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The correlation of the ultraviolet absorption spectra of benzotriazole with its molecular structure

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THE CORRELATION OF THE
ULTRAVIOLET ABSORPTION SPECTRA OF BENZOTRIAZOLE
WITH ITS MOLECULAR STRUCTURE

by

John Edward Fagel, Jr.

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

By John E. Fagel, Jr.

Approved by Galen W. Ewing

January 1950

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Dedicated to

GALEN WOOD EWING

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

146824

May 17, 1950

Thesis

ACKNOWLEDGEMENTS

Part of the work reported in this thesis was done during the summer of 1949 under a grant from the Research Corp., New York, awarded to Dr. Ewing. I spent a most enjoyable summer working on the project, and would like to express formally my sincere thanks and appreciation to Dr. Ewing for extending to me the privilege and opportunity of working with him on the project.

I should also like to acknowledge the helpful suggestions offered by Drs. Harry F. Herbrandson, Howard E. Sheffer, and Robert W. Finholt in the several interesting theoretical discussions we had on the subject.

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ABSTRACT

The purpose of this research was to derive, on a theoretical basis, a correlation between the ultraviolet absorption spectra and the molecular structure of benzotriazole.

The ultraviolet spectra of buffered aqueous solutions of benzotriazole at numerous pH values from strong acid to strong base have been determined with a Model DU Beckman Spectrophotometer, and an attempt has been made to correlate these spectra with the molecular structure of the compound.

As a check on the validity of the theory proposed in correlating the absorption spectra with the molecular structure, the spectra of 5,(6)- chlorobenzotriazole have been determined under the same conditions and compared with the spectra predicted on the basis of the proposed theory for the 5,(6)- chloro derivative.

Further minor evidence, not related to the absorption spectra, is also presented which, in part, substantiates the proposed theory.

NOTE

The reader will note that in the following introductory remarks the term "light" is used in a loose sense to refer not only to those electromagnetic radiations which are responsible for the sensation of visible color but also to all such radiations in the near-ultraviolet and infra-red regions of the spectrum. The author feels that such usage is justified on the grounds that it is easier to comprehend the general phenomenon of "light" absorption when it is approached first from the point of view of those interactions which lead to readily observable results than when it is approached from an opposite point of view. It is easier for one to understand a phenomenon if it appeals directly to the physical senses rather than indirectly. Once the basic idea is understood, it may readily be transferred to those situations which demand the use of instrumental methods. The phenomenon of "light" absorption is perfectly general in any region of the electromagnetic spectrum; the only difference involved being one in the magnitude of the energy transitions.

INTRODUCTION

It is not at all surprising that man, endowed with an active curiosity, should have attempted to discover why certain substances in his environment possess color and others do not. All about him are nature's colorful displays; ranging from certain sands and rocks to the myriad colors of autumn foliage. What is it, he must have wondered, that causes some substances to appear brightly colored and others to be completely devoid of any color at all? And of the many colored substances, why are some red, others green or blue, and still others intermediate in shade?

These and related questions have been the source of exhaustive study and investigation throughout the history of scientific endeavour. Only comparatively recently, however, with the advent of quantum mechanics and the theory of resonance, has man been able to answer these questions with any real facility. Even at his present state of learning, many of the answers he has devised are empirical at best, and he is apparently still a long way from fully understanding the really fundamental reasons underlying the cause of color.

INTRODUCTION (cont.)

Much work remains to be done before it will be possible to predict and fully explain color in the material substances about us, but eventually, through the fusion of empirical and theoretical data, we shall find the answer to our questions.

It is hoped, then, that the work reported herein will be a true contribution, and in some small way aid in furthering our general knowledge of the relationship between color and chemical constitution. If, however, this contributes no more than hitherto unpublished absorption data, the work will have been justified in that it has added to the bulk of empirical data on the phenomenon of light absorption; thus placing us one step closer to our ultimate goal.

HISTORICAL

It was early recognized that certain physical properties of substances are intimately related to their molecular structure and not merely to their physical state of aggregation. For example, crystalline quartz exhibits the phenomenon of optical rotation, but quartz in a non-crystalline form fails to do so. Clearly then, the crystal itself and not the individual quartz molecules must be responsible for the observed activity.

As early as 1815 - 1817, however, Biot (1,2,3) discovered that certain organic compounds exhibit optical activity not only in their solid states but in their liquid and gaseous states as well. Clearly then, in this case, the observed activity must be due to some inherent property of the individual molecules themselves and not merely to their physical arrangement in any particular state.

Similar considerations have likewise been found to exist in the phenomenon of light absorption. Miller (4), for example, writing in 1864 on his measurements of absorption in the ultra-violet region, states, "The most interesting fact, however, disclosed by these various experiments is the persistence of either the diactinic or the absorbent property in the compound whatever be its physical state-

HISTORICAL (cont.)

a circumstance which proves that the property under examination is intimately connected with the atomic or molecular nature of the body, and not merely with its state of aggregation."

A particular substance appears colored because it absorbs from the white light illuminating it all but a few of the wavelengths which go together to make up the white light. These relatively few wavelengths not being absorbed produce the sensation of color upon reaching the eye. The fact that a given substance is, say, red means merely that it is absorbing the blue, green, and yellow components of the white light and reflecting (or transmitting) the red component; that is, the red component is the left-over quantity following the interaction of the substance with the light incident upon it. It should be evident that the red or reflected component is of little interest in theoretical considerations, for, as indicated above, it is merely a left-over quantity. The components of interest are clearly those that suffer absorption by the particular substance; and the question of foremost interest is why these particular components are absorbed. In other words, some fundamental reason must exist which explains why certain substances absorb light selectively and others do not.

HISTORICAL (cont.)

It is of interest to note that the first report of the existence of a relationship between color and molecular structure was heralded in the first volume of the famous German journal Berichte der Deutschen Chemischen Gesellschaft (5,6). Shortly thereafter, Witt (5,7) presented to the world his theory of chromophores and auxochromes. While it is perfectly true that his theory was entirely empirical, it was nonetheless valid and useful. Today, seventy-four years later, it is every bit as true and useful as it was when first presented.

