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The Ultraviolet Absorption of Some Nitrogen Heterocycles, Benzotriazole, Benzimidazole, Indazole, Indole

John Edward Fagel Jr.
Union College - Schenectady, NY

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THE ULTRAVIOLET ABSORPTION OF SOME NITROGEN HETEROCYCLES

Benzotriazole, Benzimidazole, Indazole, Indole

by

John Edward Fagel, Jr.

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

By John E. Fagel, Jr.

Approved by Galen W. Ewing

May 11, 1951

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Dedicated to

GALEN WOOD EWING

-- an inspiring teacher, a fine employer, and a good friend

158339

11 May 51

Gift of Arthur

ACKNOWLEDGMENTS

The major part of the experimental work on benzotriazole was done during the summer and fall of 1949 and reported in the author's Bachelor of Science thesis (1). The theoretical treatment has since been extensively revised (2), and is included herein to serve as a basis of comparison for the newer work.

All of the work reported in this paper was supported by a Frederick Gardner Cottrell Grant from the Research Corporation, New York, awarded to Dr. Galen W. Ewing.

I want to express my sincere gratitude and appreciation to Dr. Ewing for making it possible for me, through a generous Research Fellowship, to do this work. Our association during the past two years has indeed been profitable and memorable for me. I sincerely hope that I shall prove worthy of the confidence and faith he has shown in me, and that I may some day be able to repay him at least in part for all he has so unselfishly given me.

My thanks are also due to Drs. John F. Flagg and Frank R. Mayo who read and criticized a part of this work, and to Albin J. Rzeszutarski who synthesized the sample of indazole.

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"----- the rules of the game are so simple that it can be played happily by almost anyone without any knowledge of the underlying principles involved."

M. J. S. Dewar (5)

---- on the theory of resonance

ABSTRACT

The ultraviolet absorption spectra of benzotriazole, 5, (6)-chloro-benzotriazole, benzimidazole, indazole, and indole have been determined in aqueous solutions of varying acidity in the region 210-300 mμ. An attempt has been made to correlate the absorption spectra of these compounds with their molecular structure. The acidic dissociation constants of several of the compounds have been determined graphically from the absorption data.

INTRODUCTION

The phenomenon of absorption of electromagnetic radiation (hereafter referred to as "light" absorption) is indeed complex and actually poorly understood. Theoretically the complete elucidation of this phenomenon is possible through the solution of the wave equations which describe a particular absorbing molecule, but unfortunately these extremely complicated equations cannot be solved by any mathematical method yet developed. Certain ingenious approximation methods for the solution of the wave equations have been devised, however, and the results of many of these approximations are in surprisingly good agreement with experimental data. Even the approximation methods are tedious and time-consuming, however, and the results are often unreliable (that is, they do not agree well with experimental observations).

The methods employed in this study cannot yield quantitative information regarding the theoretical nature of the "light" absorption process, but they are often particularly valuable in characterizing the structure of absorbing molecules on a comparative basis. This type of structural characterization is accomplished by comparing the absorption spectrum of the compound in question with the spectra of compounds of known structure. It is inferred, and corroborated empirically, that the chromophore of the unknown is similar to that of the known if their respective absorption spectra are similar. Information of this kind has often helped solve structural problems not readily amenable to any other mode of attack.

The attempted correlation of structure with absorption spectra presented in this paper is based on the resonance theory - not because this approach is the best possible in a study of this nature, but because it is the only one with which the author is sufficiently familiar. An alternate, and perhaps more fundamentally sound, approach is based on the molecular orbital theory. A brief discussion of this theory is included in another section of this paper.

Whether or not the resonance theory approach to the elucidation of "light" absorption studies is meaningful appears to be a somewhat moot question. In fact certain authorities (4) take the position that the use of terms such as resonance "merely tends to obscure the phenomena", and that arguments based on such "vague and unsupported terms of doubtful theoretical significance" are but a "play on words" and "may serve to obscure rather than clarify the correlations".

(To the reader not thoroughly familiar with the underlying principles of the theory of resonance, it must be pointed out and emphasized that the theory is actually but a figment of the imagination - devised to aid one in visualizing the physical significance of the quantum mechanical wave equations which quantitatively describe the absorbing molecule in question. Resonance structures for a particular molecule are drawn when a single "classical structure" does not fully describe the chemical properties of that molecule. These structures are merely the best pictures of the actual structure of the molecule that can be put on paper. The actual structure of the molecule is quite definite,

whatever it may be, but it cannot be represented by an ordinary structural formula; it is represented as a hybrid of all the resonance structures that can be drawn.

One must constantly be on guard lest he attach real significance to the resonance structures he draws. They exist only in his imagination and serve merely to aid him in forming a mental picture of a particular molecule.)

Certainly there is much to be said for the arguments against the resonance theory approach, but nonetheless it is interesting and often worthwhile to speculate on the nature of the absorption phenomenon and its correlation with the resonance structures one may draw for a given absorbing species. The resulting arguments are, to be sure, not even semi-quantitative; but an empirical formula which enables one to explain further experimental observations is better than no formula at all. While we await a rigorous theoretical correlation of absorption with structure, the pragmatic point of view seems justifiable. In the meantime we are collecting more data which may prove of value in the formulation and testing of a rigorous theory.

HISTORICAL (cf. ref. 1)

The first report of the existence of a relationship between "light" absorption and molecular structure appeared in the first volume of the famous German journal Berichte der Deutschen Chemischen Gesellschaft (5,6). It had earlier been recognized that certain physical properties of substances are intimately related to their molecular structure. Whereas quartz, for example, exhibits the phenomenon of optical rotation, non-crystalline silica does not; but certain organic compounds exhibit optical activity in the liquid and gaseous states as well as in the solid state. Clearly then the observed optical activity in these organic compounds must be due to some inherent property of the individual molecules and not merely to their physical arrangement in any particular state.

Similar observations were made regarding the phenomenon of "light" absorption (7), so it is not surprising that a correlation of absorption with molecular structure was attempted. One of the earliest and probably most significant of such attempts was made by Witt (5,8).

Briefly, Witt postulated that in order for a substance to exhibit selective absorption of "light" it must possess certain chemically unsaturated groups. Representative of such groups, to which Witt applied the name chromophores, are the carbon - carbon double bond, the carbon - oxygen double bond, etc. He further postulated that certain other groups, such as $-OH$, $-NH_2$, etc. - which he called auxochromes - have

the effect of intensifying the absorption of the chromophores, although these auxochromic groups themselves do not exhibit selective absorption.

Witt's theory, although entirely empirical, is nonetheless quite useful - as much so today, in fact, as it was seventy-five years ago when first presented. While not actually explaining the phenomenon of "light" absorption, it does successfully correlate absorption with certain structural characteristics.

A popular method currently used in the elucidation of absorption characteristics was first employed by Bury (9) in 1935. In his now well known paper he made the first attempt to explain the absorption phenomenon by a combination of Witt's auxochrome theory and the theory of resonance (10). He showed how the presence of the auxochromic groups in certain organic dyes introduced the possibility for increased resonance in the absorbing molecule, thus explaining the observed spectral shifts produced by the addition of the auxochrome to the parent molecule.

It has also been found possible to explain and predict the absorption characteristics of many different compounds on a semi-quantitative basis. This is achieved through the approximate solution of the wave equations which accurately describe a particular molecule. As mentioned earlier, however, this quantum mechanical approach is extremely complicated and tedious, so that only a relatively few workers are properly equipped to use it. Because of this the Bury or

resonance theory approach, although fundamentally less sound, remains in favor with many workers in the field.

THEORY (cf. ref. 1)

The absorption of radiant energy in the visible and ultraviolet regions of the electromagnetic spectrum is associated with certain electronic transitions in the absorbing molecule. Specifically it is believed that the energy of the absorbed radiation causes the excitation of outer or valence electrons of the absorbing molecule to orbitals of higher energy than are normally occupied in the ground state. According to an equation developed by Bohr, the difference in energy between the ground and excited state orbitals is proportional to the frequency of the radiation absorbed.

In addition to these electronic transitions, certain rotational and vibrational transitions of lower energy are also associated with the absorption phenomenon in the visible and ultraviolet regions. Therefore the absorption spectra of most atoms and molecules are quite complex, being a series of closely spaced lines or bands, each line corresponding to a particular energy transition.

It is obvious of course that not all molecules undergo the same electronic transitions. Some compounds, for example, are colored (absorb in the visible region of the spectrum) whereas others are not. What then governs whether or not a given electronic transition is possible?

The answer to this question lies in the quantum theory of atomic and molecular structure. By way of illustration, let us consider the absorption characteristics of several organic compounds.

THEORY (cont.)

Ethylene, for example, is colorless, but when examined in the ultraviolet region of the spectrum it reveals a definite absorption peak at approximately 180 mμ. No such behavior is exhibited by compounds such as ethane, pentane, hexane, etc. (the saturated hydrocarbons). Presumably then, the absorption phenomenon and chemical unsaturation are somehow related; that is, the energy differences between the ground and excited state orbitals of the valency electrons in the saturated hydrocarbons must be appreciably greater than the corresponding energy differences in the unsaturated hydrocarbons.

That this should be the case is evident upon examining the theoretical nature of the carbon - carbon molecular orbitals in each type of compound (11).

The carbon - carbon single bond is formed by the overlapping of hybrid sp^3 atomic orbitals. The resulting molecular orbital ("sigma" type bond) is particularly stable and relatively high energies are required for the excitation of an electron to the next higher molecular orbital. Hence the saturated hydrocarbons absorb only in the far ultraviolet (methane, 120 mμ.; ethane, 140 mμ.).

One link of the carbon - carbon double bond is formed by the overlapping of hybrid sp^2 atomic orbitals to form a "sigma" type bond of the same nature as the carbon - carbon single bond. The other link, however, is not equivalent to the first one, but is formed by the overlapping of

carbon $2p$ orbitals to give a "pi" type bond. The electrons in a "pi" type bond are significantly more mobile than "sigma" electrons and are excited to molecular orbitals of higher energy relatively easily (cf. the absorption maxima of methane and ethane with ethylene).

It is observed that compounds containing conjugated unsaturated linkages absorb at still higher wavelengths than the simple unsaturated compounds. Butadiene, for example, shows an absorption maximum at 210 $m\mu$. This means that the "pi" electrons in butadiene are even more mobile than the corresponding "pi" electrons in, say, ethylene. The explanation for this fact lies in the possibility for carbon $2p$ orbitals to overlap in several different ways. For example, these orbitals may overlap so as to form a double bond between the central carbon atoms of the molecule, they may overlap to form double bonds between the terminal and central carbon atoms, or they may overlap in such a way as to encompass all four carbon atoms simultaneously.

The result of these different overlapping possibilities tends to reduce the difference in energy between the ground state and excited state molecular orbitals - hence, according to the Bohr relation, the frequency of the absorbed radiation will be less than in the case of non-conjugated molecules. Further conjugation tends to reduce even more the energy difference between possible transition states, so that beta-carotene, for example, with eleven conjugated double bonds, absorbs in the visible region of the spectrum and hence is colored.

