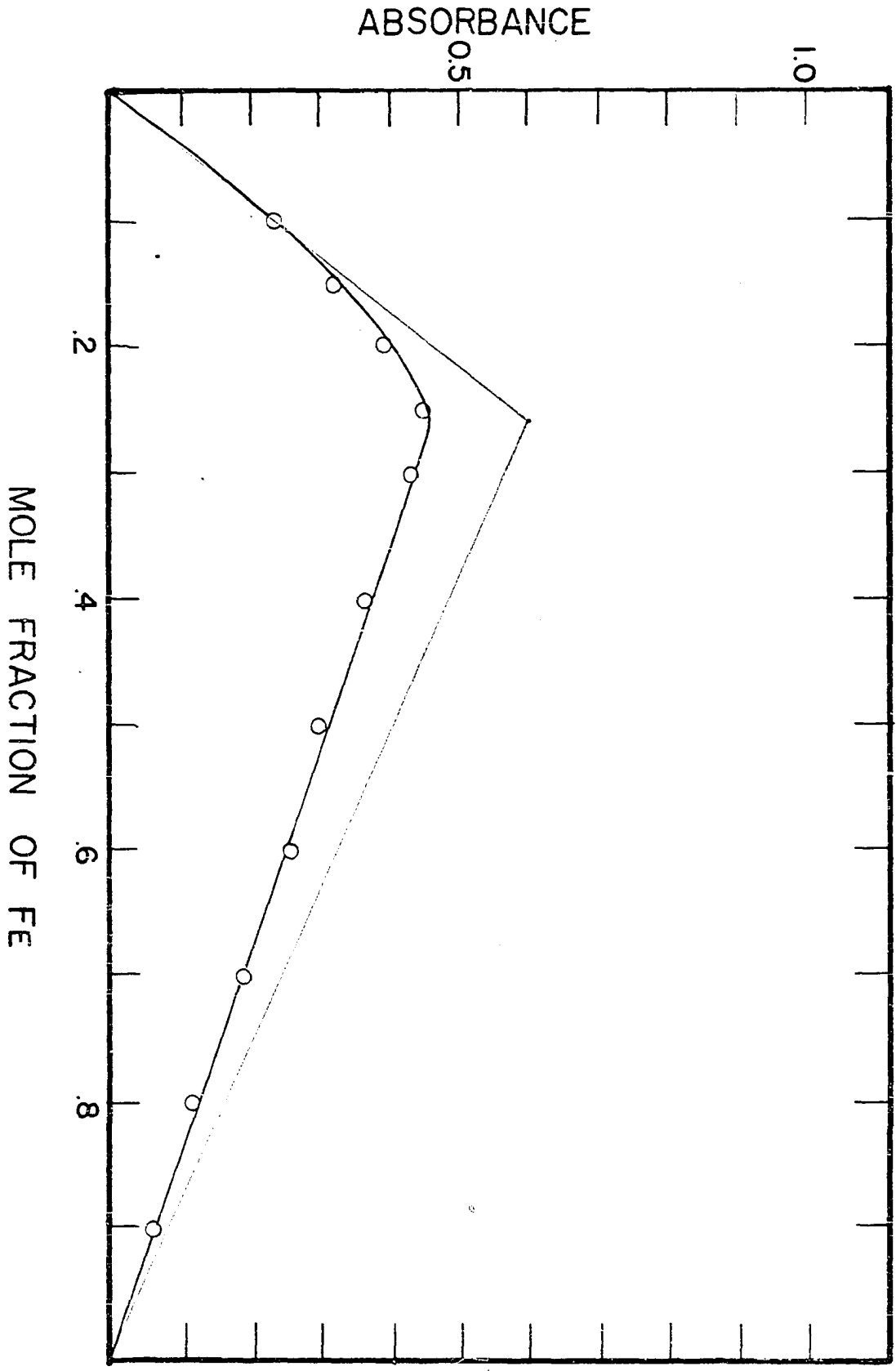
the iron and the reagent concentration to 4×10^{-3} molar when the solution was at its final volume of 25 mls. Each flask was treated with 5 mls. of sodium acetate solution (5%) and the contents were diluted to the mark and mixed. The absorbance of the solution was then measured immediately against distilled water using a Beckman Model B spectrophotometer and 2 cm. cells. A plot of the absorbance vs. the mole fraction of iron, Figure 27, indicates that three molecules of the ligand combine with a single molecule of iron.

2-amino-4,6-dipyridyl-s-triazine

The stock solutions of iron and the reagent used in the determination of molar absorptivity and the applicability of Beer's Law to the complex were prepared as follows. A 1.002×10^{-2} molar solution of iron(III) chloride was prepared by dissolving 0.5596 g. of electrolytic iron in hydrochloric acid and diluting the resultant solution to one liter. A volume of 10 ml. of this solution was then diluted again with distilled water to give a solution of 1.002×10^{-4} molar ferric chloride. A solution of the reagent was prepared which contained 1 g. of the reagent in 100 ml. of distilled water. A few drops of hydrochloric acid were added to keep the reagent in solution.

Quantities between 5 and 40 ml. of the stock solution

Figure 27. Job's plot for 2-(2'-pyridyl)-4,6,-diamino-s-triazine and iron
--- Theoretical
— Actual

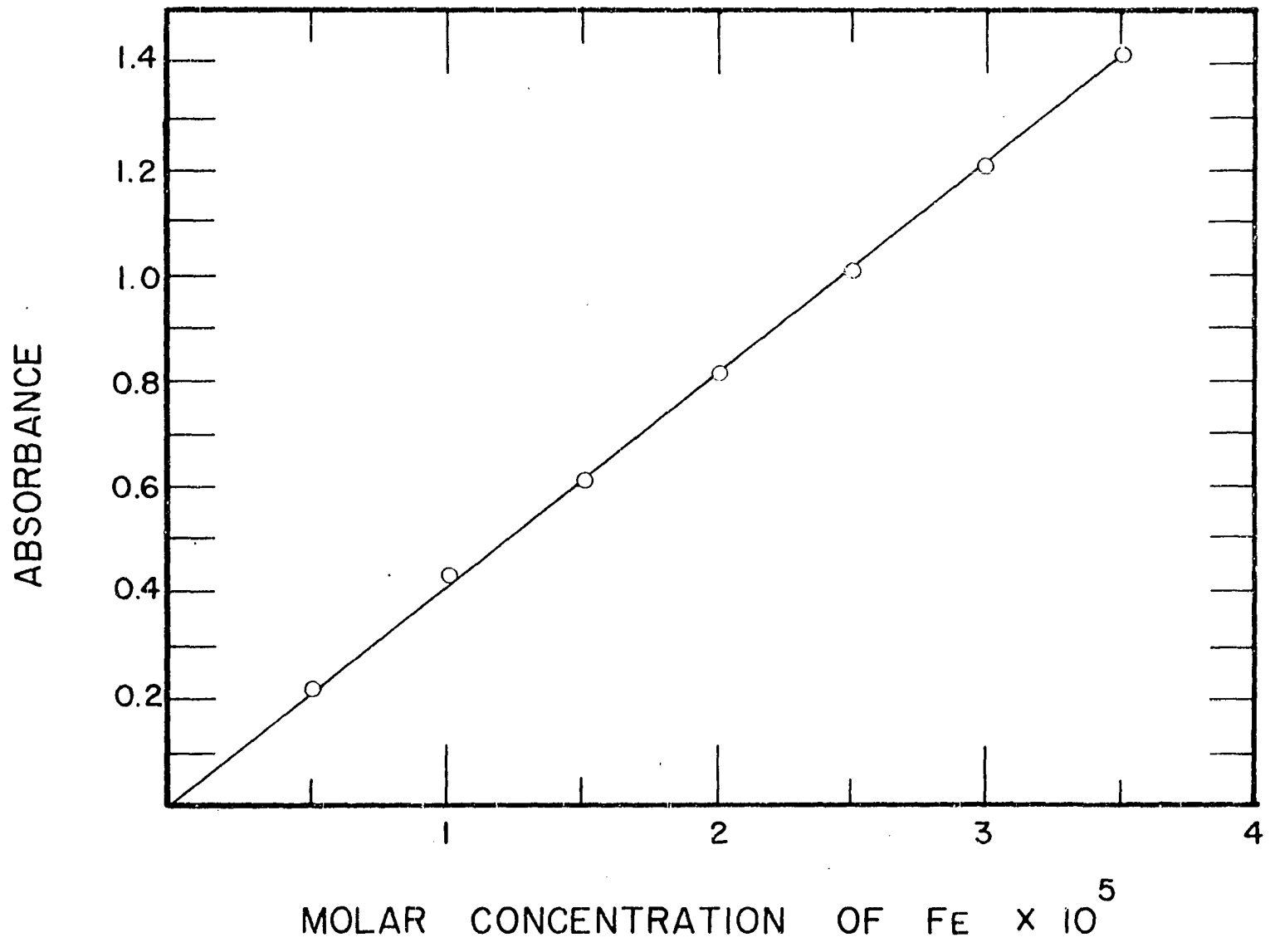


of iron(III) chloride were introduced into a series of 100 ml. volumetric flasks. These solutions were then treated successively with the following reagents; 5 ml. of hydroxylammonium chloride solution (5%), 10 ml. of the 2-amino-4,6-bis-(2'-pyridyl)-s-triazine solution (1%), and 5 ml. of the sodium acetate solution (5%). The contents of the flasks were then diluted to the mark and mixed. The absorbance of the solutions were then measured against distilled water using the Cary Model 12 spectrophotometer and 5 cm. cells. The results of this determination are reproduced as Figure 28.