Briefly, Witt postulated that in order for a substance to possess color it must contain certain characteristic unsaturated groups, which he called chromophores. Representative of the class are the carbon - carbon double bond, the nitrogen - oxygen double bond, etc. He further postulated that the color of compounds containing such groups was intensified by the presence of other groups, which he called auxochromes, such as $-OH$, $-NH_2$, etc.

In the years that followed, Hartley, Baly, Henri and others (5,8), working with the rapidly accumulating bulk of absorption spectral data, attempted to correlate the absorption spectra with the chemical constitution of the absorbing compounds.

HISTORICAL (cont.)

In addition to Witt's theory, it was soon discovered, for example, that similar structures had similar absorption spectra. Thus it was found that all simple ketones and aldehydes exhibit absorption peaks, characteristic of the carbonyl group, in the same general region of the spectrum (the near ultraviolet). With observations such as these in mind, Henri (8) extended Witt's definition of a chromophore to include any group which produces a characteristic absorption peak in any region of the spectrum - not only in the visible, but the ultraviolet and infra-red as well.

Following the initial periods of experimentation in the field of light absorption, wherein many empirical relations were observed and noted, several theories were proposed to account for the phenomenon. Amongst the earliest of these was the belief advanced by Hartly (5,9) that the absorption was characteristic of the parent compound and was merely altered by the presence of substituent groups on the parent; that is, the parent compound responsible for the absorption retained its identity from one situation to another.

Contrary to Hartley's belief, however, and representative of modern theory, the theories of Baly (5,10), Kauffmann (5,11), and Hantzsch (5,12) embodied the general principle that color (light absorption) is due to valency changes in a particular molecule (5).

HISTORICAL (cont.)

The similarity of certain of these theories to modern theory (based on quantum mechanics and the theory of resonance) is indeed remarkable. Hantzsch (5,12), for example, "attributed color to changes in the distribution of affinity without accompanying changes in the relative positions of atoms, a phenomenon which he called valency isomerism."

During this same period the belief was also advanced (Baeyer - 5,13) that color in certain compounds is caused by a tautomeric shift of some particular atom in the compound.

Apparently Campbell (5,14) was the first to attribute the phenomenon of light absorption to vibrating electrons. His stand was later championed by both Lewis (5,15) and Wells (5,16).

The theory of light absorption as we know it today was probably conceived by Bury (17) in 1935. In his now well known paper he made the first attempt to explain color (- of certain organic dyes) by a combination of Witt's theory of auxochromes and the theory of resonance (17a). In brief, he showed how the presence of the auxochromic groups introduced the possibility for resonance in the molecule.

HISTORICAL (cont.)

The post-Bury period has yielded a great wealth of new data and ideas on the general subject. Probably the greatest single impetus to carry out research in the field came in the early 1940's in the form of the Beckman Quartz Spectrophotometer (18) - a versatile, reasonably priced instrument of high precision and accuracy, yet simple enough to be operated by a relatively unskilled operator. This one instrument must be credited for the majority of the work done in the field in this country in recent years. It has made possible the extensive application of the methods of light absorption in both the visible and ultraviolet regions, and through such application has greatly expanded the bulk of available information on the general subject.

It would be out of place in a paper of this sort to attempt to develop further the history of such a broad field of endeavour. It is hoped that the above gives a reasonably representative and accurate picture of the field as a whole.

For further and more detailed information, the reader is referred to the many excellent and interesting reviews on the subject which have appeared in recent years (5,19,20, and others).

THEORY

As indicated previously, the generally accepted view held today is that light absorption is intimately related to electron oscillations within a particular absorbing molecule.

Specifically, it is believed that the absorption of electromagnetic radiation causes the atom or molecule to undergo certain energy transitions; that is, the energy of the absorbed radiation increases the energy of the absorbing species above its normal or ground state energy. The Bohr equation tells us that the difference in energy between the ground and excited states is proportional to the frequency of the radiation absorbed: $E_1 - E_0 = h\nu$, where ν is the frequency, h the Planck constant, and E_0 and E_1 the energies of the ground and excited states, respectively. (Note that the excited state is the state resulting upon the absorption of energy by the atom or molecule.)

We are now in a position to ask just what happens when an atom or molecule passes from its ground state into an excited state. The answer in the case of individual atoms is quite simple: the absorbed energy causes certain electrons in the atom to move from their normal energy levels to levels of higher energy. Since such transitions are restricted according to the principles of quantum mechanics, only a definite number of discrete excited states are possible for any given atom.

THEORY (cont.)

When dealing with a simple monatomic substance, composed of a tremendous number of individual atoms, all of the possible transitions are observed simultaneously; that is, some of the individual atoms will undergo one of the possible transitions, others a second, still others a third, etc. The net result, of course, is an instantaneous appearance of all the excited states. The observed result is the familiar and characteristic line spectrum - each line of which corresponds to a single energy transition.

The answer in the case of even the simplest polyatomic molecule is, however, much more complicated than that given above for an individual atom. Not only are the same relative electronic transitions possible, but also, associated with each, certain rotational and vibrational transitions. The energies required for the latter two are of a much smaller magnitude than those required for the former. Many rotational and vibrational transitions will therefore accompany each electronic transition. This results in a series of lines very close together; many of which are so close that existing dispersing instruments are unable to separate them. The spectrum, for this reason, is known as a band spectrum.

THEORY (cont.)

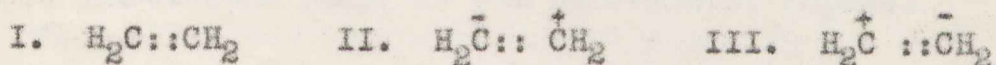
Having thus considered the fundamental aspects of the theory of light absorption, we may now take up a specific case: absorption by organic compounds. The following presupposes the reader to be familiar with the general principles of the theory of resonance.

The organic compound ethylene appears colorless in the visible region of the spectrum, but when examined in the ultra-violet region it reveals a definite absorption peak at approximately 180 mmu. (21). No such behavior is exhibited by compounds such as ethane, pentane, hexane, etc. (the saturated hydrocarbons). We must conclude, then, that color and unsaturation are somehow intimately related. In the light of modern resonance theory, the explanation is quite simple.