Instead of using the molecular orbital theory, it is often possible to arrive at similar conclusions by means of the resonance approach. The latter, although of "doubtful theoretical significance", is easier to handle than the molecular orbital approach, particularly in the case of more complicated structures than the relatively simple ones thus far discussed. The general technique employed in the resonance treatment will be evident upon reading the following theoretical speculations in regard to the spectral behavior of benzotriazole, benzimidazole, etc.

THEORY (cont.)

Part Two

The fundamental relation of absorption photometry, the Beer-Lambert law, relates the fraction of the incident monochromatic radiation absorbed to the number of absorbing molecules present in the path of the incident beam (12). In mathematical terms:

$$dI/I = -Kdn$$

where I is the intensity of the monochromatic radiation, K a proportionality constant, and n the number of absorbing molecules.

Integrating this equation between the limits I₀ to I and 0 to n:

$$\ln I/I_0 = -Kn \quad \text{or} \quad \log I_0/I = kn$$

At constant temperature, the number of absorbing molecules is proportional to the concentration and the amount of absorbing material present (that is, the length of path through the absorbing medium).

The law may then be stated in its usual form:

$$\log I_0/I = \epsilon_g bc = A_g$$

where g is the concentration and b is the length of path.

The logarithm term is given the name absorbancy, optical density, or extinction; and the corresponding symbols A_g, D, or E. The first term is a part of the new terminology in use by the National Bureau of Standards (13). This terminology will be followed in the present work.

THEORY (cont.)

Part Two

The units of the proportionality constant are clearly dependent on the units chosen for the concentration and path length. (Since we are here concerned only with absorption in solution, the path length corresponds to the inside dimension of the cell used to hold the solution, and will hereafter be referred to simply as the cell length.)

Almost without exception the centimeter is chosen as the unit of cell length, but no such uniformity of usage is true regarding the units of concentration. Among the several possibilities, two of the more widely used are grams per liter and gram-moles per liter. The latter is, of course, the more fundamental and will be used herein.

The proportionality constant is numerically equal to the absorbancy of a solution of unit concentration contained in a cell of unit length. If centimeters and grams per liter are chosen as the units of cell length and concentration respectively, the proportionality constant is given the symbol a_s or k and is known as the absorbancy index or the specific extinction coefficient.

If centimeters and gram-moles per liter are chosen as the units, the proportionality constant is given the symbol a_M or the Greek "epsilon" and is known as the molar absorbancy index or the molar extinction coefficient.

EXPERIMENTAL

The spectra were determined with a Model DU Beckman Spectrophotometer (14), Serial No. 3210.

The instrument was set at minimum sensitivity for all determinations, thus allowing measurements to be made at wavelengths as low as 210 mμ. Slit widths were varied from approximately 1.6 to 0.2 mm. Except in the lower wavelength region, the nominal band width isolated was approximately 1 mμ.

Readings were taken at wavelength intervals no greater than 5 mμ. In the vicinity of the maxima and minima readings were taken every 1 mμ.

Matched, fused-silica, cells of square cross-section, 10 mm. \pm 0.01 mm. on the inside, were used.

Melting point determinations were made with a calibrated Thiele apparatus. All buffer solutions were checked with a glass-electrode pH meter.

EXPERIMENTAL (cont.)

Preparation of the Compounds

1. Benzotriazole.

The material used in this study was obtained by benzene extraction from a photographic anti-foggant, Orthazite, manufactured by the Edwal Laboratories and purchased from a retail photographic dealer.

After extraction, the material was recrystallized from benzene until a sharp melting point was obtained. The melting point of the white product, after drying in vacuo at 77° C, was 98-99° C (corr.). Literature values are 98.5° C (15) and 96-97° C (16).

2. 5,(6)-Chlorobenzotriazole.

The chloro-derivative was synthesized from 4-chloro-o-phenylenediamine by diazotization and self-coupling, by adaptation of the procedure (16) for the synthesis of benzotriazole from o-phenylenediamine.

The crude material was recrystallized from xylene. After drying in vacuo at 100° C, the white product melted at 156-157° C (corr.). Literature value is 156° C (17).

3. Benzimidazole.

The benzimidazole used in this study was purchased from the Eastman Kodak Company (Organic Chemical #2621). After twice re-

EXPERIMENTAL (Cont.)

Preparation of the Compounds

crystallizing from water and drying at 100° C, the white product melted at 170-171° C (corr.). Literature value for the melting point is 170-172° C (24).

4. Indazole.

The sample of indazole was furnished by Albin J. Rzeszutarski (29), Dept. of Chemistry, Union College, who synthesized it according to the procedure of Barclay, Campbell, and Dodds (25).

The melting point of the white product was 147-148° C (corr.). Literature value given for the melting point is 148° C (25).

5. Indole.

The C. P. material used was purchased from Eimer and Amend (Lot #484728). The melting point of the sample as received was 52-53° C (corr.), and the boiling point 253° C at 760 mm. The picrate (red needles when wet with benzene) melted at 175.5-176.5° C (corr.).

Literature values of these constants are: melting point 52-53° C; boiling point (762 mm.) 253° C; melting point of the picrate 176° C (26).

EXPERIMENTAL (cont.)

Preparation of Solutions.

Solutions of all the compounds varied in concentration between approximately 10 and 15 mg. per liter. The reference liquid used in each determination was from the same batch of solvent used in preparing the solution.

Because of the extremely limited solubility of 5,(6)-chloro-benzotriazole in aqueous buffers, it was found expedient to affect solution of the compound by first dissolving it in a few ml. of ethanol. No solvent effect on the spectra was observed.

Except in the pH range 2-6, the Clark and Lubs buffers were found ideally suited as solvents for the present work. (In the range excepted, a biphthalate salt which absorbs below 300 mμ. renders these buffers unsuitable.) Sorensen's glycine-hydrochloric acid buffers were found to possess the necessary transparency in the range not covered by the Clark and Lubs buffers, but there is some evidence that the glycine component of these buffers exerts an undesirable "salt effect" on the spectra.

It was not possible to determine the absorption of indole in either strongly acidic or basic solutions. The compound undergoes polymerization in strong acids (red-orange solution), and is essentially completely insoluble in strong alkali.

DISCUSSION

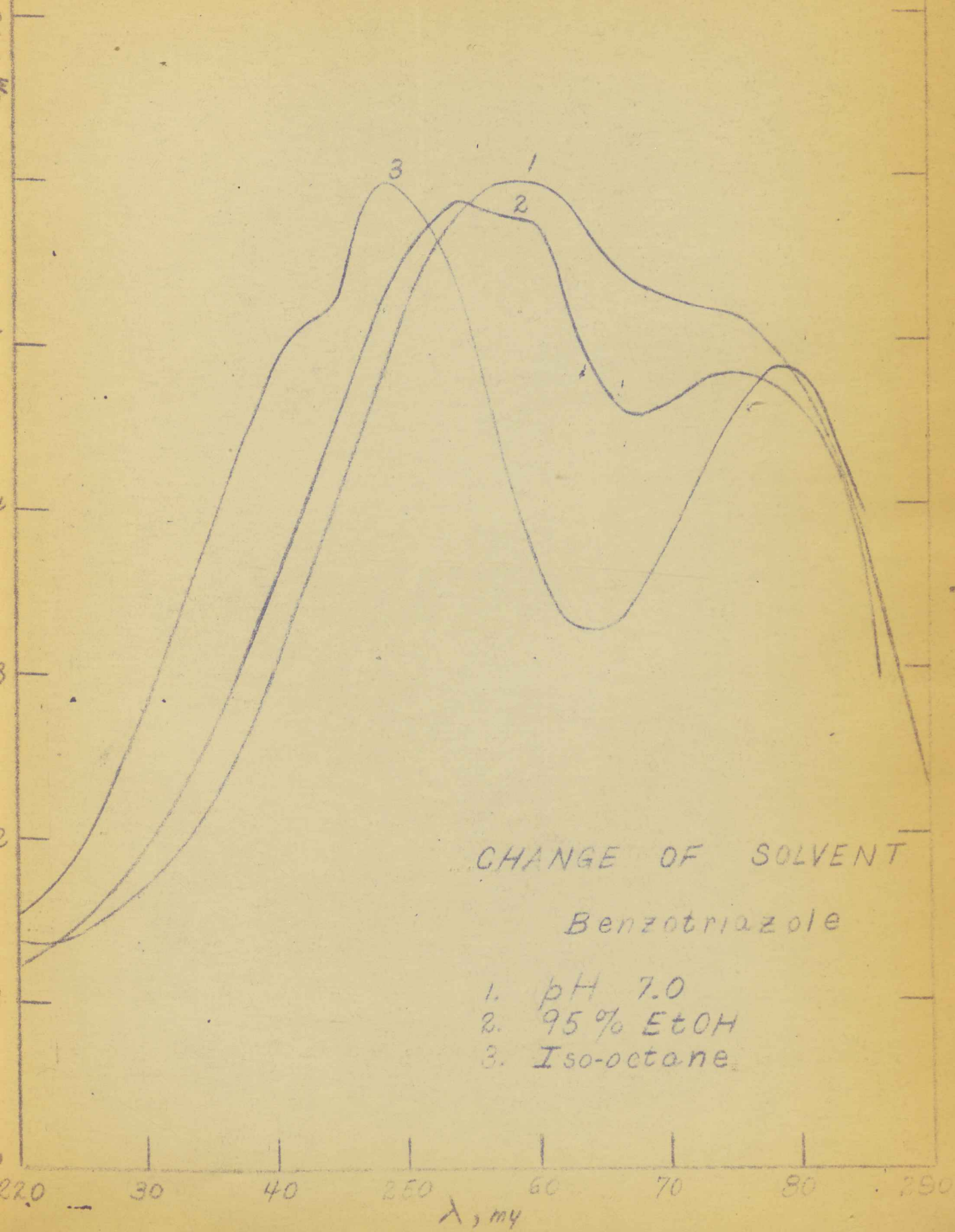
Benzotriazole.