The combining ratio of the ligand with iron(II) was determined by the method of continuous variations. For this purpose stock solutions of both the free reagent and iron(III) chloride were prepared with a molar concentration of 1.002×10^{-3} .

Quantities of the iron(III) chloride solution varying between 1 and 20 ml. were introduced into a series of 100 ml. volumetric flasks. A volume of 5 ml. of hydroxylammonium chloride solution (5%) was added to each of the flasks. Sufficient amounts of the reagent were then added to bring the total of the iron and the reagent concentration to 2.004×10^{-4} molar when the solution was at its final volume of 100 ml. The contents of each flask were then treated with 5 ml. of sodium acetate solution (5%) and then diluted to the mark

Figure 28. Beer's law plot for bis(2-amino-4,6-bis(2'-pyridyl-s-triazine)-
iron(II)
Wavelength: 497 m μ ; cell length: 5 cm.

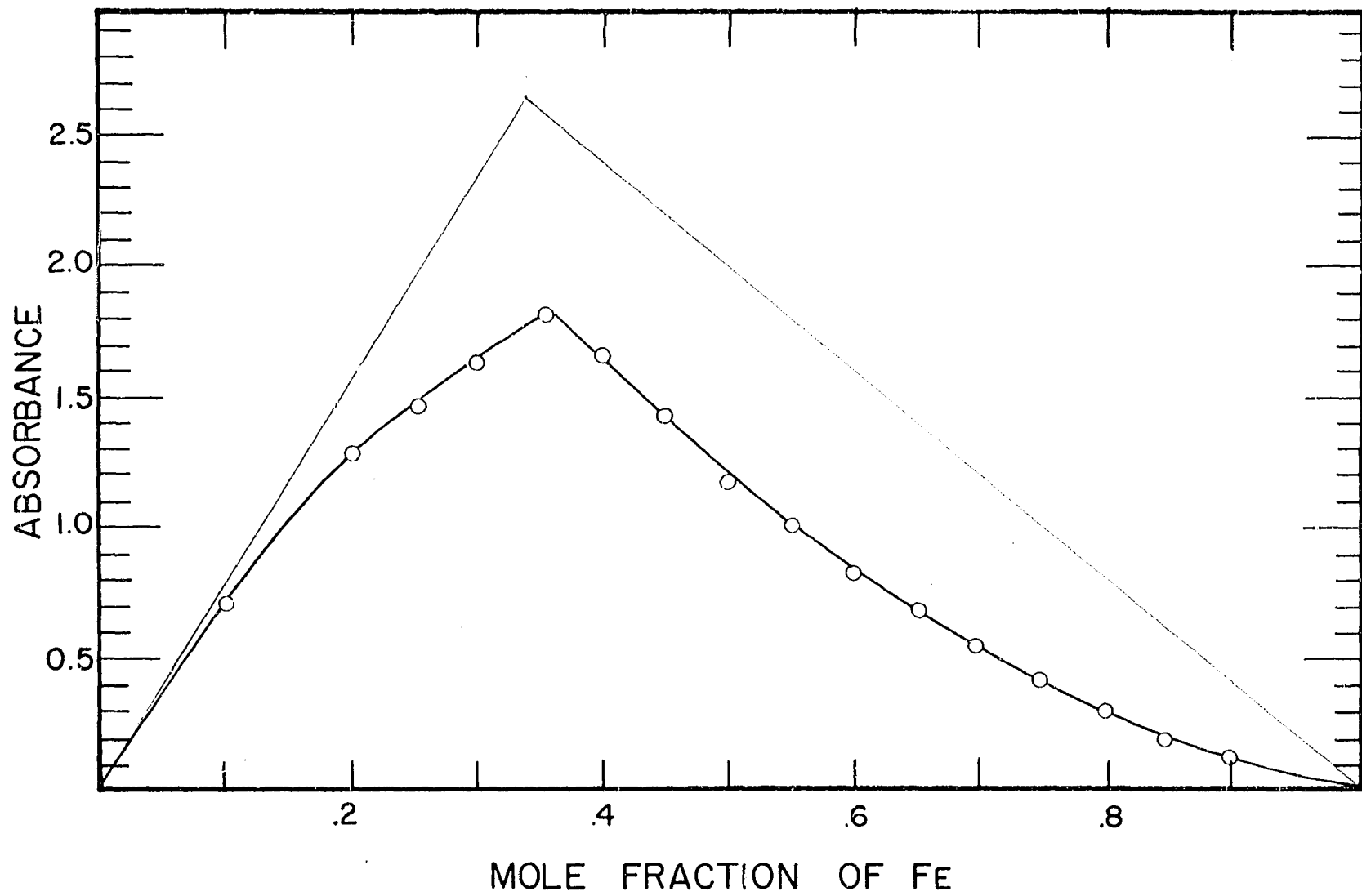


and mixed. The absorbance of this series of solutions was then measured against distilled water using the Cary Model 12 Spectrophotometer and 5 cm. cells. A plot of the absorbance vs. the mole fraction of iron, Figure 29, indicates that two molecules of the ligand combine with a single molecule of iron.

The curvature of the points in Figure 29 indicate that there might be a second type of complex produced. This possibility was investigated by means of a simulated spectrophotometric titration. The term simulated titration is used inasmuch as several solutions were used in the preparation of the titration curve. This technique eliminates the necessity of a correction due to the dilution of the solution with each addition of titrant. In practice this simulated titration was carried out by adding 20 ml. of a 4.008×10^{-4} molar solution of the 2-amino-4,6-bis(2'-pyridyl)-s-triazine to a series of 100 ml. volumetric flasks. To each flask was then added a volume of iron(III) chloride solution, 1.002×10^{-4} molar, varying between 5 and 50 mls. A more concentrated iron(III) chloride solution, 4.008×10^{-4} molar, was used for those points on the graph above 50 ml. of titrant and the concentrations are expressed in terms of a volume in ml. of 1.002×10^{-4} molar iron(III) chloride. The iron was reduced with 5 ml. of a hydroxylammonium chloride solution (5%) and the solution buffered with 5 mls. of a sodium acetate solution (5%). The

Figure 29. Job's plot for 2-amino-4,6-bis(2'-pyridyl)-s-triazine and iron(II)