From the wavelength position of the absorption peak we see that, relatively speaking, the energies involved are rather great (that is, the frequencies corresponding to such relatively low wavelengths are large). According to the Bohr relation, this means that the difference in energy between the ground and excited states must be relatively great. Such may indeed be shown to be the case if we consider resonance in the molecule.

THEORY (cont.)

We may conveniently picture the ground state of the ethylene molecule as having structure I, below. The possibilities for resonance permit structures II and III plus contributions from other resonance hybrids of these two for the excited states (22, p. 147). Since relatively great energies are necessary to maintain a charge separation, the energy of the excited state is necessarily much greater than that of the ground state; that is, the ground state is far more stable than the excited state.



The above explains the absorption of ethylenic compounds, but does not indicate why such absorption is characteristic of unsaturated and not of saturated compounds. The answer to this aspect of the general question lies in the nature of the bonding electrons in the two types of compounds.

In the case of the unsaturated compounds, one pair of the four bonding electrons of the unsaturated linkage is considered less rigidly fixed in position than the other pair; that is, one of the two pairs is relatively free or mobile. (Such electron pairs are often referred to as "unsaturation", "mobile", or "pi" electrons). (21, p. 108-09).

THEORY (cont.)

These mobile electrons are easily displaced by energies of the magnitude corresponding to electromagnetic radiations of the ultraviolet region of the spectrum; thus leading to excited states such as postulated above for ethylene.

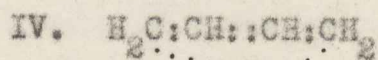
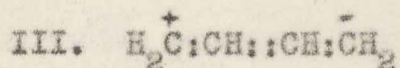
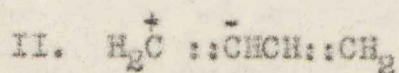
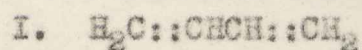
The saturated hydrocarbons possess no such mobile electrons, however, and are thus unable (upon interaction with energies of the magnitude considered) to yield corresponding excited states. They therefore show no electronic absorption spectra in any easily accessible range of the ultraviolet region.

In conclusion, let us consider the absorption of butadiene as representative of conjugated unsaturated compounds.

Whereas it is observed that a compound such as pentadiene-1,4 (containing two isolated unsaturated linkages) absorbs in the same general region of the spectrum as ethylene (but with the magnitude of absorption about twice that for a single unsaturated linkage) (e.g. 21, p. 112-13); it is found that butadiene absorbs at relatively much greater wavelengths (approximately 217 mμ.) (21, p. 114). The Bohr equation tells us in this case, then, that the difference in energy between the ground and excited states must be relatively less than in the case of ethylene; that is, the excited states must somehow be stabilized relative to the ground state. Resonance theory gives us the answer.

THEORY (cont.)

If we picture the ground state of the butadiene molecule as having structure I, the excited states, corresponding to those drawn for ethylene, are represented by II and III plus contributions from other resonance hybrids of these two. (22, p.148). In addition, however, one further resonance structure may be drawn: IV, in which the dotted line represents a formal bond. Resonance theory tells us that the energy difference between these two states is indeed smaller than the corresponding energy difference in the case of the ethylene molecule; and that, therefore, the absorption peak should be located at a relatively greater wavelength.



For a more detailed and complete account, the reader is again referred to existing texts, articles, and reviews. (8,24,17,20,23,26,29,5,19,21,25,27,28).

THEORY (cont.)

Part Two

The fundamental law of absorption photometry, the Beer-Lambert law, relates the fraction of the incident light absorbed to the number of absorbing molecules present in the path of the light beam (e.g. 21, p. 107). Mathematically stated:

$$dI/I = -Kdn$$

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

Integrating between the limits $I_0 - I$ and $0 - n$:

$$\ln I/I_0 = -Kn \quad \text{or} \quad \log I_0/I = k'n$$

At constant temperature, the number of molecules is determined by 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 working form:

$$\log I_0/I = kcl$$

where c is the concentration and l is the length of path.

THEORY (cont.)

Part Two

The logarithm term is given the name optical density, extinction, or absorbancy; and the corresponding symbols D , E , or A_s . The latter term is a part of the new terminology in use by the National Bureau of Standards. (30). Throughout the present work, the former term will be used.

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 the gram per liter and the gram mole per liter. The latter is, of course, the more fundamental and will be used in the present work.

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

THEORY (cont.)

Part Two

If the centimeter and the gram mole per liter are chosen as the units, the proportionality constant is given the symbol ϵ or a_M and is known as the molar extinction coefficient or the molar absorptancy index. (In both cases the latter expressions are from the National Bureau of Standards terminology).

Historically, it is of interest to note that the fundamental law was not derived as a unit as presented above, but in two parts: Lambert's law (31,33), which relates absorption to the length of path through an homogeneous medium (successive layers of equal thickness absorb equal fractions of the radiation at constant wavelength); and Beer's law (32,34), which relates absorption to the concentration of absorbing material at constant cell length. The two laws are easily combined to give the final fundamental law as already presented.

There are no known exceptions to Lambert's law, but often Beer's law does not hold (that is, density does not always vary linearly with apparent concentration at constant cell length). It is now generally accepted, however, that deviations from Beer's law result only when there is a change in the nature of the absorbing species (through dissociation, association, etc.); that is, as long as the nature of the absorbing molecules remains the same, Beer's law is strictly followed.

EXPERIMENTAL PART

Apparatus.

The spectra were determined with a Model DU Beckman Spectrophotometer (18), Serial No. 3210, equipped for ultraviolet measurement.

The sensitivity control of the instrument was set at its counterclockwise limit (minimum sensitivity) for all determinations, thus allowing measurements to be made down to 210 m μ . wavelength. Slit widths varied from approximately 1.6 to 0.3 mm., as the extreme limits. Except at the lower wavelengths (210-220, approximately), the average slit width used was in the range 0.5 to 0.3 mm. (This corresponds to a nominal band width (35) isolated of 1.0 ± 0.2 m μ .).