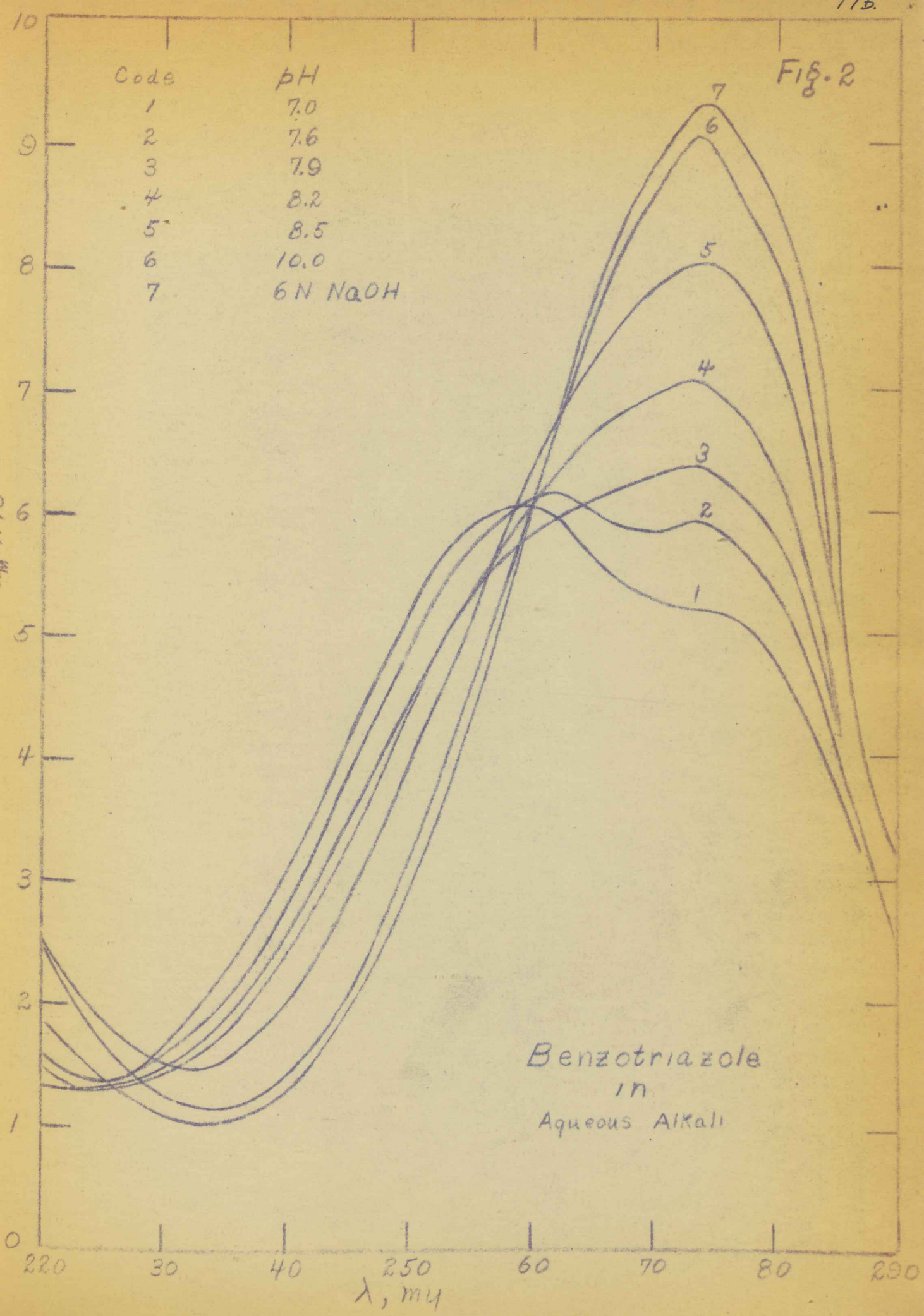
The ultraviolet absorption of benzotriazole was determined initially in solvents of varying polarity. As may be seen in Fig. 1, a bathochromic shift accompanies the change from non-polar to polar solvents. This may be explained by assuming that the more polar solvent tends to isolate separated charges in the excited state of the molecule, hence lowering the energy relative to the ground state. Such a decrease in the energy difference between the ground and excited states results in the observed bathochromic shift.

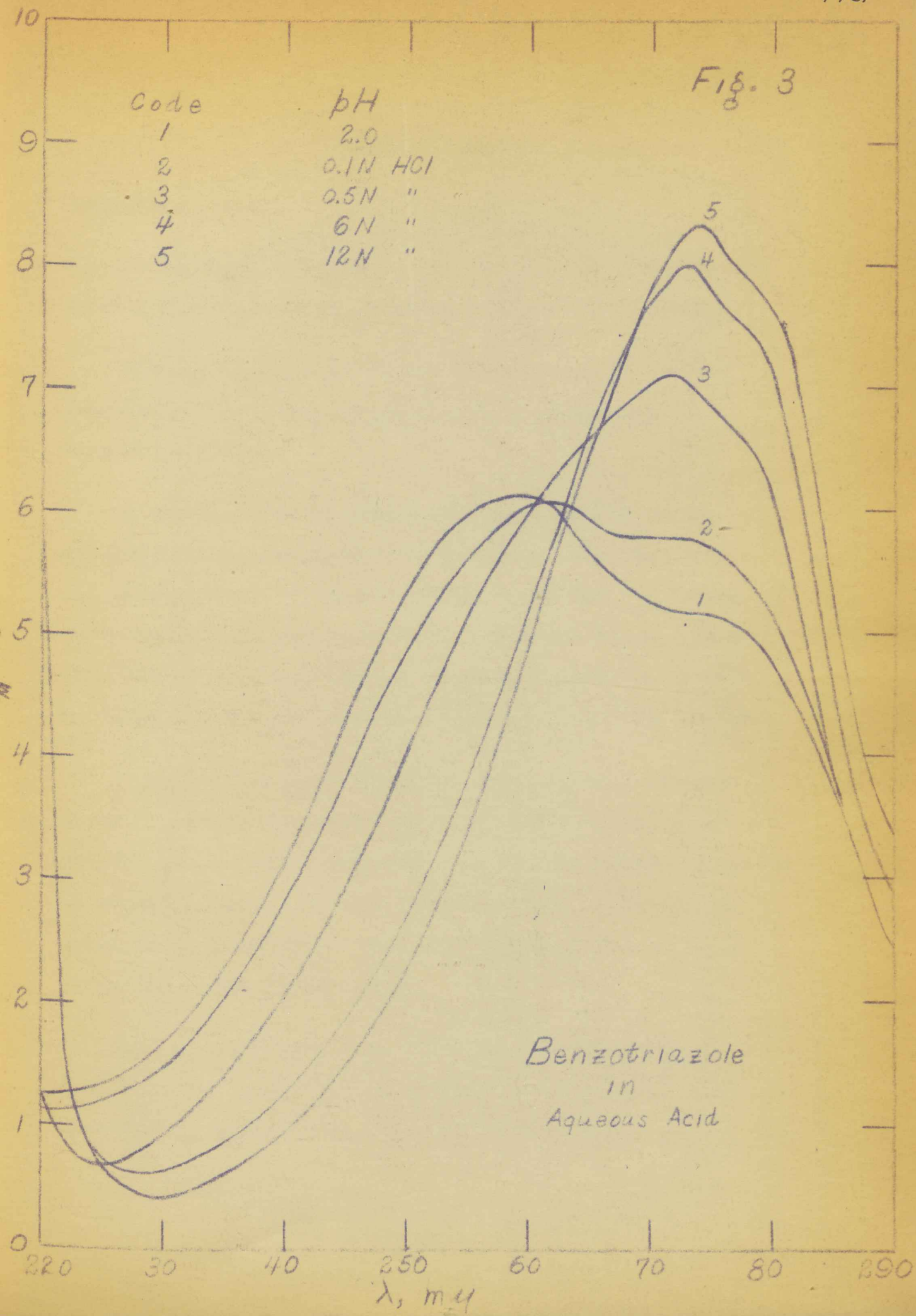
Upon examining the spectra of benzotriazole in solutions of widely varying pH (Figs. 2-3), two fundamental spectral types are noted. The spectra of strongly acidic and basic solutions exhibit a single maximum, whereas the spectra of mildly acidic and neutral solutions exhibit two maxima.

It is assumed that the principle^{a/} contributing forms of the molecule in neutral, acidic, and basic solutions are, respectively, the neutral molecule (I), the cation (II), and the anion (III). (Roman numerals refer to the table of resonance structures in the Appendix.) It is further assumed, by analogy with the known spectra of benzene and q-quinone, that the lower wavelength absorption band is characteristic of the benzenoid chromophore (such as I, II, or III),

Fig. 1







DISCUSSION (cont.)

Benzotriazole (cont.)

and that the higher wavelength band is characteristic of the quinoid (such as IV or V) or semi-quinoid (such as VI or VII) chromophore.

(The term "semi-quinoid" is used herein for want of a better designation. No relation with the free radical semiquinone is intended or implied.)

The purpose of the following is to inquire which of the many possible resonance structures of the various molecular forms most closely approximates the actual structure of each form. It is to be emphasized, however, that the attempted correlation between resonance structures of the ground state and the observed spectra is empirical in the main and may well prove to be inadequate in the final analysis.

It is observed that the absorption maximum of basic solutions occurs in the higher wavelength region (274 m μ .). In accordance with the previous postulations, this means that the resonance structures of the ground state of the anion which most closely approximate the actual structure are quinoid (such as V) or semi-quinoid (such as VI) rather than benzenoid (such as III).

There are two probable forms of the cations: the 1,2- and the 1,3-. Since the spectra in strongly acidic and basic solutions are observed to be similar, it seems reasonable to assume that the

DISCUSSION (cont.)

Benzotriazole (cont.)

structures of the cation and anion are also similar. Upon examining typical resonance structures of each form of the cation and comparing them with the resonance structures of the anion and neutral molecule, it is noted that the principle structures of the 1,2- form are similar to those of the anion (quinoid), whereas the structures of the 1,3- form (VIII, IX) are similar to those of the neutral molecule (benzenoid). Therefore the conclusion is that the cation exists in the 1,2- rather than the 1,3- form.

Evidence in support of the postulation of a mono-acid form in strongly acidic solutions was obtained by analyzing a sample of benzotriazole hydrochloride (18). The hydrochloride was dissolved in water and passed through a cation exchange column saturated with hydrogen ions. The effluent was then titrated with standard base. Within the limits of experimental error, one equivalent of hydrogen ion was found per equivalent of benzotriazole, indicating the salt to be a mono-hydrochloride.

In both mildly acidic and neutral solutions, two absorption maxima of approximately equal intensity are observed. The inference is that the actual structure of the ground state of the molecule in these media

DISCUSSION (cont.)

Benzotriazole (cont.)

is most closely approximated by the benzenoid resonance structures (such as I). This conclusion is in agreement with that of other investigators (18,19). It also seems possible that tautomerism of I to the quinoid structure X may occur to some extent, thus accounting for the appearance of the higher wavelength maximum as well as the lower.

5,(6)-Chlorobenzotriazole.

The absorption spectra of 5,(6)-chlorobenzotriazole (Figs. 5-6) exhibit roughly the same shape and variation with pH as do the spectra of the parent compound. The slight differences observed are presumably the result of the weighting, inductive, or resonance effects of the chlorine.

With reference to the first of the three effects, it is generally observed that increasing the weight of a chromophore leads to both batho- and hyperchromic spectral shifts, although the exact nature of the effect of the added weight on the electronic energy levels is not readily apparent.