— Theoretical
— Actual

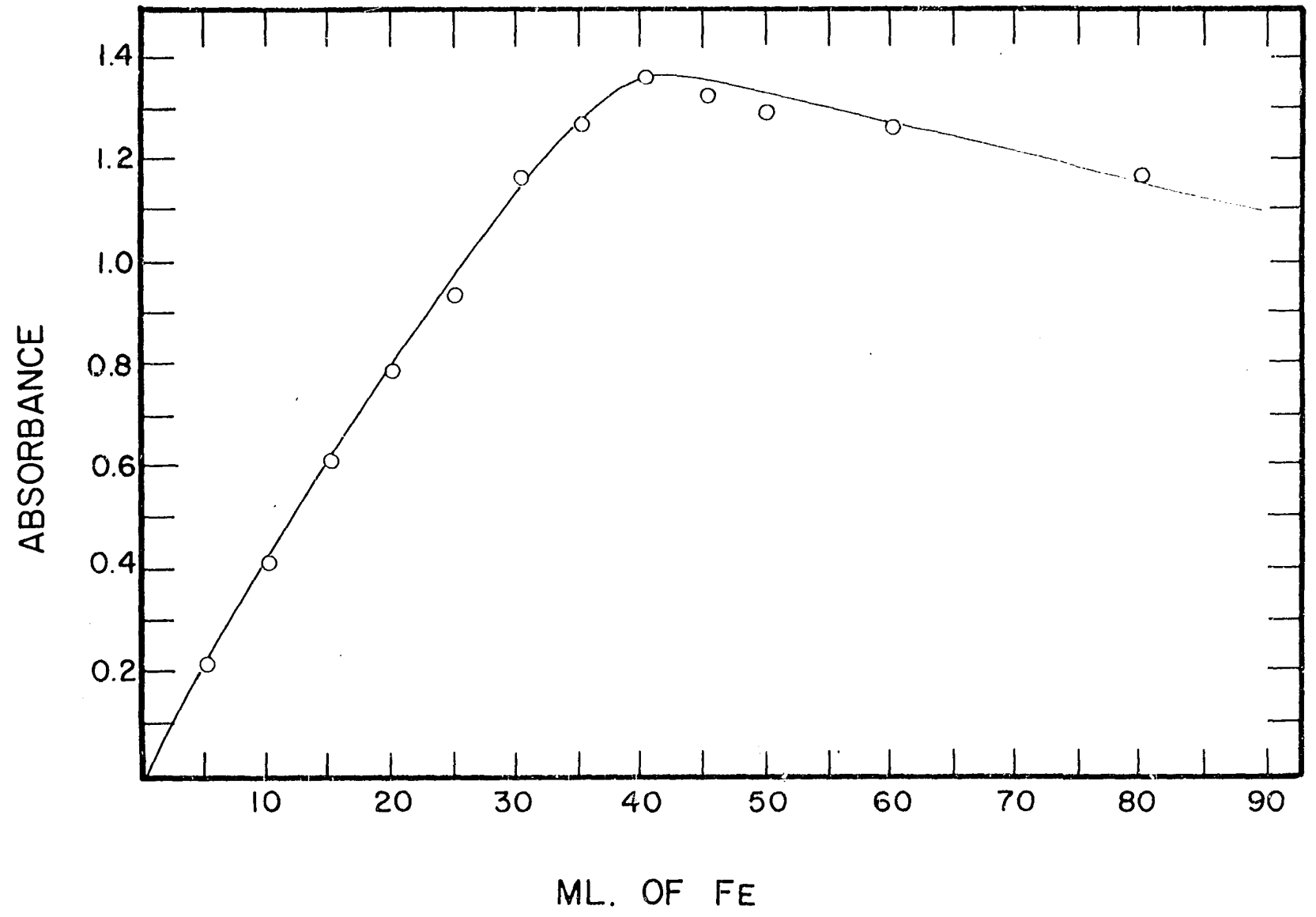


contents of each flask were diluted to the mark and mixed. The absorbance of each solution was then measured with a Cary Model 12 spectrophotometer using 5 cm. cells and a blank solution of distilled water. The results of this experiment are reproduced as Figure 30. The decrease in the absorbance beyond the equivalence point, 40 ml. of iron(III) chloride, is a strong indication of the presence of a complex with a combining ratio of one to one.

In order to definitely establish that the complex exists in a two to one ratio an attempt was made to isolate the compound in crystalline form and analyze it directly.

The preparation of the crystalline complex was accomplished in the following manner. An aqueous solution of the complex was prepared and treated with a solution of sodium perchlorate. The perchlorate salt of the complex was then extracted into nitrobenzene. The nitrobenzene solution was then washed several times with an aqueous solution of sodium perchlorate and finally once with distilled water. The volume of the nitrobenzene solution was then reduced by evaporation in vacuum. The concentrated solution was filtered and added dropwise with good stirring to a volume of light petroleum ether four times that of the nitrobenzene. A dark blue powder precipitated and was filtered from the resultant solution. This powder was placed in a Soxhlet extractor and extracted with

Figure 30. Titration curve of 2-amino-4,6-bis(2'-pyridyl)-s-triazine with
iron(II)
Concentration of 2-amino-4,6-bis-2' pyridyl-s-triazine 8.160×10^{-3}
millimoles
Concentration of the titrant 1.002×10^{-4} molar



light petroleum ether to remove any excess of the organic reagent or nitrobenzene which might have adhered to the surface of the powder. The powder was then dissolved in a minimum quantity of hot glacial acetic acid, from which it deposited upon cooling as dark violet needle shaped crystals. These crystals were analyzed for their components, iron, triazine, and perchlorate.

The direct analysis for the perchlorate ion on a semi-micro scale is difficult and therefore, the perchlorate ion was reduced to the chloride ion in a parr bomb, by the method recommended by Crump and Johnson. The chloride was then determined by the Volhard procedure.

In the procedure recommended by Crump and Johnson advantage is taken of the catalytic effect of the perchlorate ion on the oxidation of organic material (24). In its ordinary usage the Parr bomb is charged with sodium peroxide, sugar, the sample and a small quantity of an alkali perchlorate. For the present purpose the charge is the same with the exception that the perchlorate is omitted. After firing the bomb the contents were leached with deionized water, acidified with dilute nitric acid and treated with a measured amount of a standard silver nitrate solution. The excess silver nitrate was determined by a back titration with standard potassium thiocyanate

to the iron(III) thiocyanate end point. Four samples were analyzed by this scheme and the results obtained were as follows: 24.1 %, 23.8 %, 24.2 % and 24.1 % perchlorate present.

The crystals were next analyzed for their iron content in the following manner. Two samples of 7.20 and 7.49 mg. of the complex were taken and dissolved in 250 ml. of water. A 100 ml. aliquot of this stock solution was then treated with nitric and perchloric acids to destroy the organic matter present, and then with sulfuric acid to remove the perchloric acid. The sample was evaporated to near dryness with the sulfuric acid and then taken up again in deionized water. It was treated with 5 mls. of hydroxylammonium chloride solution (5%), 5 mls. of 1,10-phenanthroline solution (1%) and 5 mls. of sodium acetate solution (5%). The solutions were diluted to 100 mls. and the absorbance of each was measured with a Beckman Model DU spectrophotometer using 1 cm. cells and distilled water for a blank. By comparison to a standard curve the iron content was determined to be 6.45% and 6.56% in the two samples.

The triazine portion of the molecule was determined spectrophotometrically by taking advantage of the fact that at a constant pH there are several points in the ultraviolet region of the spectrum where the molar absorptivity of the complex and the free reagent are identical. Thus, an absorp-

tivity measurement at one of these points would measure the triazine content of the solution regardless of whether the material in solution was complexed with iron or in the free state. In order to test this idea, several spectra were run using the same concentration of triazine but different amounts of iron. Such a group of spectra are reproduced in Figure 31. They were obtained by recording the ultraviolet spectrum of the solutions used in the spectrophotometric titration of 2-amino-4,6-bis(2'-pyridyl)-s-triazine with iron. It should be noted that there is a true isocabsorptive point at 235 m μ which might serve for this analysis. In order to determine the effect of the concentration of the triazine on the absorptivity at this particular wavelength a series of solutions were prepared in the following manner. Volumes of 10 ml., 20 ml., 30 ml. and 40 ml. of a 1×10^{-3} molar solution of the free base were introduced into a series of four 100 ml. volumetric flasks. Each of the flasks was then treated with 5 ml. of a hydroxylammonium chloride solution (5%) and 5 ml. of a sodium acetate solution (5%). The contents of the flasks were then diluted to the mark and mixed. A second series of solutions containing identical quantities of the above materials plus 10 ml. of a 1×10^{-3} molar solution of iron(III) chloride was also prepared. The absorption spectra of these solutions were then recorded with a Cary Model 12 spectrophotometer using 1 cm. cells and a blank solution of distilled water. These

Figure 31. The ultraviolet spectrum of a series of solutions containing identical quantities of reagent but different quantities of iron