In no instance were readings taken at wavelength intervals greater than 5 m μ . Near the regions of main interest readings were taken every 2 m μ ., and in the immediate vicinity of the maxima and minima readings were taken at 1 m μ . intervals.

The cells used were matched, fused-silica cells of square cross-section; 10 mm. \times 0.01 mm. on the inside.

The pH of all buffer solutions was checked with a Model G Beckman pH Meter.

Melting point determinations were made with a simple Thiele tube apparatus calibrated at various intervals with compounds of known purity and melting points.

EXPERIMENTAL PART (cont.)

Calibration of the Apparatus.

The spectrophotometer was checked and calibrated against the hydrogen α -line (656.3 m μ .) approximately once a month.

A complete wavelength - density test spectrum of standard chromate solution (36) was run approximately every two months. In all cases, it was found that accurate and reproducible results were obtained for both wavelength and density values over the range 210-500 m μ ..

The pH meter was checked and calibrated periodically with National Technical Laboratories concentrated buffer solution (1:25) at pH 7.0. When solutions of high or low pH were to be measured (greater than pH 10 or less than pH 2), the meter was calibrated against National Technical Laboratories buffer solutions of pH 10.0 or pH 2.0; since it was found that a discrepancy of a few tenths of a pH unit was introduced in the ends of the scale if calibration was made in the middle of the scale (at pH 7).

EXPERIMENTAL PART (cont.)

Preparation of the Compounds.

1. Benzotriazole

The material used was obtained by benzene extraction from a photographic anti-foggant, "Orthazite", distributed by the Edwal Laboratories and purchased from a retail photographic dealer. Apparently the benzotriazole was present as a mechanical mixture with a benzene-insoluble residue of unknown composition.

After extraction the material was recrystallized from benzene solution until a reasonably sharp melting point compound was obtained. The melting point of the final white product, after drying in vacuo at 77° C, was 98-99° C (corr.)

2. 5,(6)-Chlorobenzotriazole

The chloro-derivative was synthesized from 4-chloro-o-phenylenediamine (Eastman Pract.) by diazotizing and self-coupling, according to the procedure of Damschroder and Peterson (37) for the synthesis of benzotriazole from o-phenylenediamine (37,38).

The crude yield was recrystallized from xylene. After drying in vacuo at 100° C, the final white product melted at 156-157° C (corr.).

EXPERIMENTAL PART (cont.)

Preparation of Solutions.

Solution concentrations used for both the parent compound and the chloro-derivative varied between 10 and 15 mg. per liter. The reference liquid used in every determination was from the same batch of solvent that was used to make the solution.

Because of the extremely limited solubility of the chloro-derivative in aqueous solvents, it was found necessary (for reasons of ease and economy in the time of preparation of solutions) to dissolve the samples in 2 ml. of stock ethanol before attempting to achieve an aqueous solution. The presence of even such small ethanol concentrations was sufficient to hold the samples in solution.

Because of the presence of the ethanol in the final solutions, a solvent effect on the spectra was possible. In order to determine this effect, if any, a solution was prepared according to the procedure outlined above and checked against a solution of the chloro-derivative in pure aqueous solvent (pH 7.0 buffer in both cases). Identical molar extinction coefficient values (well within the range of experimental error) were obtained for both solutions at like wavelengths over the range 210-300 mμ.

EXPERIMENTAL PART (cont.)

Buffer Solutions.

It was found impossible to obtain a single series of buffers which were suitable for the present use over the entire pH range. The main difficulty is that the buffer necessarily has to be free of ultraviolet-absorbing materials in order not to interfere with or mask completely the absorption of the material being studied.

The Clark and Lubs buffers (39,40) were found ideally suited as solvents, however, except in the range pH 2.0 to pH 6.0. (In this region the buffer solution is made with a biphthalate salt, which causes the solution to become opaque below approximately 300 mμ.). Sørensen's glycine - hydrochloric acid buffers (41,42) were found to possess the necessary transparency in the region not covered by the Clark and Lubs buffers, and were therefore used; although they presented additional difficulties in that they prove themselves excellent media for the growth of fungi.

EXPERIMENTAL PART (cont.)