The inductive effect of the chlorine should tend to stabilize those resonance structures which bear negative formal charges on the

Fig. 4

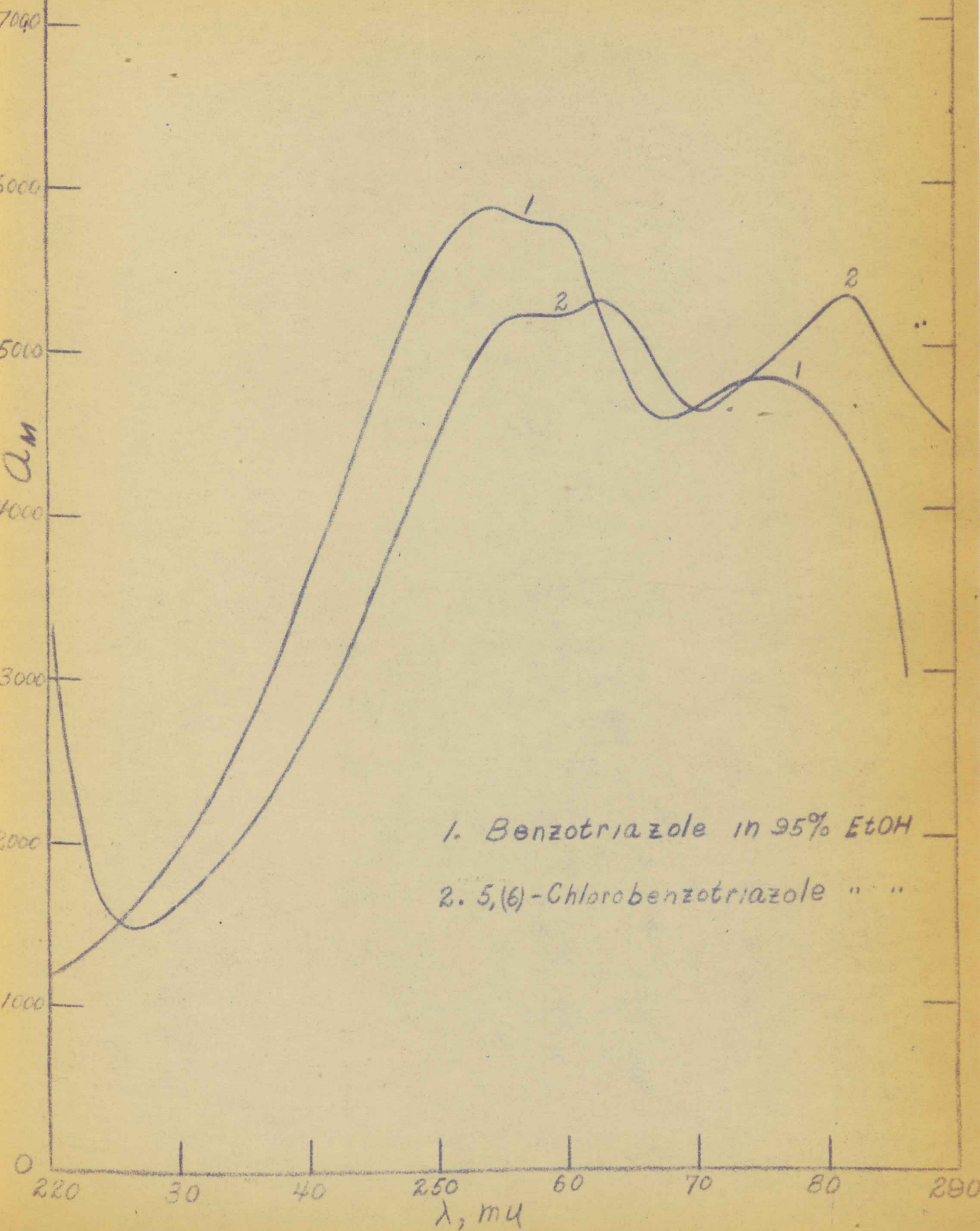
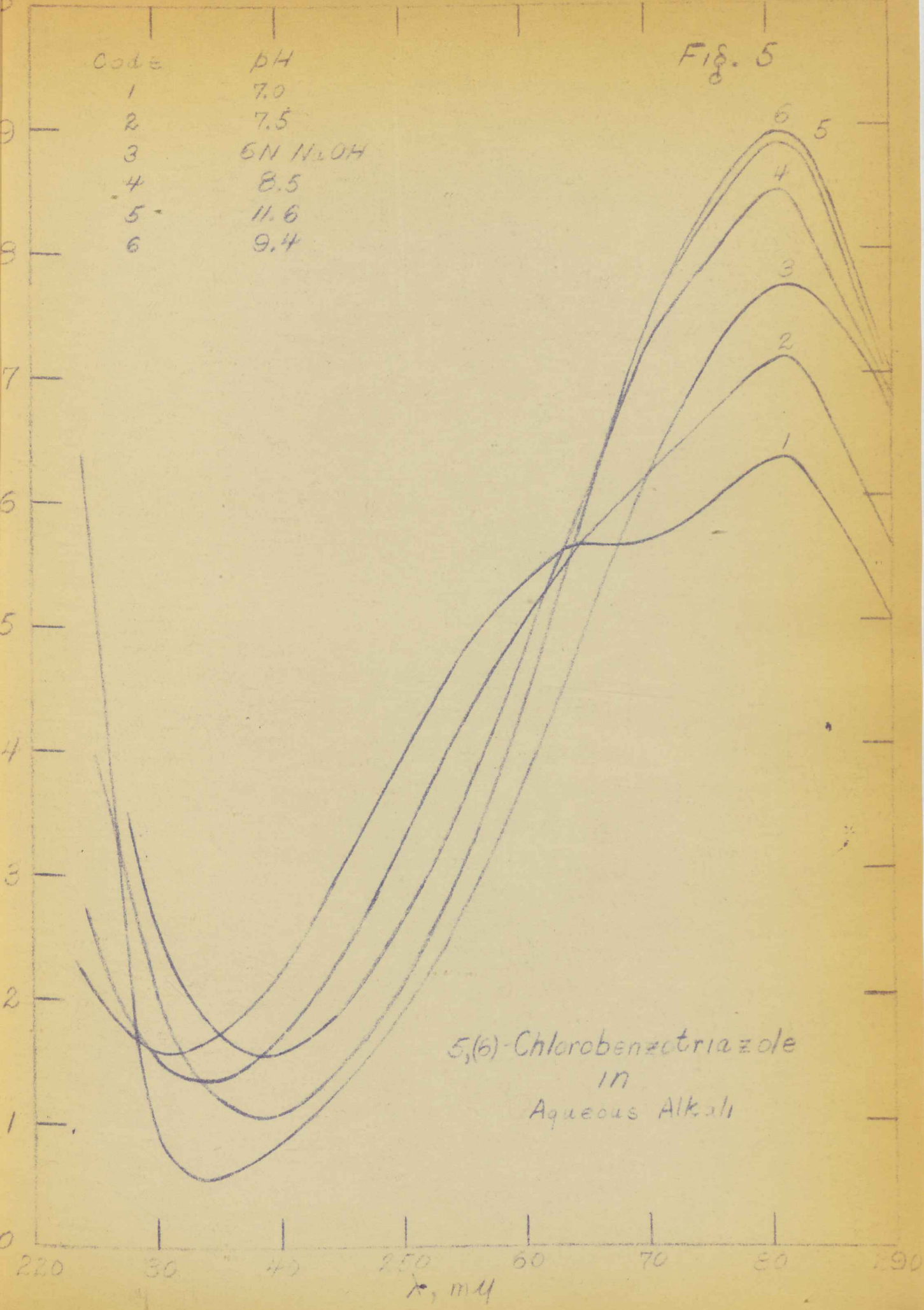


Fig. 5

| Code | pH |
|------|------------------|
| 1 | 7.0 |
| 2 | 7.5 |
| 3 | 8N NaOH |
| 4 | 8.5 |
| 5 | 11.6 |
| 6 | 9.4 |





DISCUSSION (cont.)

5,(6)-Chlorobenzotriazole (cont.)

benzene ring, particularly at the 5- or 6- position (such as VII). If it is assumed that these charge-separated structures are among the principle resonance contributors to the excited state of the neutral molecule, then the added stabilization due to the inductive effect of the chlorine will decrease the energy difference between the ground and excited states, thereby resulting in the observed bathochromic shift. Similar reasoning may also account for the observed shift in basic and acidic solutions, although the elucidation of the excited states of the anion and cation appears impracticable.

The resonance effect is not immediately evident, for the chlorine cannot easily resonate with the ring. It should be noted, however, that the presence of the chlorine destroys the equivalence of structures such as VI and XI, thereby increasing the energy of the ground state of the anion. This increased energy of the ground state (assuming the energy of the excited states remains constant) would account for the observed bathochromic shift on passing from neutral to basic solutions.

DISCUSSION (cont.)

Benzimidazole⁻(cf. ref. 28)

Whereas the spectra of benzotriazole exhibit little or no fine structure, the spectra of benzimidazole (Fig. 7) show pronounced fine structure, even in aqueous solutions, in the 270-280 mμ. region. In accordance with the "loose-bolt" hypothesis of Lewis and Calvin (27), this may be interpreted as evidence that the N-C-N linkage in benzimidazole (XII) is somewhat strained relative to the N-N-N linkage in benzotriazole.

(Fine structure in an absorption spectrum is the result of certain rotational-vibrational transitions superimposed on the principle electronic transitions. Lewis and Calvin have postulated that large, loosely held groups in an absorbing molecule are akin to loose bolts in a piece of machinery in that they are able to dissipate energy by entering into low frequency vibrations. A rigid or constrained molecule without any "loose-bolts" cannot dissipate energy absorbed in an electronic transition as well as a flexible molecule with "loose-bolts". Hence the molecule as a whole is set into vibration, the result appearing as fine structure in the absorption spectrum.)

It is observed that the spectral behavior of benzimidazole on passing from neutral to acidic and basic solutions is roughly analogous to the behavior of benzotriazole under similar conditions (Fig. 8).