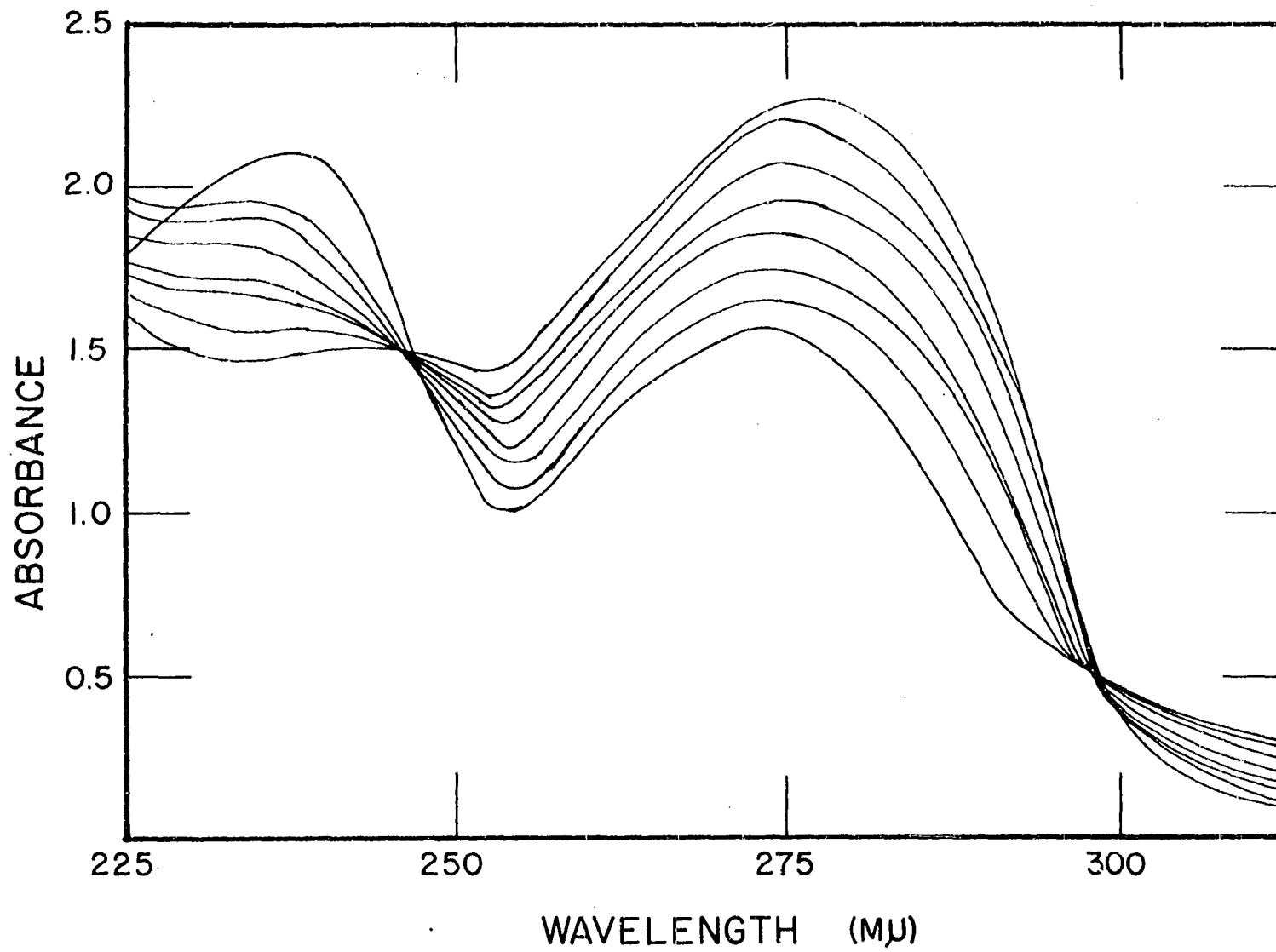


Figure 32. The effect of different concentrations of triazine on the absorptivity of the solution in the ultraviolet

	Triazine	Fe
1 - —	1×10^{-4} molar	
2 - —	2×10^{-4} molar	
3 - —	3×10^{-4} molar	
4 - —	4×10^{-4} molar	
1 - ---	1×10^{-4} molar	1×10^{-4} molar
2 - ---	2×10^{-4} molar	1×10^{-4} molar
3 - ---	3×10^{-4} molar	1×10^{-4} molar
4 - ---	4×10^{-4} molar	1×10^{-4} molar

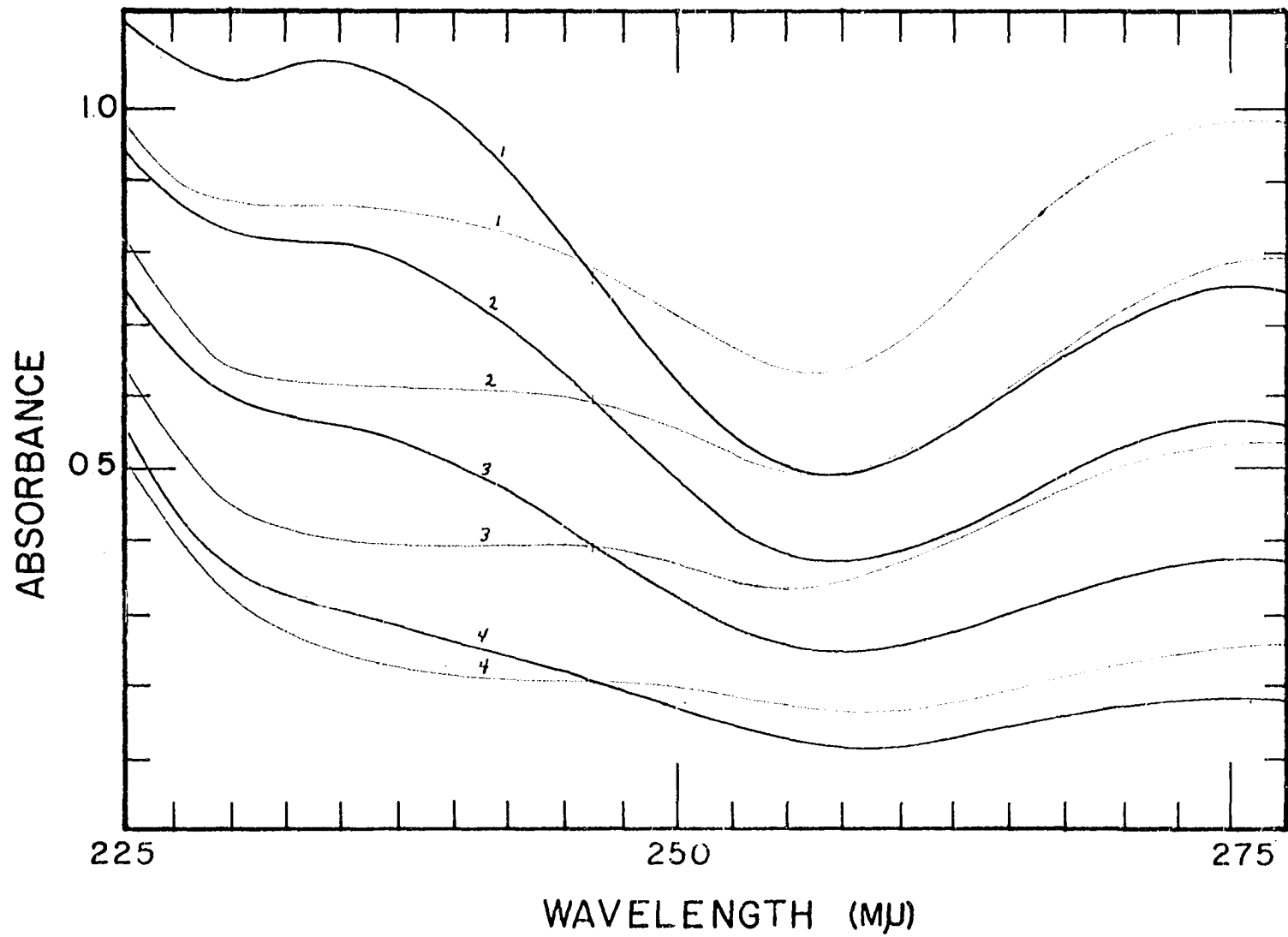
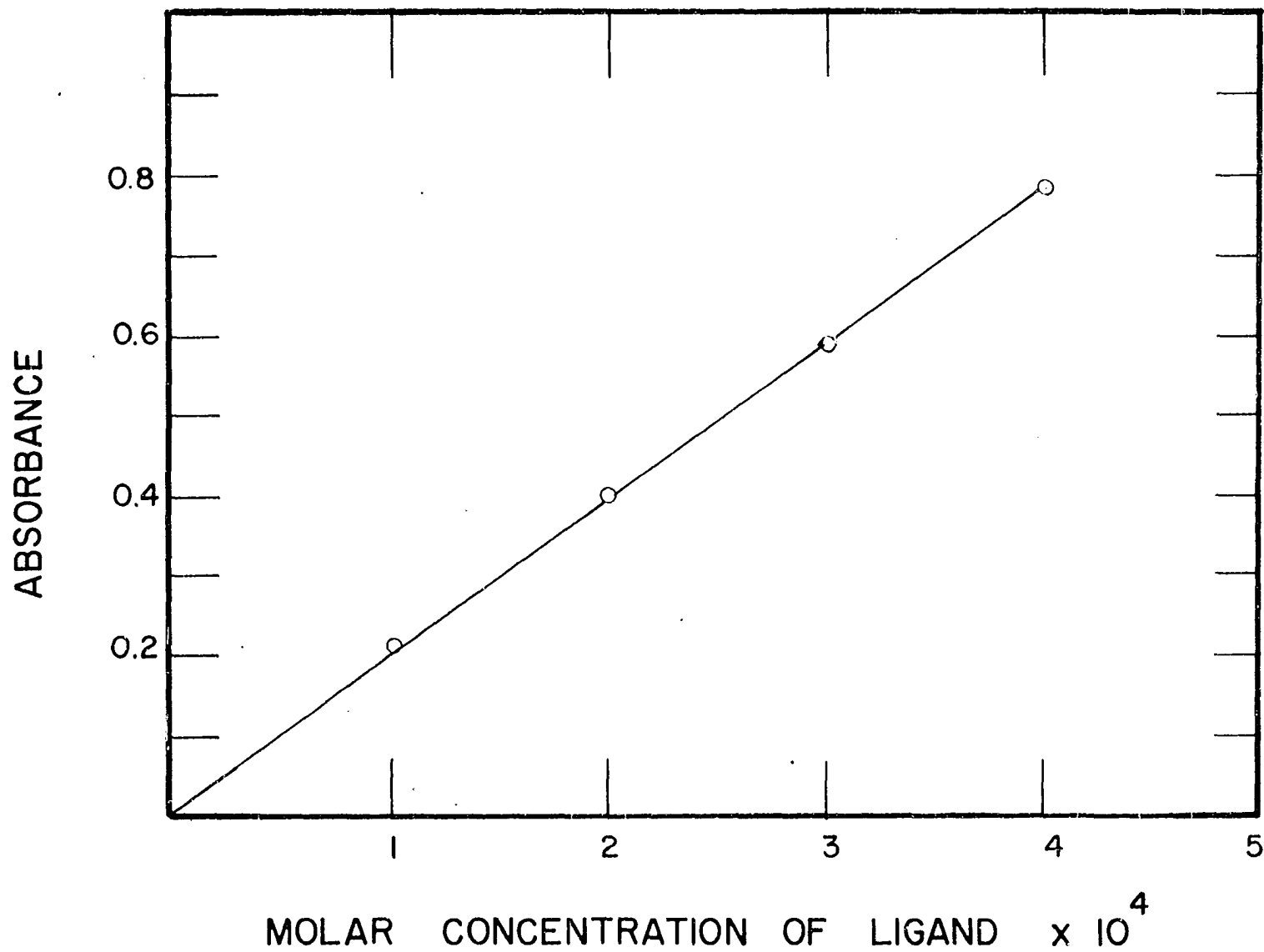