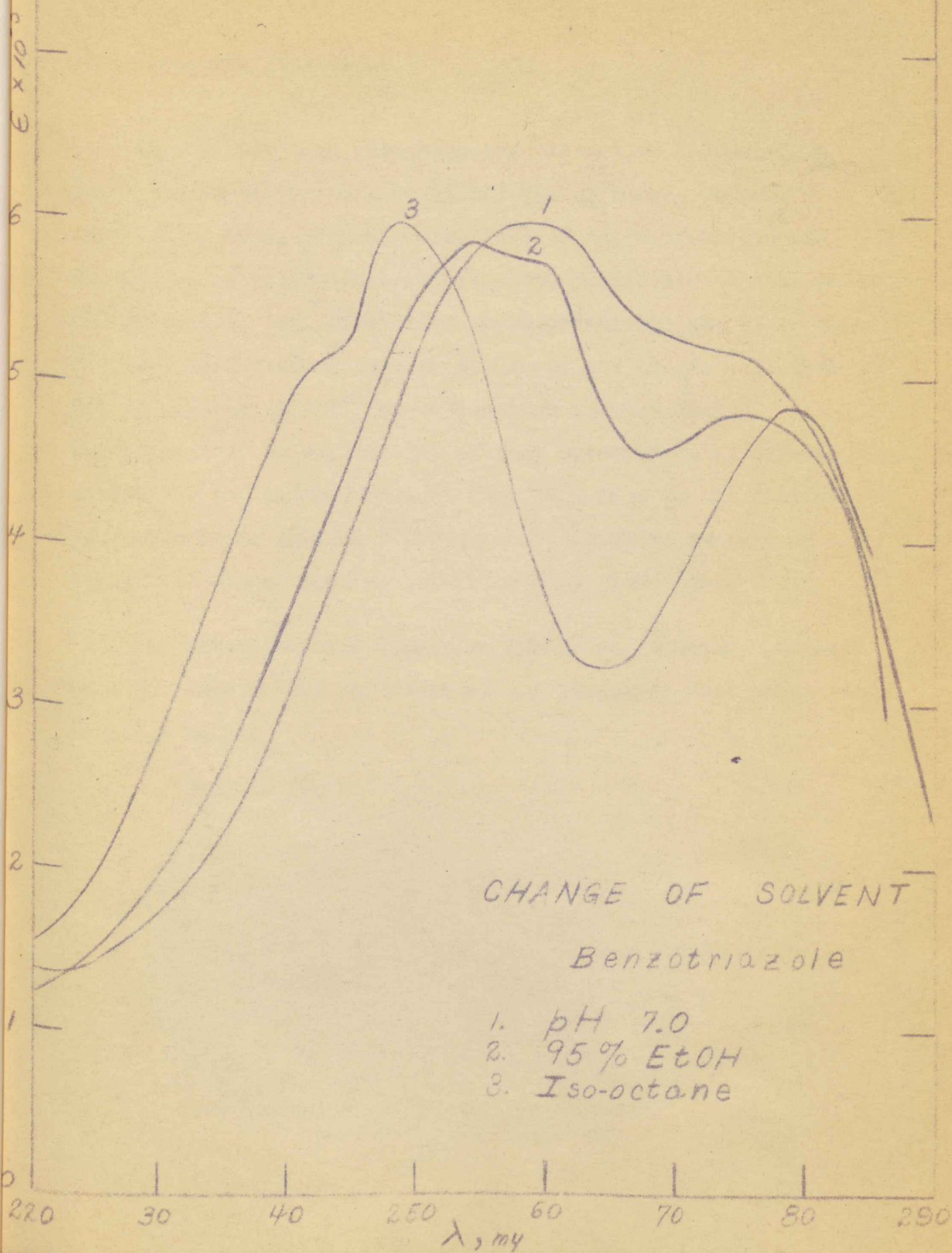
Temperature Effects.

All determinations were made at room temperature. The extreme variations in temperature encountered were 17° C and 33° C. In the main, however, temperature fluctuations were confined to the region $20-25^{\circ}$ C.

The spectra determined at the temperature extremes were subsequently rechecked at $20-25^{\circ}$ C in order to determine if there were any temperature effects on the spectra in the normal temperature range encountered. No apparent deviations resulting from temperature fluctuations were detected in any case.

Solvent Effect.

The effect of solvents of varying polarity on the spectra was found to be in accordance with previous observations recorded for the solvent effect (23,43). It is readily apparent (see curves on next page) that on passing from polar to non-polar solvents the spectra exhibit a general hypsochromic (24, p. 214) shift accompanied by a noticeable increase in the resolution of the fine structure. (See also 21, p. 109).

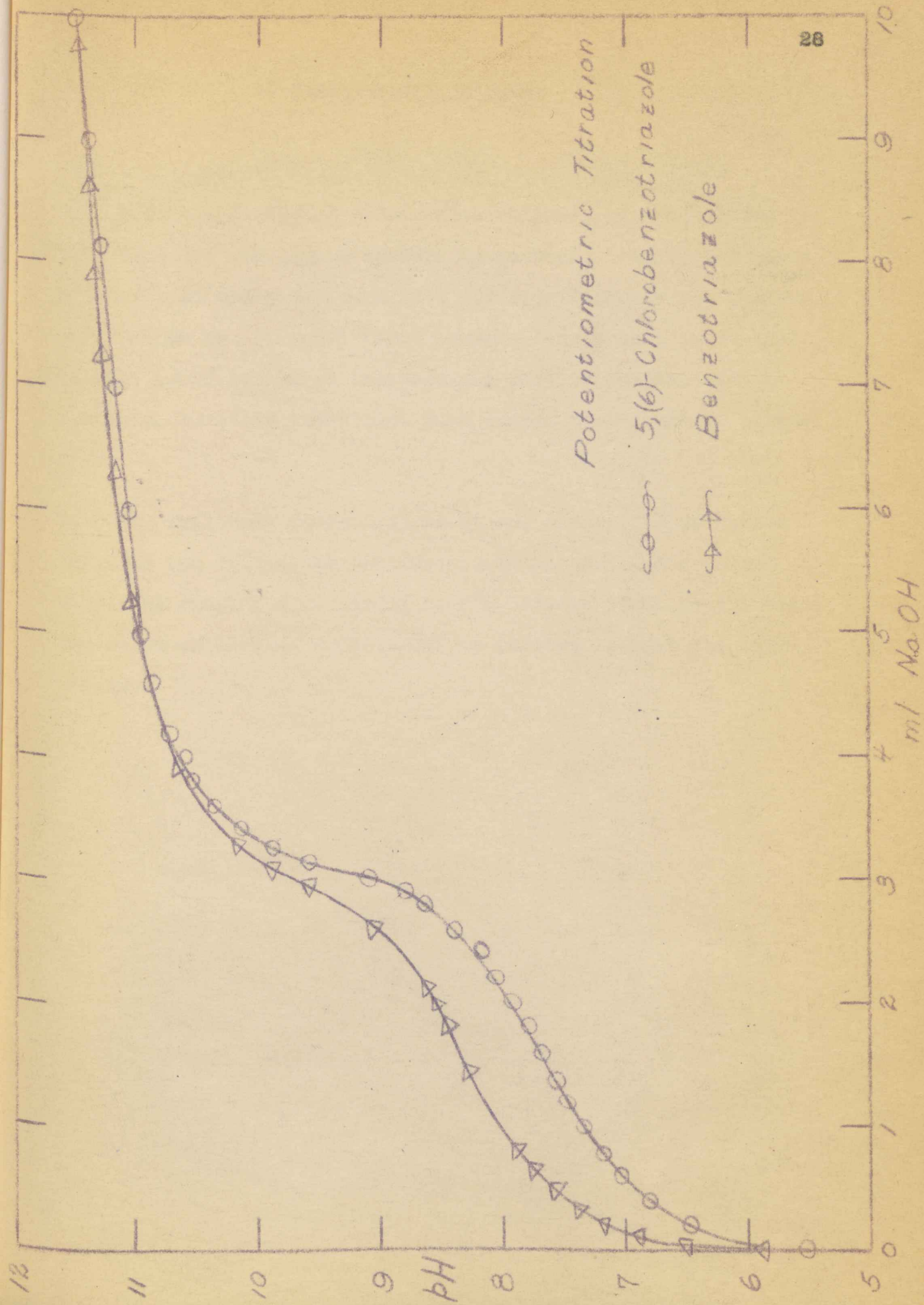


EXPERIMENTAL PART (cont.)