Fig. 7

Benzimidazole

1. pH 7.0
2. Isooctane

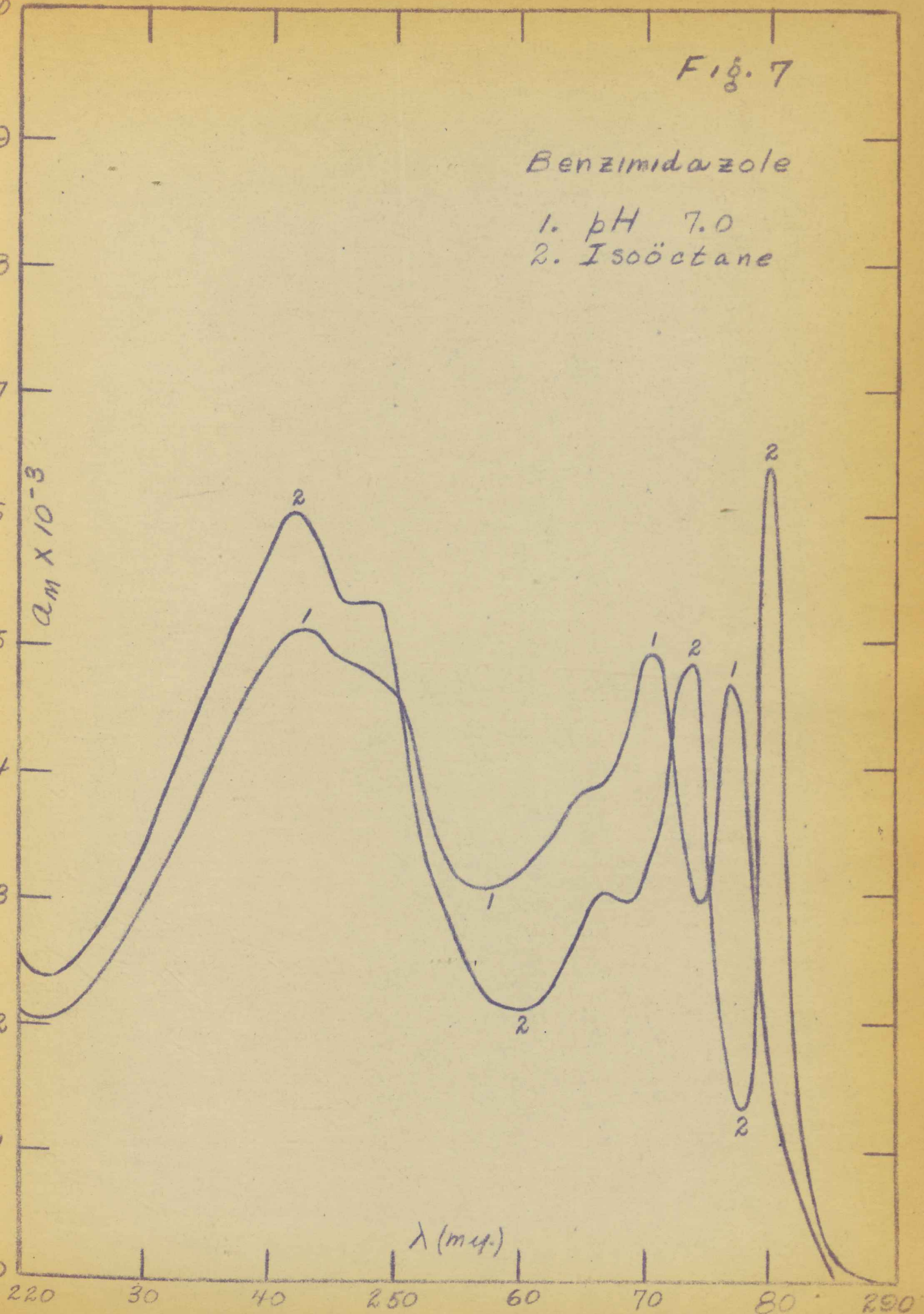
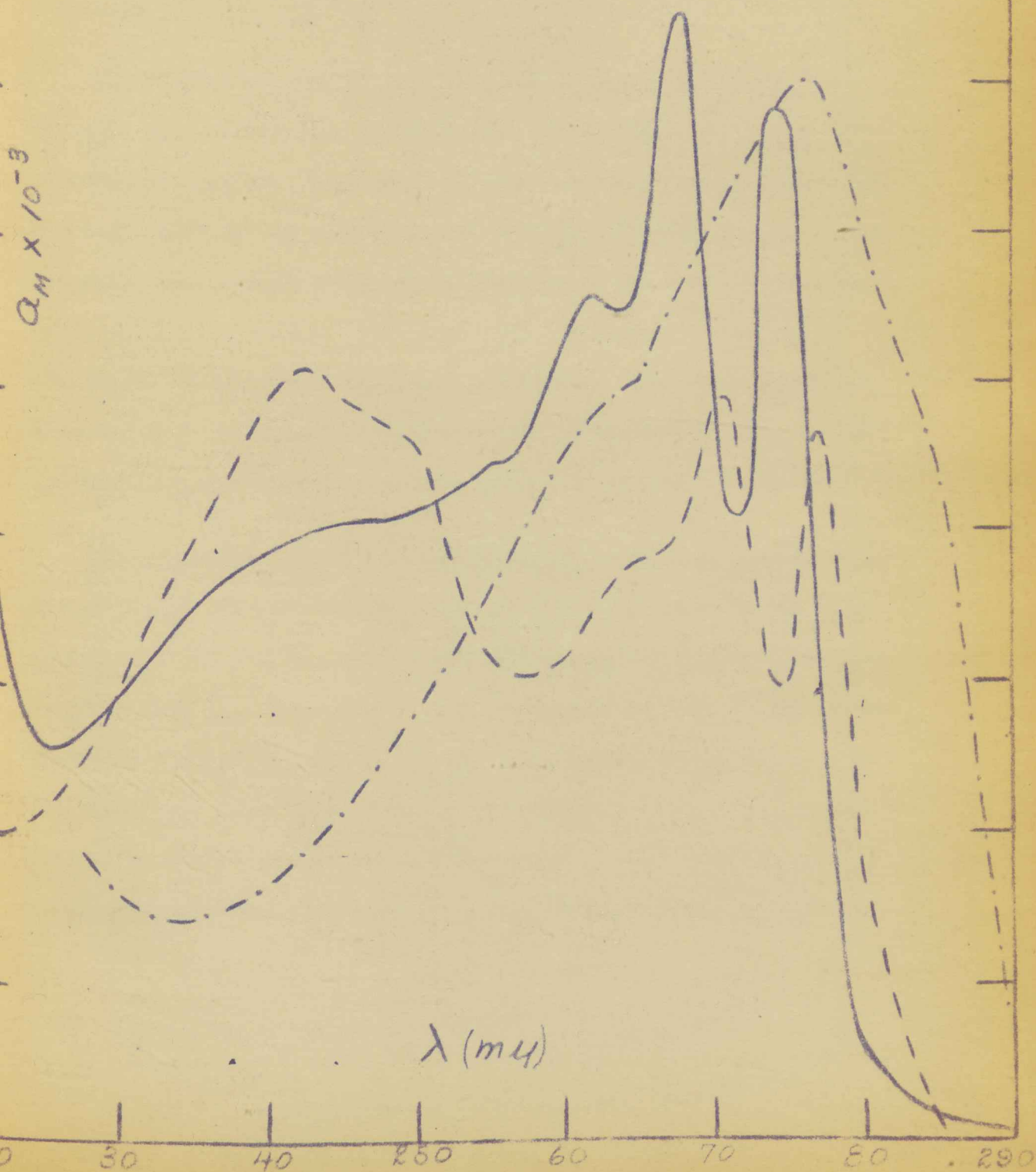


Fig. 8

Benzimidazole

- 12N HCl
- - - pH 7.0
- · - · - 6N NaOH



DISCUSSION (cont.)

Benzimidazole (cont.)

The following structural speculations are therefore based on assumptions similar to those employed in the discussion related to benzotriazole.

The absorption spectra of benzimidazole and benzotriazole in strongly basic solutions are quite similar; a single maximum in the 270-280 m μ . region. Therefore it seems reasonable to postulate that the structures of the anions of each compound are also similar. Upon examining some typical resonance structures of the benzimidazole anion (XIII, XIV, etc.), it is noted that they are exactly analogous to comparable benzotriazole resonance structures. The inference drawn, then, is that the actual structure of the benzimidazole anion is best approximated by the quinoid or semi-quinoid resonance structures.

The absorption spectra of benzimidazole in strongly acidic solutions suggest that the structure of the cation is somewhat different than that of the anion. The significant absorption in the lower wavelength region (242 m μ .) would lead one to believe that the benzenoid resonance structures (such as XV) are more important contributors to the actual ground structure of the benzimidazole cation than are the comparable benzotriazolium structures to the actual structure of the benzotriazole cation. That this might be true is also suggested by

DISCUSSION (cont.)

Benzimidazole (cont.)

the resonance structures one can draw for the benzimidazole cation.

It is observed that all of the resonance structures of the quinoid or semi-quinoid type (such as XVI) involve separated charges whereas the structures of the benzenoid type (XV) do not. The conclusion then is that the actual structure of the benzimidazole cation is less quinoid than that of the anion, but somewhat more so than that of the neutral molecule -- which presumably is best represented as a benzenoid structure (XII) (by comparison of both the spectra and resonance structures of benzimidazole and benzotriazole in neutral solutions).

It is also noted that the absorption spectrum of 2-aminobenzimidazole (28) in acidic solutions is essentially identical to the spectrum of benzotriazole in basic solutions. Since the resonance structures of the cation of 2-amino-benzimidazole and the anion of benzotriazole are analogous, this is taken as further evidence in support of the structural-spectral correlation theory presented herein.

Indazole

There has been much discussion in the past in respect to the location of the acidic hydrogen atom in the pyrazole ring of indazole. Chemical evidence, in fact, suggests that the hydrogen is on the

DISCUSSION (cont.)

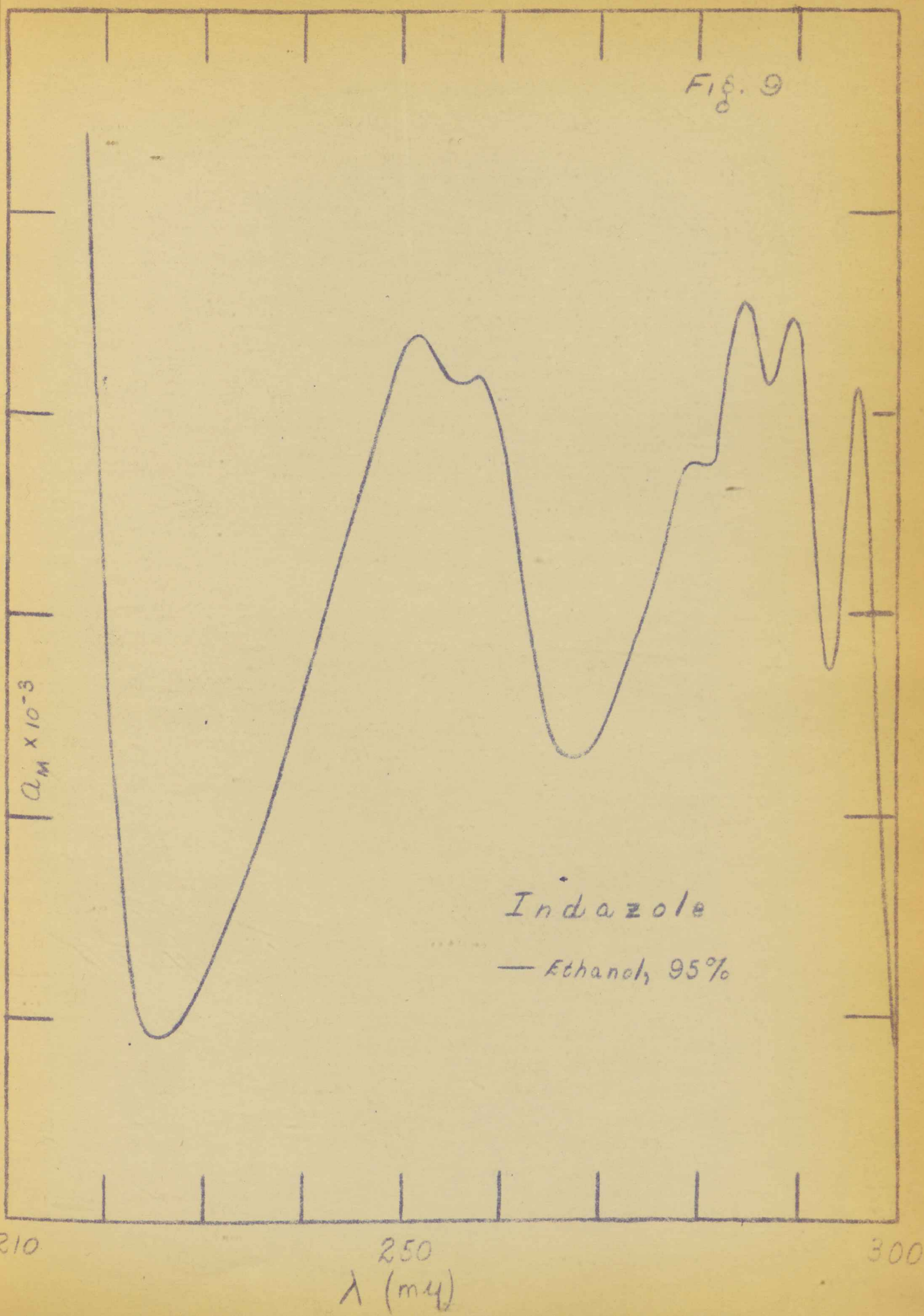
Indazole (cont.)