Figure 33. Beer's law plot for triazine at 235 m μ



spectra are reproduced as Figure 32. The variation of the absorptivity of the solutions with the concentration of the triazine is also given as Figure 33.

With the method thus established, the amount of triazine in the complex was determined by measuring the absorptivity of the stock solutions used for the determination of iron. The results of these two determinations gave a value of 60.5% and 61.5% for the percentage of 2-amino-4,6-bis(2'-pyridyl)-s-triazine in the crystals.

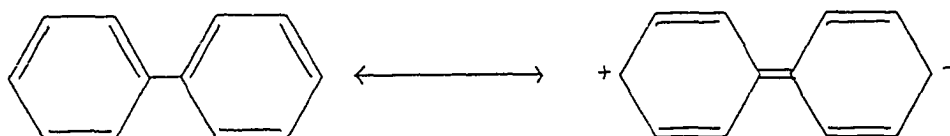
2,4,6-tris(2'-pyridyl)-s-triazine

No experimental work was done on the complex resulting between this compound and iron(II), as the properties of this particular complex together with its analytical applications are being studied by another worker. Any conclusions drawn on this compound are taken from data provided by him.

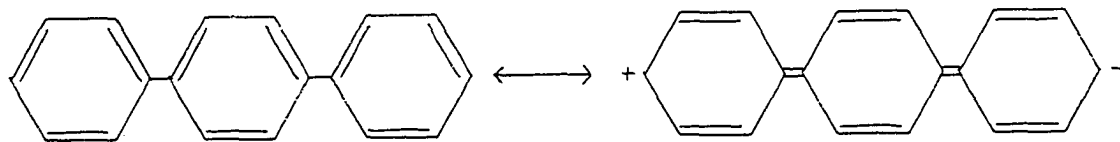
RESULTS AND CONCLUSIONS

The ultraviolet spectra of the polypyridyl compounds studied show many of the same characteristics as their polyphenyl analogues. Thus the interpretation of the spectrum of these compounds will rely heavily upon the interpretation placed upon the spectrum of their polyphenyl counterparts.

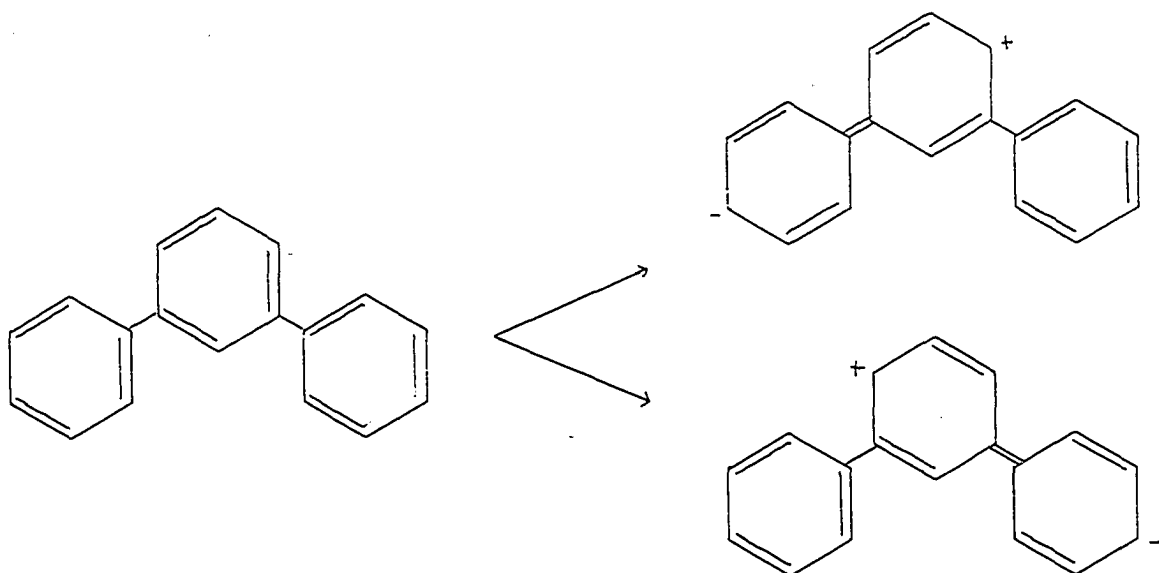
Biphenyl exhibits a single absorption peak at 247 m μ with a molar absorptivity of 20,000. The size of the molar absorptivity indicates that this must be a conjugation band and it is attributed to the transformation between the ground state and the para-quinoid excited state, i.e.:



This assignment is corroborated by the effect of a second phenyl substituent. If the second phenyl group is attached para to the position of attachment of the first phenyl group, the length of the possible conjugation chain is increased and the energy required for the transition is decreased. The net result is that the absorption peak undergoes both a bathochromic and a hyperchromic shift. The transition producing the absorption peak in p-terphenyl then is considered to be the following:



On the other hand when the phenyl group is attached in a meta position no such decrease in the energy is possible as the two groups then can not conjugate, and the two must act independently of the other. However, as there are now two possibilities of excitation, the molar absorptivity of the compound should increase. These two possibilities for excitation are:



In fact the observed molar absorptivities of the meta terphenyl is twice that observed for the biphenyl.

In the case of the polypyridyls the situation is slightly more complicated. Experimentally there is observed not the

single peak of the polyphenyls but rather two peaks. As nearly all of the polypyridyl compounds investigated showed these two peaks in the ultraviolet, a deviation from this should be considered the exception rather than the rule. The position of the peaks have been found to be nearly constant throughout the entire series of compounds investigated. Thus, it is concluded that the same type of transition is responsible for a particular absorption peak in the spectrum of these compounds. Therefore, the transition accounting for the absorption peak at 240 m μ will be designated as "Transition I" and that which accounts for the absorption at 275 m μ as "Transition II".