Potentiometric Titrations.

It was felt that potentiometric titration curves might yield useful information regarding the pH ranges wherein significant changes in the structure of the compounds occur. The following potentiometric titration curves indeed show points of inflection, but, as will be shown presently, the pH regions of these inflection points do not correlate at all well with the pH regions in which the absorption spectra change significantly. No explanation of this observation is offered, except for the general thought that it points to the conclusion that absorption spectra afford a more sensitive measure of structural change than do potentiometric titrations.

The potentiometric titration curves do, however, indicate that a change in the structure of the compounds does occur with a change in pH.

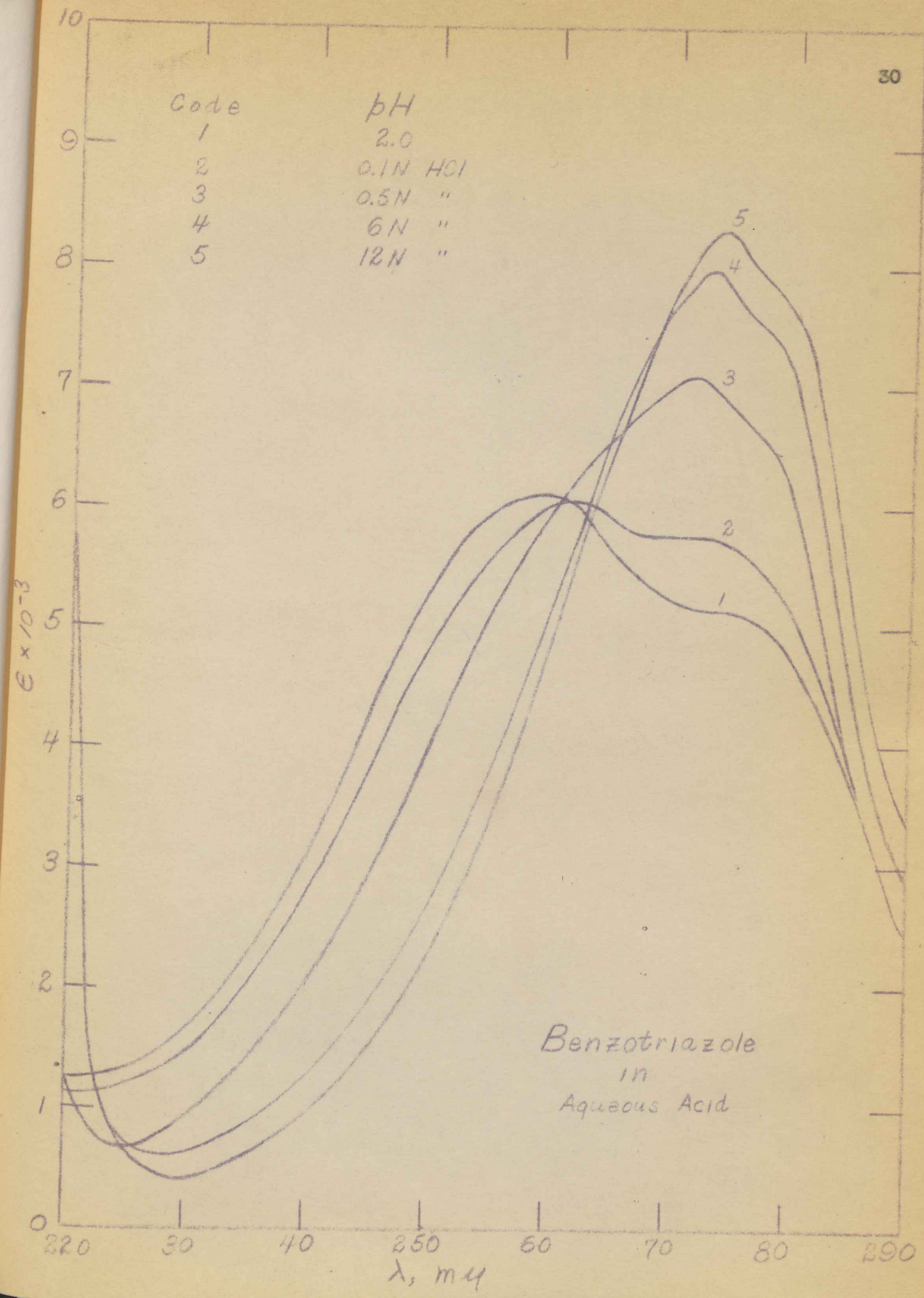


EXPERIMENTAL RESULTS

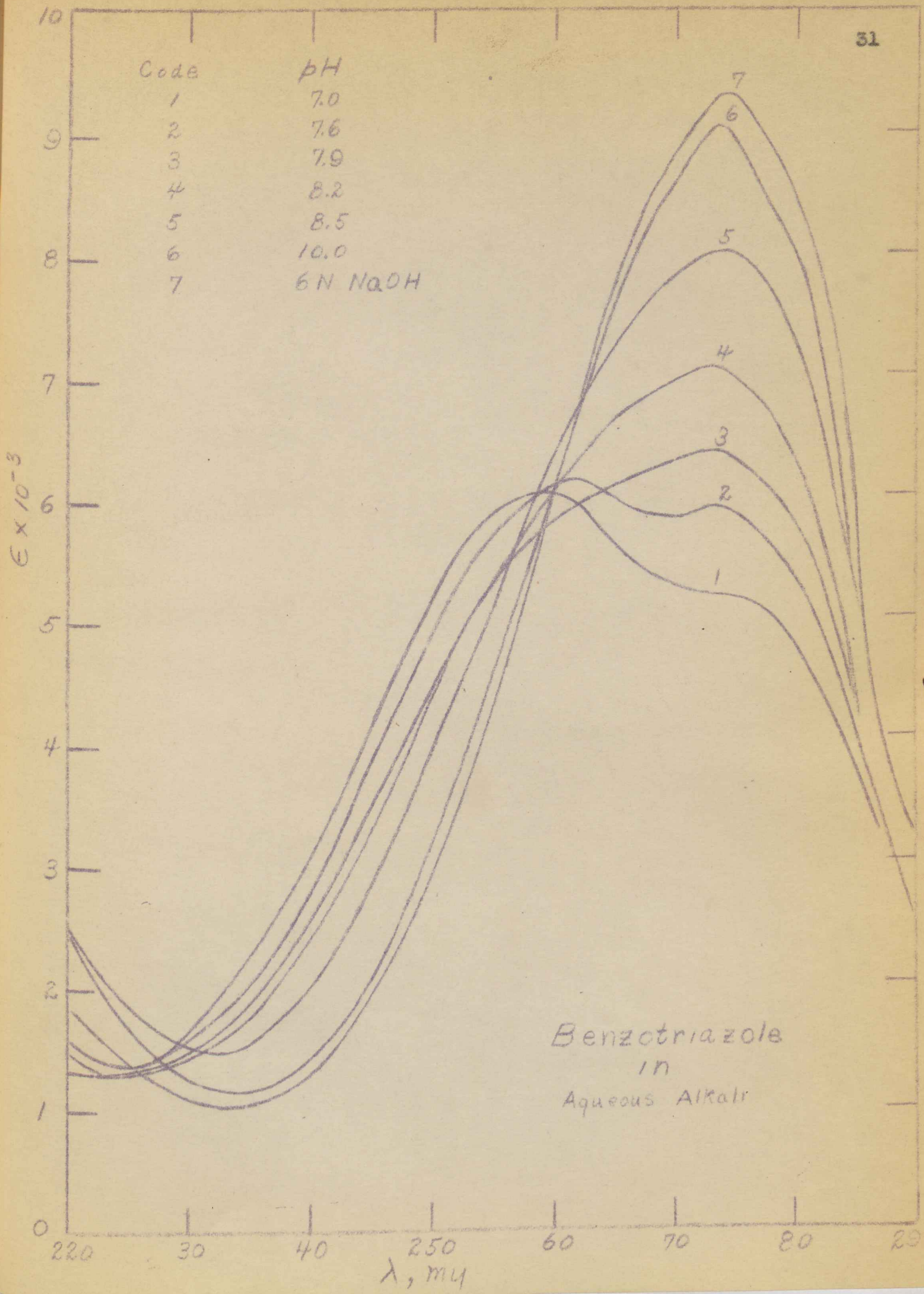
With the foregoing information at hand, it was decided to determine the absorption spectra in neutral, acidic, and basic solutions in order to learn just how significantly the spectra varied with pH. If significant changes were noted, additional spectra could be run at intermediate pH's to complete the spectrophotometric titration. Such indeed turned out to be the case.

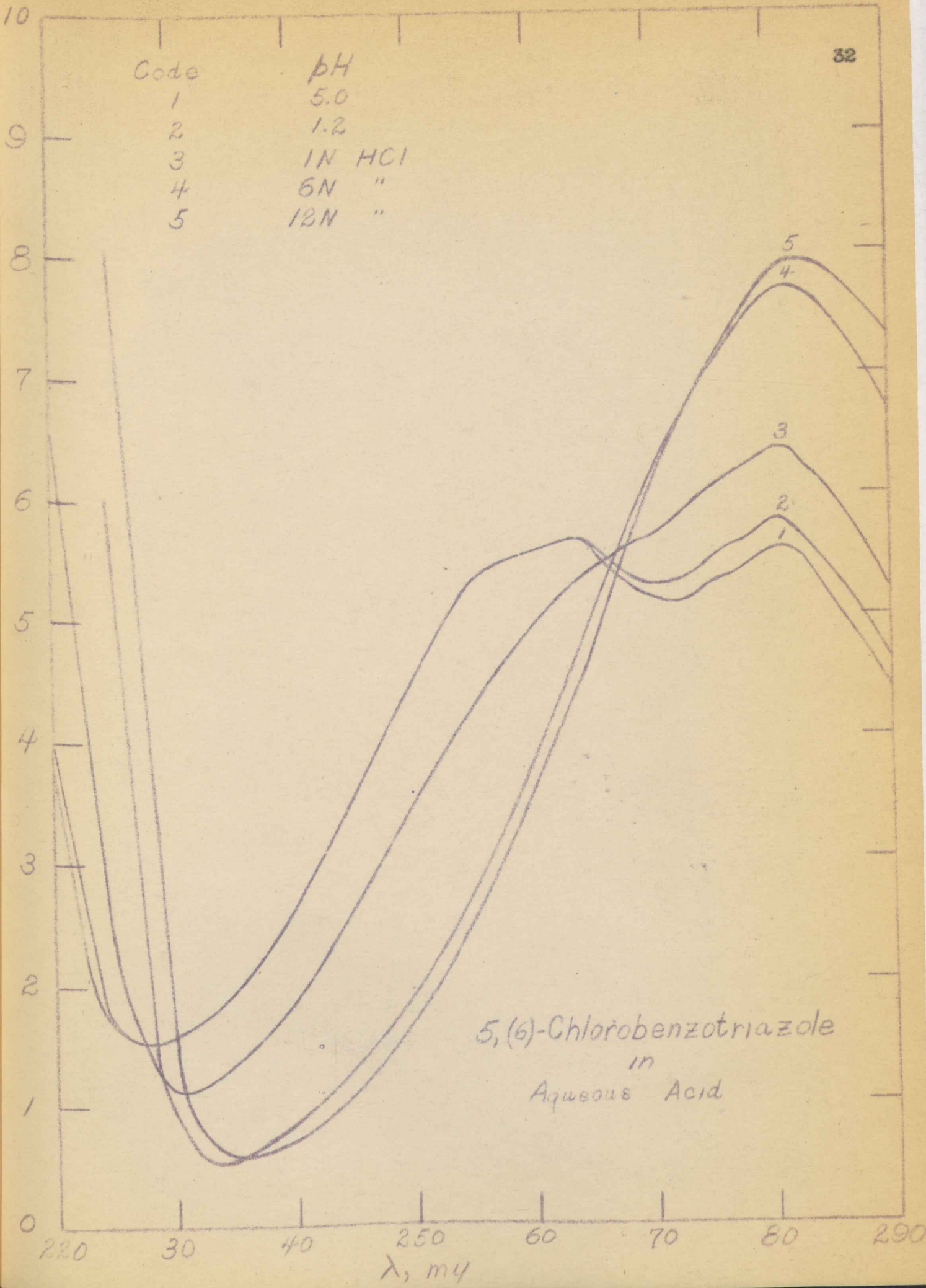
The following curves represent the absorption of benzo-triazole and 5,(6)-chlorobenzotriazole in buffered aqueous solutions ranging from strong acid to strong base. In all cases the molar extinction coefficient is plotted against the wavelength.