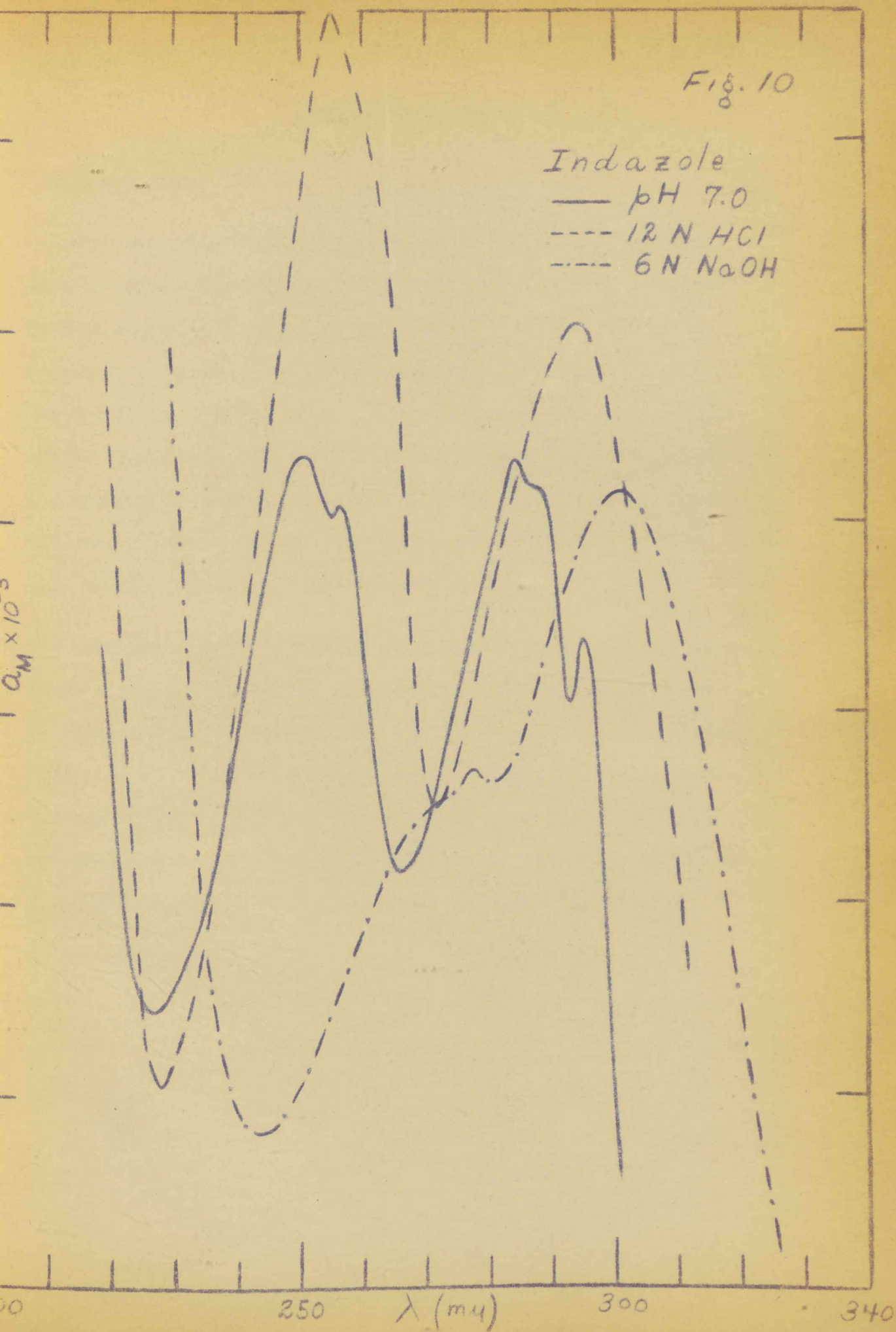
1- nitrogen in some cases and on the 2- nitrogen in other cases (isindazole and indazole, respectively), although it has been found impossible to isolate two distinct forms of the compound (alkyl derivatives of indazole can, however, be prepared in both the 1- and 2- forms). Barclay, Campbell, and Dodds (25) have shown on the basis of cryoscopic data that the "old distinction between isindazole and indazole is no longer valid". The present interpretation of the ultraviolet absorption spectra of indazole confirms this viewpoint.

On the basis of the fine structure resolved in the absorption spectra of indazole, it would seem that the strain in the N-N-C linkage is intermediate between that of the N-N-N linkage in benzo-triazole and the N-C-N linkage in benzimidazole. The spectrum of indazole in ethanol (95%) shows significant fine structure (Fig. 9), but most of this is smoothed out on passing to aqueous solutions.

The spectral behavior of indazole is such that it seems reasonable to postulate a tautomeric equilibrium between the 1- and 2- forms of the compound. In neutral and acidic solutions, two pronounced absorption maxima are observed. In strongly basic solutions there is some diminution in the height of the lower wavelength maximum, but it is still significant (Fig. 10).

Fig. 9





DISCUSSION (cont.)

Indazole (cont.)

Following the assumptions previously outlined, this suggests that the actual structure of the neutral molecule in the 1- form is best approximated as benzenoid (such as XVII), whereas the actual structure of the 2- form is best approximated as quinoid (XVIII). The cation is presumably more of a hybrid between the benzenoid and quinoid structures. The anion must also be considered a hybrid, but the spectrum in strongly basic solutions suggests that the quinoid structures (such as XIX) are more important contributors to resonance than are the benzenoid structures (such as XX).

The important point is that the hydrogen atom is probably in a state of dynamic equilibrium between the 1- and 2- nitrogen atoms. Since the principle resonance structures of the 1- form are benzenoid whereas those of the 2- form are quinoid, this agrees well with the observed spectral behavior of the compound in solutions of varying acidity. The spectra further suggest that the tautomeric equilibrium is displaced in favor of the 2- form as the medium becomes more basic.

DISCUSSION (cont.)

Indole

Little fine structure is resolved in the spectra of indole in aqueous solutions (Fig. 11). On the basis of the previous arguments, this suggests that the N-C-C linkage is relatively free from strain.

It is observed that the absorption spectra of indole in solutions ranging from acidic to basic are all essentially identical; that is, there is no shift in the wavelength of maximum absorption on passing from neutral to acidic and basic media as is observed in the case of benzotriazole, benzimidazole, and indazole. That this should be true is somewhat surprising, but it may be explained on the basis of either of two different assumptions.

If the compound exhibits no tendency to react as either an acid or a base in the media involved (0.2N HCl to 0.2N NaOH), then the structure of the absorbing entity will remain the same in all solutions and its absorption characteristics will of course remain the same also. (As noted earlier, it was not possible to examine the absorption of indole in either strongly acidic or basic solutions. The compound polymerizes in strong acid (26), and is insoluble in strong alkali. This latter point may be taken as further evidence that there is little or no tendency for the compound to ionize as an acid, even in strongly basic solutions.)

Fig. 11

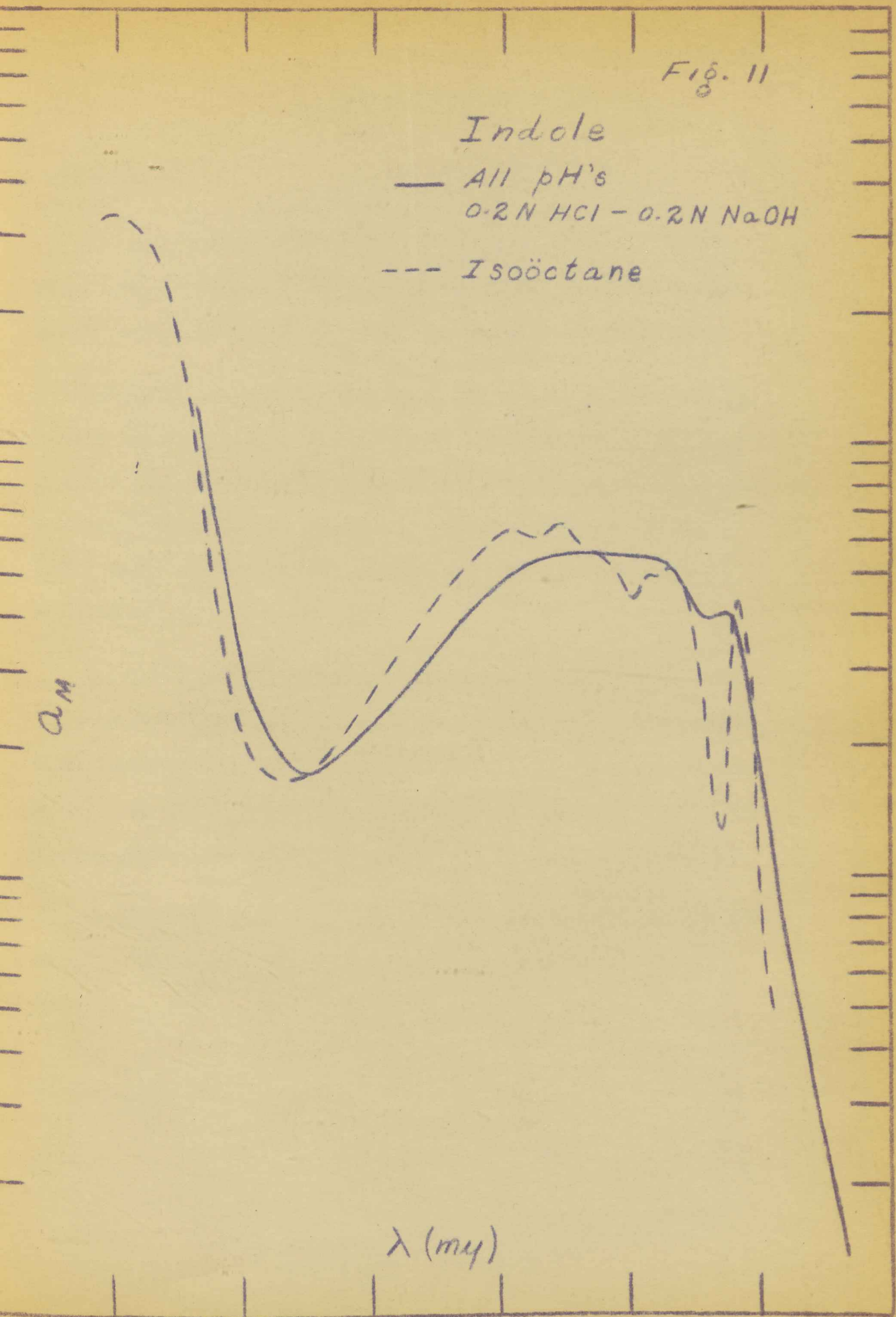
Indole

— All pH's
0.2 N HCl - 0.2 N NaOH

--- Isooctane

 α_M λ (m μ)

00 215 230 245 260 275 290 305



DISCUSSION (cont.)