The fact that the π electron skeletons of the polyphenyl and polypyridyl analogues are approximately the same, and that both of these series of compounds have an absorption peak in the vicinity of 240 m μ leads to the conclusion that this absorption peak is probably caused by the same type of transition. Inasmuch as the transition in the case of the polyphenyl series is known to be due to a transition from the ground state to a para-quinoid type of structure it is probable that the transition in the polypyridyl system designated as "Transition I" is of the same type, i.e.



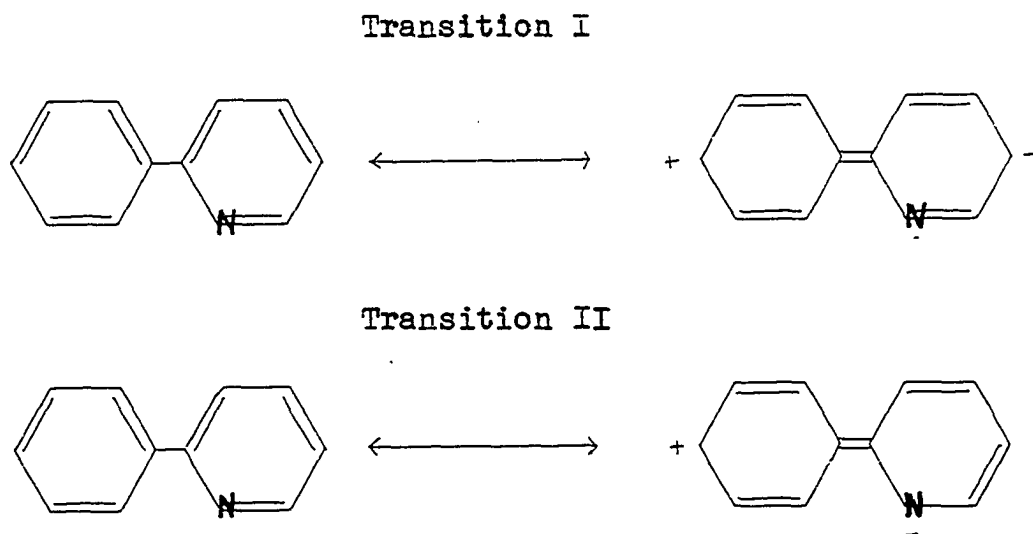
Inasmuch as the only difference between the polyphenyl and the polypyridyl system is the presence of the ring nitrogen atoms, and since the presence of the nitrogen atoms gives rise to a new absorption band, the transition accounting for this new band must involve the nitrogen atoms. The change most probably results from the greater electronegativity of the nitrogen atom. The molar absorptivity indicates that this peak is also a conjugation peak, and therefore, one would conclude that the nitrogen was in some manner entering into conjugation with the second pyridine ring. The simplest transition of this type would then be a transition from the ground state to an ortho-para-quinoid structure for an excited state. Thus the transition designated as "Transition II" is postulated as being the following:



In order to test this postulate the spectra of the phenylpyridines were examined in an attempt to determine the effect that the relative position of the nitrogen atom and the phenyl group would have upon the spectrum of the compound. It was thought that with but a single nitrogen atom the effect would be most pronounced. 2-Phenylpyridine (Figure 2) exhibits two absorption peaks, one at $247 \text{ m}\mu$ and the other at $275 \text{ m}\mu$.

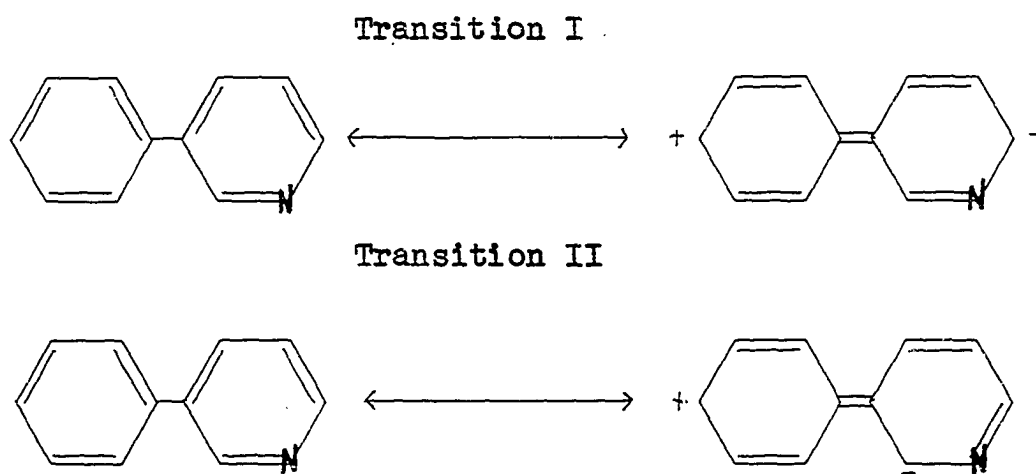
Thus the two transitions are represented in this molecule.

It should also be noted that the two peaks have about an equal molar absorptivity, indicating approximately equal transition probability. The transitions accounting for these two peaks are written as:



With the nitrogen atom and the phenyl group situated relative to each other as in 3-phenylpyridine there are again two peaks as is evidenced in Figure 2. The wavelengths at which these absorption bands occur are the same as before, namely, 247 and 275 $m\mu$. Thus one could say that the same type of transition is again responsible for these peaks. There is, however, an important difference between the two spectra. The molar absorptivities of the two peaks in the case of the 3-phenylpyridine are by no means equal. The peak corresponding to "Transition I" is enhanced over that observed in the case of

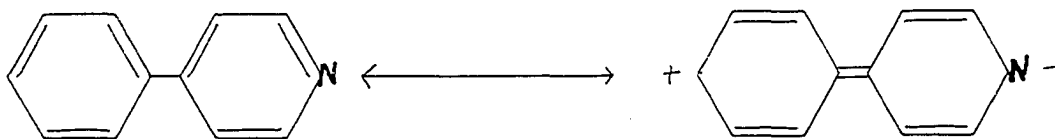
2-phenylpyridine whereas, the peak ascribed to "Transition II" is considerably diminished when compared to that observed for 2-phenylpyridine. This diminution is caused by the decrease in the electronegativity of the atom in the pyridine nucleus ortho to the phenyl group. The transitions which account for the two peaks in 3-phenylpyridine are then written as:



Finally when the nitrogen atom and the phenyl group are situated para to each other as in the case of 4-phenylpyridine a new situation arises. The spectrum of 4-phenylpyridine shows but a single peak, at a wavelength of 260 m μ . This, happily, is the proverbial exception which proves the rule. With the nitrogen located in a position para to the phenyl group the electronegativity of the positions ortho to the phenyl group is so reduced that a transition involving that position is no longer probable. Indeed, the greater electronegativity of

the nitrogen atom located in the para position reduces the energy difference between the ground and the excited state of the para quinoid transition to such an extent that a bathochromic shift is observed for this transition. The transition spoken of is represented as:

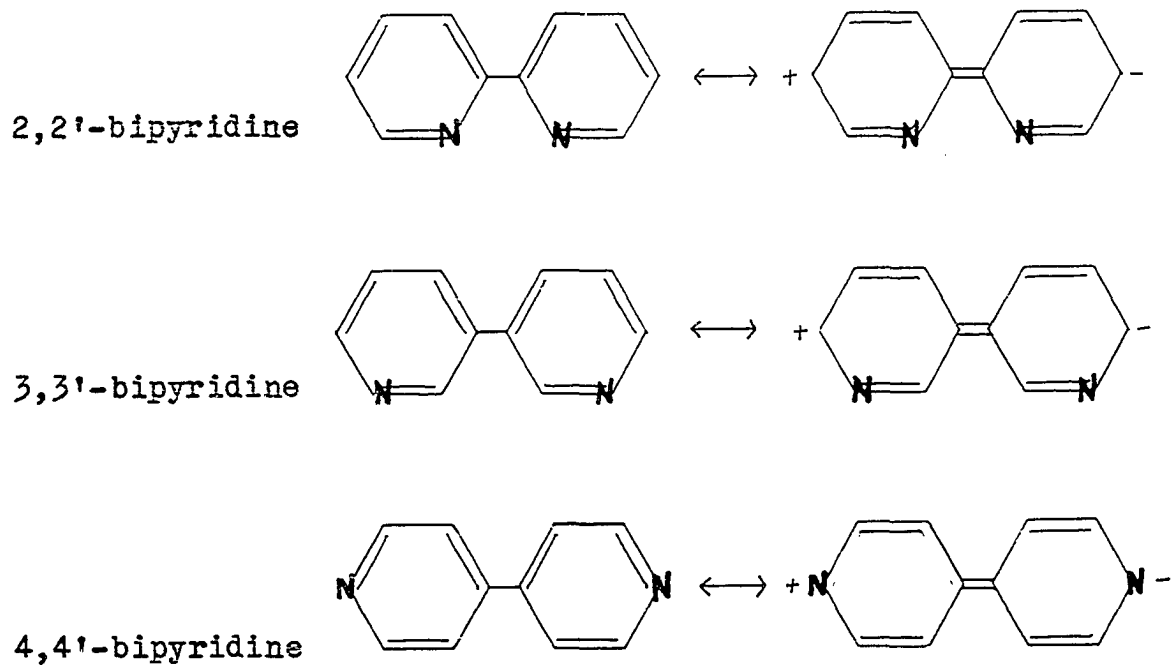
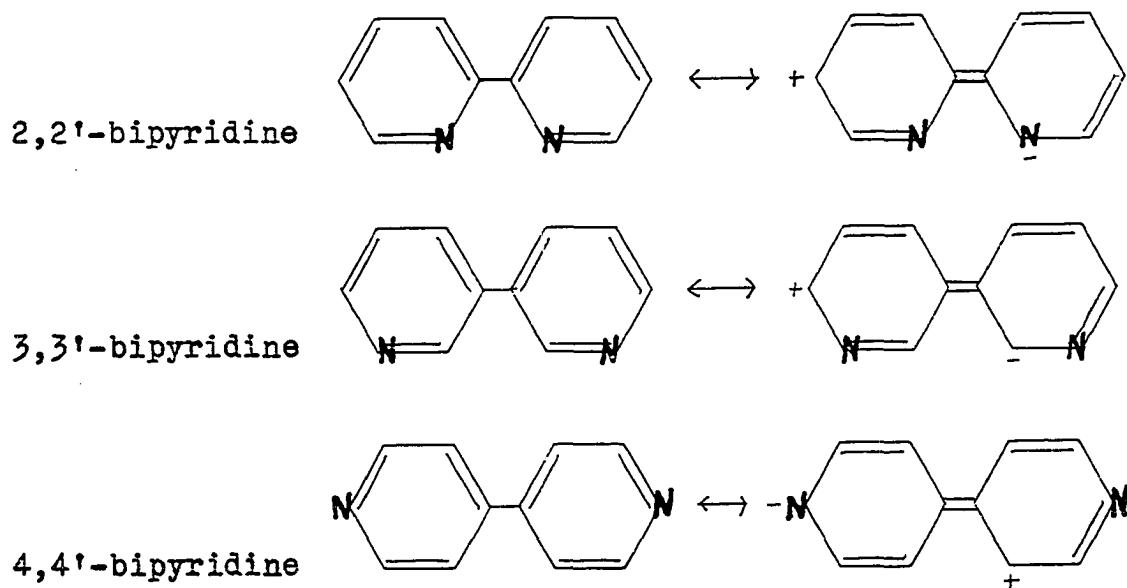
Transition I



and no "Transition II" is observed.

With the introduction of a second nitrogen atom, that is, in the bipyridines, the spectra obtained are very similar to those of the corresponding phenylpyridines. Figure 3 shows that there are again two transitions as evidenced by two absorption peaks. And inasmuch as these absorption peaks occur in the same relative positions as before, it may be concluded that they represent the same type of transition. Again it is observed that as the nitrogen atoms are shifted from the ortho positions to para positions with respect to the other pyridine group, "Transition I" assumes a more dominant role, while that of "Transition II" is diminished. Again the transitions accounting for each of the peaks would be as follows:

Transition I

Transition II (280 m μ)

Here it should be noted that there is one important difference between the bipyridine and the phenylpyridine systems. In the case of the 4-phenylpyridine only one absorption peak was observed. However, in the case of 4,4'-bipyridine there are two peaks observed and there is no change in the wavelength at which they occur. The transition assigned to account for this second peak is again an ortho-para quinoid type excited state, despite the fact that the electronegative centers of the molecule are located exclusively in the para positions. Indeed, this is the very cause of the presence of "Transition II". Inasmuch as both para positions are now sites of negative charge, and the para quinoid structure requires that one of them acquire a positive charge; this transition is now energetically less favorable than in the case of 4-phenylpyridine. Thus the path is again opened for an ortho-para quinoid type transition, "Transition II".

Figures 8 through 14 show the effect of the methyl substituent on the spectrum of the 2,2'-bipyridine as a function of the position of the methyl group. Figure 8, which shows the ultraviolet spectrum of 3,3'-dimethyl-2,2'bipyridine, is considerably different than the spectrum of any of the other compounds studied. The spectrum shows but a single peak which is much reduced in intensity. This decrease in intensity of absorption is the direct result of the presence

of the two methyl groups. In the 3 position the methyl groups sterically hinder the free rotation about the carbon carbon linkage between the two rings. In effect they prevent the two rings from becoming coplanar; a condition which is required if the electrons of the two rings are to interact and produce a conjugation band in the spectrum.

With the methyl groups removed to the 4 and 4' positions the spectrum again shows the two peaks in the bipyridine spectrum. The effect of the methyl groups in these positions is twofold; they reduce the intensity of the peak ascribed to "Transition I" and cause the peak of "Transition II" to spread out over a greater wavelength range. These effects are probably due to the fact that the methyl group tends to increase the electron density of the ring by both the inductomeric and electromeric processes. This increase in electron density is not, however, uniformly distributed over all elements of the ring. The mesomeric effect requires that the largest portion of this increase be assigned to positions 1, 3 and 5. Indeed, the inductive effect would place the largest concentration on the nitrogen of position 1. Thus the increase in the general electron density of the rings has the effect of spreading out the absorption peak on the long wavelength side while the increased electron density on the nitrogen atom in particular causes "Transition II" to

become the dominant transition.

When the methyl groups are located in the 5 and 5' positions the spectrum shows the two peaks of the bipyridine system. And again the peaks are spread out on the long wavelength side. The cause of this spreading is the general increase in the electron density of the rings, and occurs in the same manner as in the case of 4,4'-dimethyl-2,2'-bipyridine. The effect upon the nitrogen atom would be much smaller however, as the nitrogen is now located in a position which is meta to the methyl group and therefore, the mesomeric effect can not operate. An increase in the electron density of the nitrogen atom, and therefore an increase in the basicity of this atom must occur only through an inductive mechanism. Thus the basicity of the nitrogen atom is decreased in comparison to that of the 4,4'-dimethyl-2,2'-bipyridine. The fact that the peak of "Transition II" is not decreased correspondingly is the result of the methyl group in the 5 position, which is more readily capable of accepting the positive charge of the excited state than a hydrogen atom would be. Accordingly, both transitions should take place with greater ease and an examination of the spectrum does indeed indicate this, as both peaks have undergone batho- and hyperchromic shifts.

The final member of this series, 6,6'-dimethyl-2,2'-bipyridine shows a spectrum which is again considerably dif-

ferent from the others. There is but a single absorption peak located at 280 m μ which corresponds to the wavelength of the absorption due to "Transition II". Indeed, the presence of the methyl group in this position would tend to increase the electron density of the nitrogen atom considerably. With the methyl group located adjacent to the nitrogen atom, one would expect that the hyperconjugation effect would operate more effectively than in any other position on the ring. This increase in electron density of the nitrogen atom, and therefore, its basicity, should then promote "Transition II". The observed spectrum indicates that this promotion is so effective that "Transition I" is eliminated.

If the spectrum of 2,2',2"-tripyridine were to agree with that of the terphenyl series one would expect that there should be two peaks, each with an increase in molar absorptivity but not changed with respect to their position on the wavelength scale. Examination of the spectrum of 2,2',2"-tripyridine, Figure 6, does not substantiate the above prediction. In place of the predicted two peaks there occurs but a single diffuse peak. It must be concluded then that in some manner the three rings are entering into conjugation. Such a conjugated structure would indicate that the group acting as a connector between these two rings must be a rather poor insulator. It is known that nitrogen with its extra

pair of electrons is a poor insulator toward conjugation and will often allow conjugation where it would otherwise be impossible.

Finally the effect of the pyridyl group on the spectrum of s-triazine was observed. The spectrum of triamino-s-triazine was used to determine the type of ultraviolet spectrum to be expected from the s-triazine nucleus itself. As shown in Figure 15 the nucleus has only a very small absorption peak located almost at the short wavelength cut off. With the introduction of a pyridyl group, forming 2-pyridyl-4,6-diamino-s-triazine there occurs two peaks in the ultraviolet absorption spectrum. Indeed, the spectrum strongly resembles that of bipyridine and therefore, the assigned transitions accounting for the absorption peaks should be the same.