Indole (cont.)

If it is assumed that indole does exhibit acidic and basic properties, it must be inferred that the structures of the neutral molecule, the cation, and the anion are essentially identical.

Following the previous arguments, the neutral molecule is presumably best represented by a benzenoid structure (XXI). It is apparent that the cation (XXII) also must have a benzenoid structure, for any structure of the quinoid or semi-quinoid type (such as XXIII) would involve a doubly charged nitrogen and hence would be expected to contribute very little.

On the basis of the resonance structures one can draw for the anion (such as XXIV), it would seem that the actual structure might well possess some quinoid characteristics. If an anion does exist, however, we must infer that it is principally benzenoid -- otherwise a spectral shift on passing to basic solutions would be expected.

Which of the above arguments, if either, is correct is difficult to say. Very likely the true explanation involves a combination of both.

GRAPHICAL DETERMINATION OF THE ACIDIC DISSOCIATION CONSTANTS

According to Stenström and Goldsmith (20), it is possible to determine the apparent dissociation constant of a compound by measuring its absorption in solutions of varying acidity. In Figs. 12-15 the molar absorptancy index (a_M) is plotted against the pH of the solutions. The apparent pK is equal to that value of the pH at which a_M is midway between its upper and lower limits.

The values of the dissociation constants so determined agree closely with potentiometrically determined values reported in the literature (21,22,23).

It is noted that the chlorine substitution in benzotriazole shifts the pK value in accordance with the expected inductive influence of the chlorine.