The introduction of the second pyridyl group to form a 2-amino-4,6-bis(2'-pyridyl)-s-triazine results in a compound which has an absorption spectrum of the same type as would be predicted from a study of the polyphenyls. That is, the wavelengths of the peaks do not shift from those of the mono-pyridyl compound. However, the intensity of the absorption does increase. Indeed, the increase is such that the resultant spectrum shows peaks which are nearly twice that observed in the case of the mono-pyridyl derivative. It would

be concluded from this that the extra pair of "p" electrons on the connecting nitrogen atom must be so involved with the resonance of the central ring that they are no longer available to act as a conductor of the resonance between the rings as they were in the case of the 2,2',2"-tripyridine.

With the introduction of the third pyridine ring the absorption spectrum is again accounted for by considering the polyphenyl system. In this case, however, the fit is not as good as in the case of the di-pyridyl substituted derivative. The absorption peak corresponding to "Transition I" has been reduced, rather than increased as might be predicted. The peak corresponding to that of "Transition II" does increase as the theory would predict. Thus this peak is found to increase uniformly, depending upon the number of pyridine rings attached to the central nucleus.

The effect of iron(II) on the spectrum of these compounds is invariably an increase in the peak ascribed to "Transition II". And in many cases the absorption peak ascribed to "Transition I" is decreased at the same time. If the original assignment of transitions to the absorption peaks were correct then this effect would be a logical result. Iron(II) reacts with these compounds, utilizing the unshared "p" electrons of the nitrogen atoms. The location of a positive charge at these sites should by the inductive effect increase

the pull on the electrons from other parts of the molecule and thus cause the transition designated as "Transition II" to be easier.

In certain instances the effect is very striking. Whereas the ultraviolet spectrum of the 2,2',2''-tripyridine is composed of only one peak and it was postulated that this anomalous behavior was the result of the mobility of the "p" electrons on the nitrogen which separated the two rings. With the formation of a complex with iron, these "p" electrons are used to bond to the iron and are no longer mobile, therefore the nitrogen atom should again become a good insulator. With the cross conjugation eliminated the spectrum should acquire the ordinary two peaks of the meta conjugated system. Indeed, the spectrum of the iron complex does show the two peaks that are present in the spectrum of the other compounds of this type. It should be noted that these peaks have, however, undergone a bathochromic shift and at the present time the cause of this shift is unknown.

If the interpretation that the absorption of "Transition II" is increased by withdrawing electrons from the nitrogen towards the iron is correct, then a hydrogen ion should have the same effect upon the ultraviolet spectrum. Figures 21 through 24, which show the absorption spectra of the substituted triazines in solutions of various acidity do show this

effect. Namely, an increase in the hydrogen ion concentration results in an increase in absorption of that peak assigned to "Transition II". This change in the absorption spectrum is identical with the change observed when the compound is complexed with iron. Of those compounds studied for this comparison between the effect of iron(II) and the proton only the tripyridyl-s-triazine showed any significant difference in the effect of these two ions. A study of Figure 20 and Figure 24 indicates that the proton is more effective than iron(II) in this regard. However, inasmuch as iron(II) can operate on only two of the appended nuclei, whereas the proton is capable of operating on all three of the appendages, this difference is to be expected.

Bipyridine and its derivatives are known to act as bidentate chelating agents, forming complexes with iron in the ratio of three ligands to one iron(II). Tripyridine, on the other hand, acts as a tridentate ligand, forming complexes with iron in the ratio of two ligands with one iron(II) ion. It has been determined that the monopyridyl-s-triazine acts as a bidentate ligand in the same manner as bipyridine while the dipyridyl and tripyridyl substituted s-triazines act as tridentates in the same manner as tripyridine.

Thus the constitutional elements of the compounds have been determined. The spacial configuration can also be deter-

mined from this work. The ultraviolet band presented by each of these complexes are conjugation bands. Such bands cannot exist unless the rings acquire a planar configuration. Therefore, one can reasonably conclude that the ligand must assume a planar configuration in the chelate. In the case of iron, where the complex is octahedral, one must then assign positions 2,3, and 4 to one ligand and positions 1, 5 and 6 to the other when the ligands are tridentate. In brief, the spacial configuration must be such that the two tridentate ligands must enter the complex in a planar configuration perpendicular to each other. Thus one can substitute bipyridine in a 6 position, provided the substituent group is capable of occupying a coordination position of the iron, and still obtain the ferroine reaction with the product. 2,2',2''-tripyridine is indeed an example of such a substitution. The corresponding derivative of 1, 10 phenanthroline should be a very interesting compound. The presence of the large pyridine ring should tend to prohibit the cuproine reaction, thus making the reagent more specific for iron.

SUMMARY

A new series of compounds, the pyridyl substituted s-triazines, has been found to yield colored compounds with iron(II), that is to give the ferroine reaction.

The molar absorptivity of the iron derivative and therefore the sensitivity of the compound as a reagent for the determination of iron, has been found to increase as the number of pyridine rings attached to the central triazine ring increased. Thus the molar absorptivity of the mono-pyridyl derivative is 300, of the dipyridyl derivative 8,000, and of the tripyridyl derivative 23,500. The sensitivity of the latter compound toward iron approaches that of bathophenanthroline. Being much easier to produce than bathophenanthroline tripyridyl triazine should become the preferred reagent for the colorimetric determination of traces of iron.

The absorption spectra of 2,4-diamino-6-(2'-pyridyl)-s-triazine, 2-amino-4,6-bis(2'-pyridyl)-s-triazine and tris(2'-pyridyl)-s-triazine and the iron(II) derivatives of these compounds have been obtained. The ultraviolet spectra of the triazines resemble closely those of the analogous polypyridyl compounds. The visible spectra of the iron derivatives also resemble those of the iron(II) derivatives of the corresponding polypyridyl compounds.

Using as a basis the ultraviolet absorption spectra of the polyphenyl compounds two electronic transitions have been postulated to account for the ultraviolet spectra of the phenylpyridyl, polypyridyl and the triazine compounds. These transitions involve cross conjugation between the rings which results in either para-para conjugated structures, transition I, or ortho-para conjugated structures, transition II. The effects of methyl substitution has been explained in terms of the transitions postulated.

The absorption spectra of the hydrogen and iron(II) derivatives of the pyridyl substituted triazines has been obtained. The hydrogen ion and iron(II) affect the absorption spectra in the same manner. This is the result expected on the basis of the theory advanced to account for the spectra of the polypyridines and pyridyl triazines. The visible absorption spectra of the hydrogen and iron(II) derivatives of these compounds are of course not identical. The theory to account for the visible absorption of the iron(II) compounds had been previously advanced by Krumholz and extended by Bailar; support for their theory has now been advanced and the theory extended to the pyridyl substituted triazines.

The transitions postulated to account for the ultraviolet absorption spectra of the polypyridyl and pyridyl sub-

stituted triazines require that the two rings be coplanar so that the π electrons of the two rings can interact to give a cross conjugated structure. The 3,3'-disubstituted bipyridines and tripyridines often fail to react with iron(II) or at best react with a very low formation constant and molar absorptivity; this effect, which is stereochemical in nature, is explained on the basis that the inability of the molecule to assume a coplanar structure prevents interaction of the electron systems.

Substitution in the 6 or 6' positions of bipyridine prevents union with iron(II). This also is a stereochemical effect but of a different nature. Groups in the 6- and 6'-positions prevent three such molecules from approaching the iron atom sufficiently close to occupy the six octahedral positions about the atom. The exception to this is 2,6-bis(2'-pyridyl)pyridine (2,2',2''-tripyridine) which acts as a tridentate ligand, the nitrogen atom of the third pyridyl ring being in position to unite with the iron atom. In this molecule all three rings must become coplanar and two molecules unite with the iron atom, one occupying the 2,3, and 4 positions, the second the 1,5 and 6 positions. This behavior has now been extended to the iron derivatives of the pyridyl substituted triazines.

The compounds tris-(2,4-diamino-6-(pyridyl)-s-triazine iron(II) chloride and bis(2-amino-4,6-bis-(2'-pyridyl)-s-triazine iron(II) perchlorate have been prepared in a crystalline state. The composition of the former has been inferred from data obtained by the method of continuous variations applied to solutions of this compound. The composition of the latter has been determined in three different ways. First, the method of continuous variations showed that the ratio of the ligand to iron is two to one with the possibility of a one to one ratio for solutions in which the iron content is greater than that allowed by a two to one ratio of ligand to iron. Second, a spectrophotometric titration confirmed the finding of the method of continuous variations. Finally a direct analysis of the crystalline material definitely established that the compound was composed of one iron, two ligands and two perchlorate ions.

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