Fig. 12

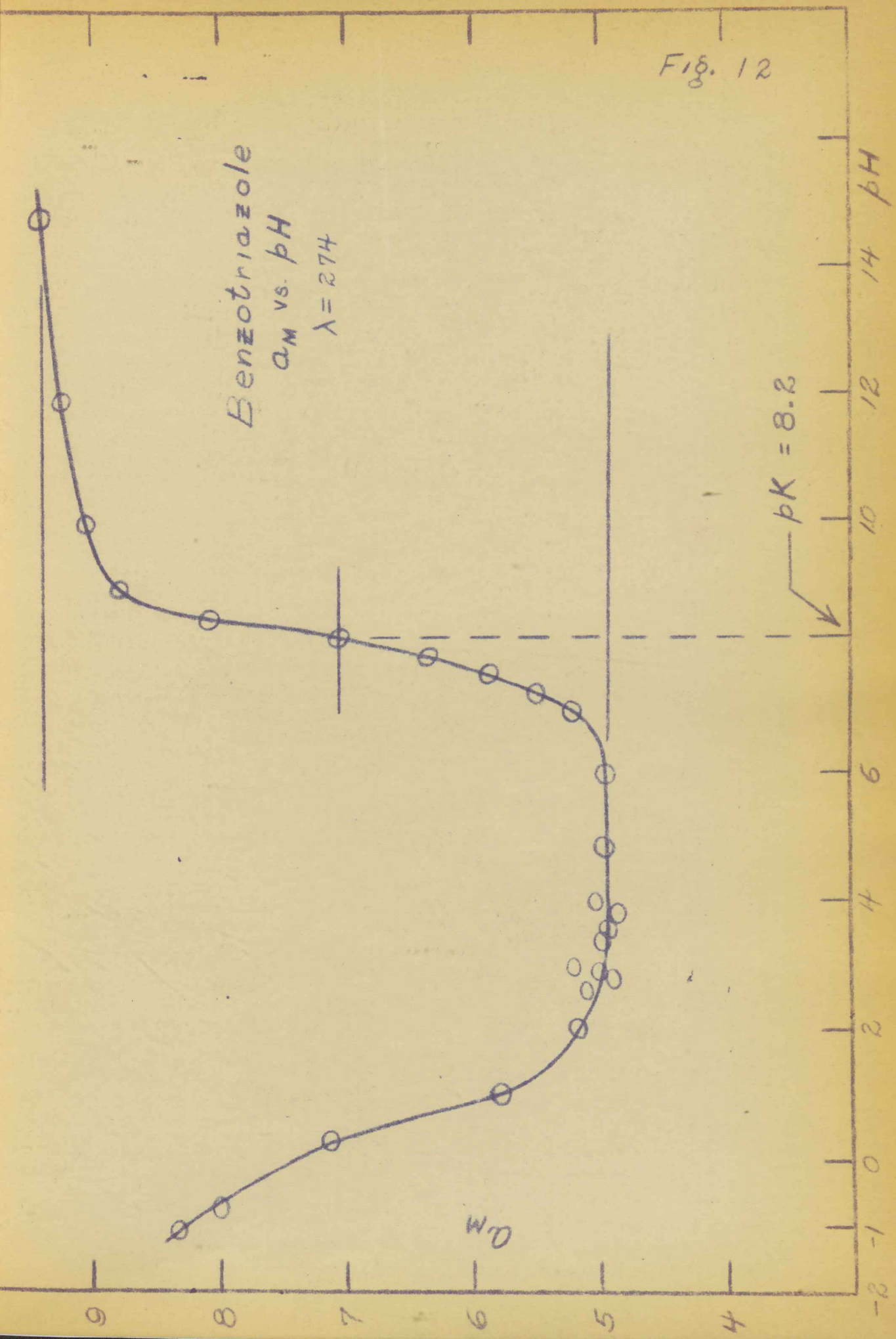


Fig. 13

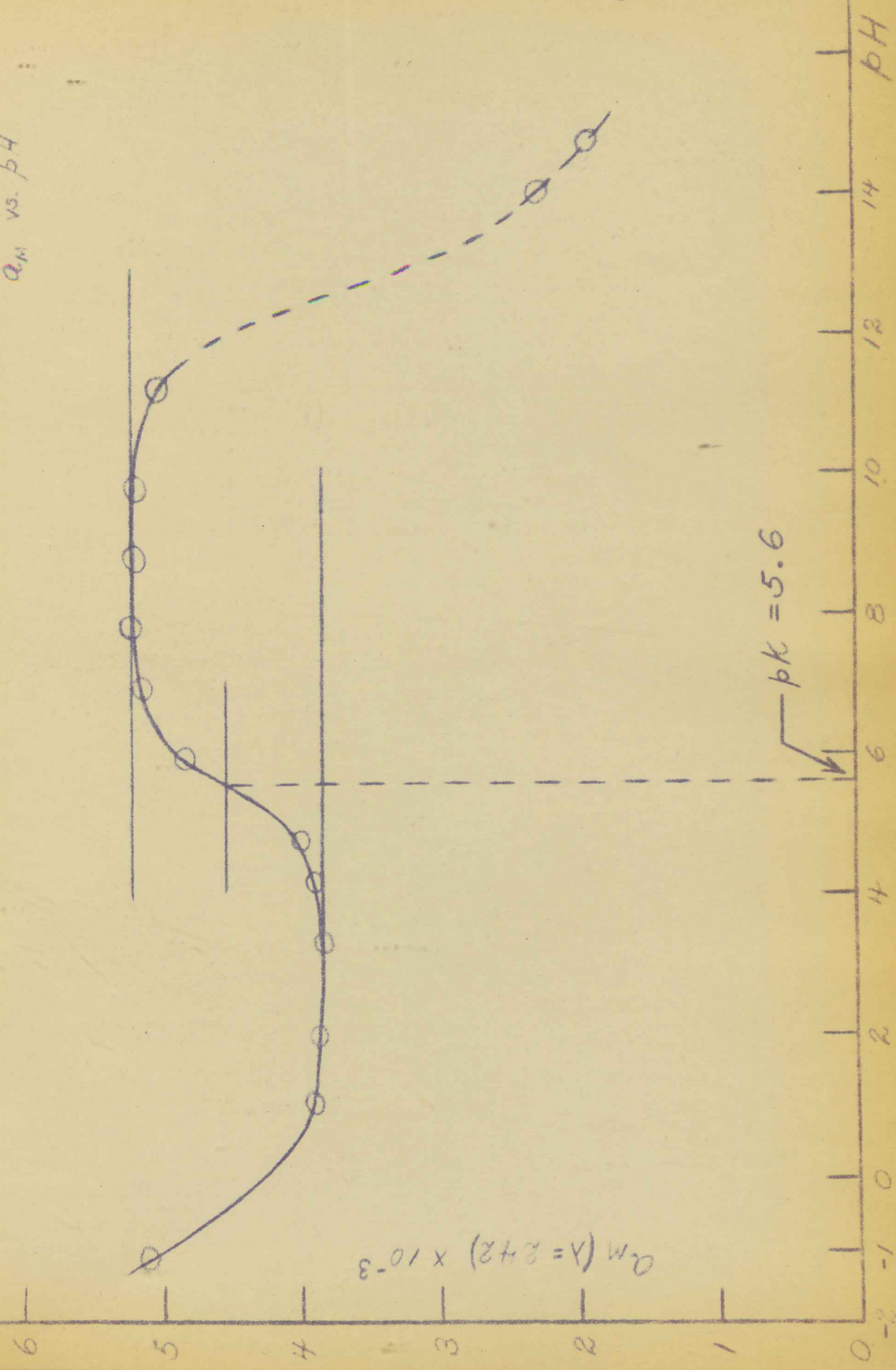
5, (6) - Chlorobenzotriazole

 a_M vs. pH $\lambda = 281$ $pK = 7.7$ a_M

pH

Benzimidazole
 a_M vs. pH

Fig. 14



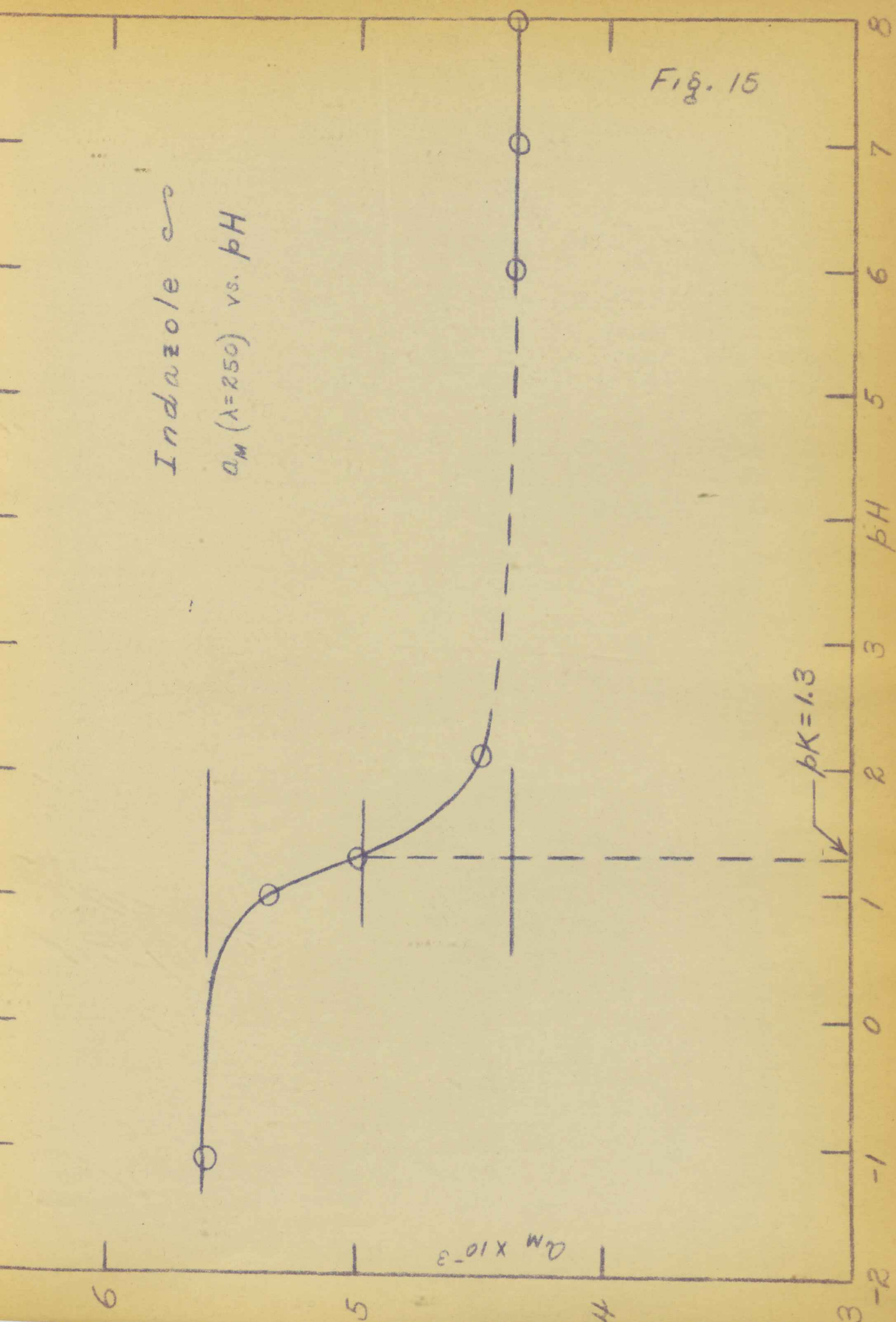


TABLE OF RESONANCE STRUCTURES

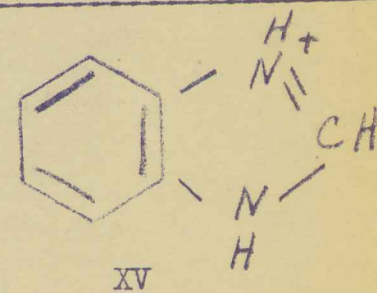
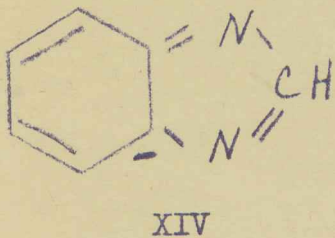
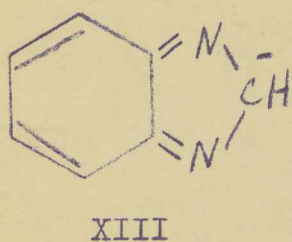
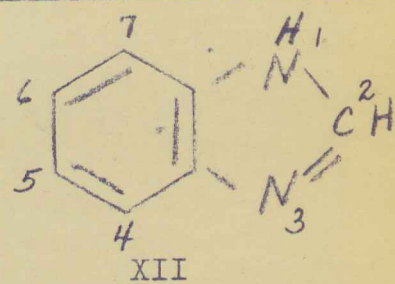
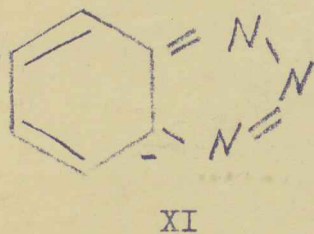
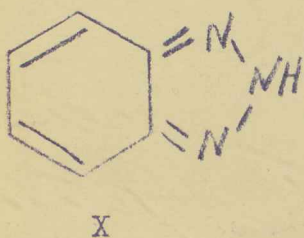
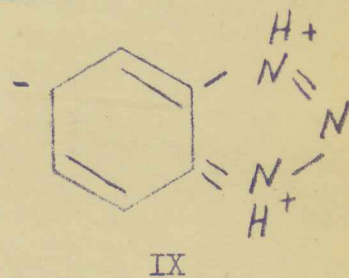
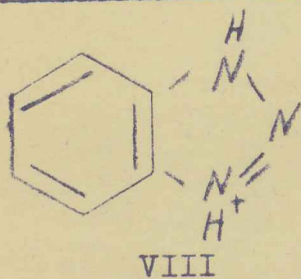
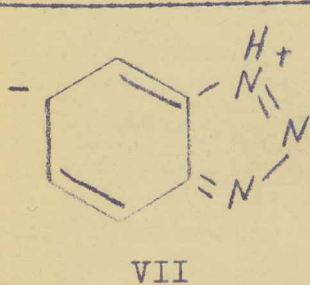
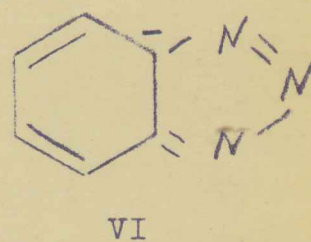
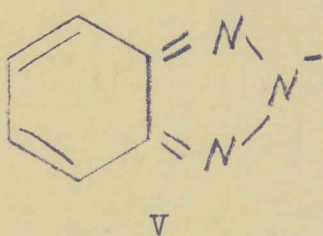
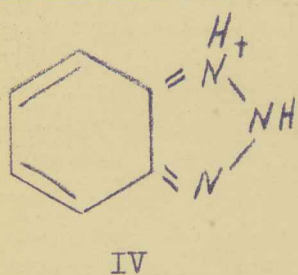
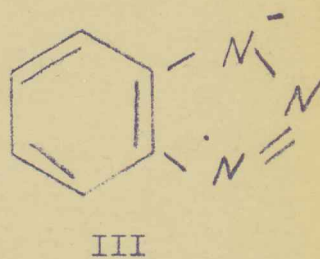
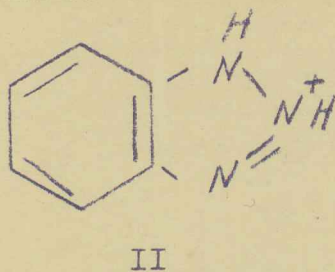
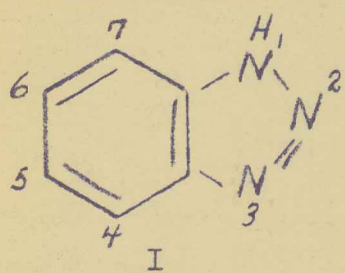
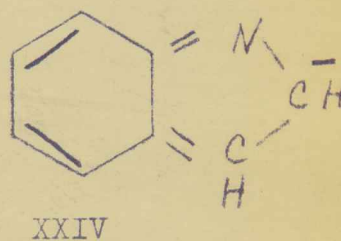
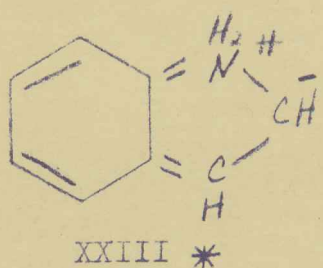
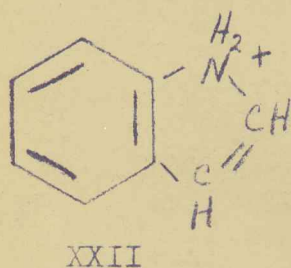
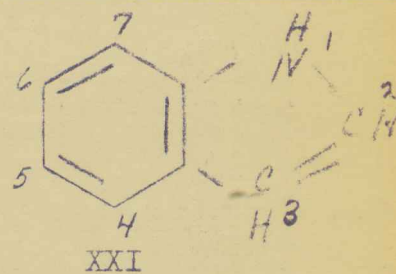
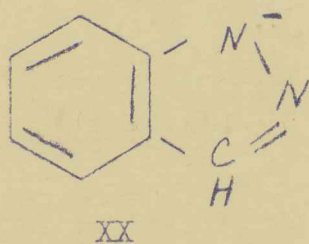
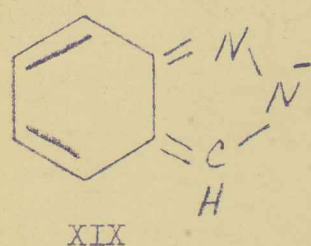
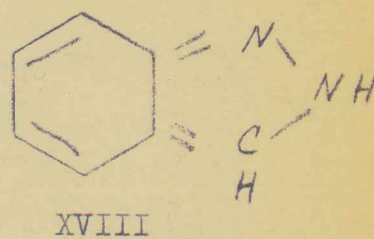
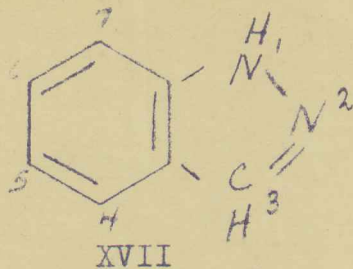
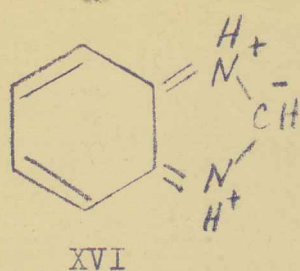


TABLE OF RESONANCE STRUCTURES (cont.)



Erratum- Resonance structure XXIII is void (ten electrons around the 1- nitrogen atom). Therefore no structure of the quinoid or semi-quinoid type is possible.

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