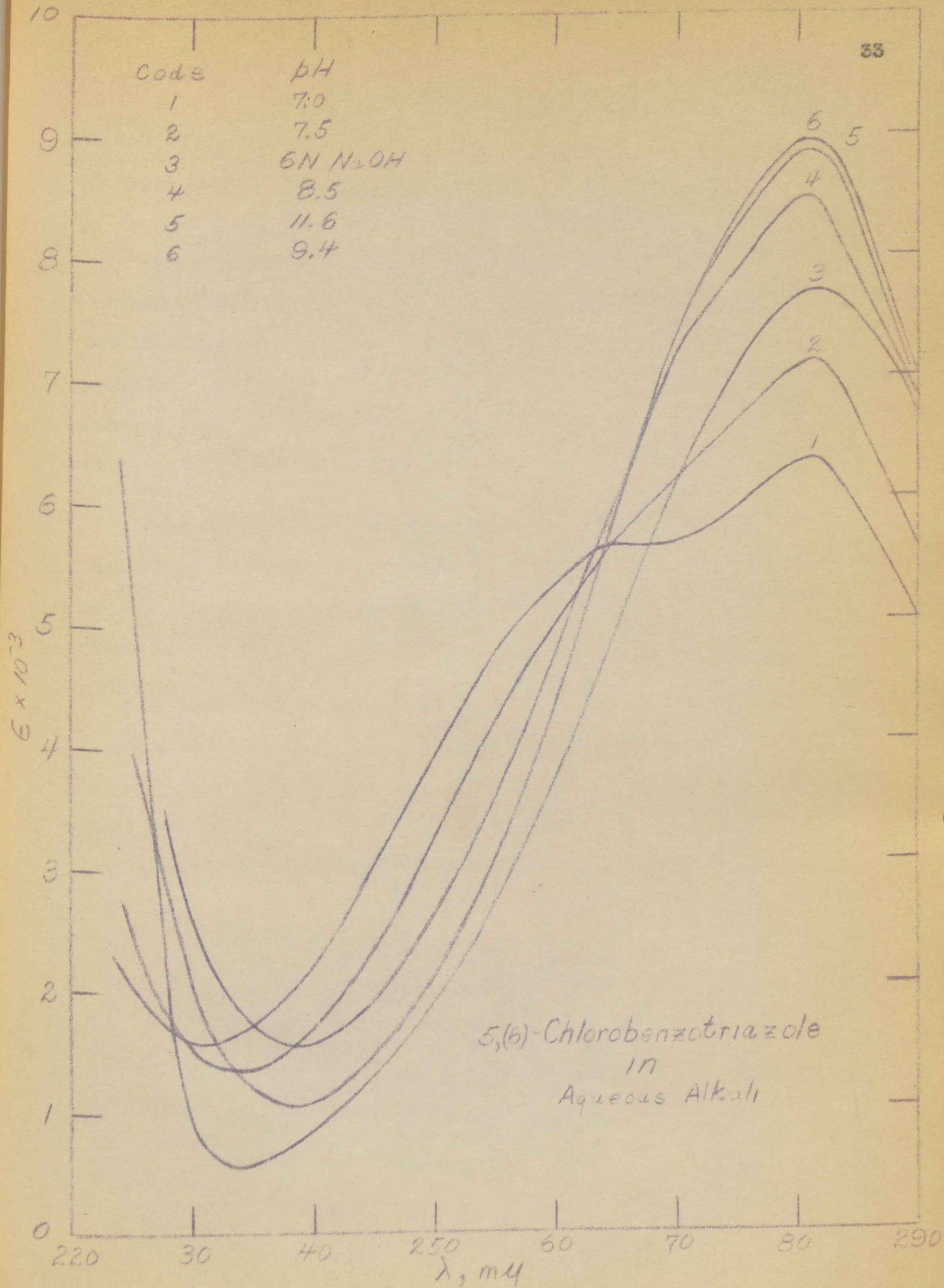
Code	pH
1	2.0
2	0.1N HCl
3	0.5N "
4	6N "
5	12N "



Code	pH
1	7.0
2	7.6
3	7.9
4	8.2
5	8.5
6	10.0
7	6 N NaOH







EXPERIMENTAL RESULTS (cont.)

Analysis of the Hydrochloride of Benzotriazole.

The hydrochloride was prepared by bubbling hydrogen chloride through an ethereal solution of benzotriazole (44). The solution immediately became cloudy and then slowly precipitated long, colorless needles of the hydrochloride. The needles were isolated, washed, recrystallized, and analyzed to determine the number of moles of HCl associated with each mole of the parent compound.

Inasmuch as benzotriazole forms a silver salt, it was impossible to conduct the analysis by silver nitrate precipitation. As an alternate means, cation exchange was employed- a method which proved highly effective.

An aqueous solution of the hydrochloride was washed through a column of "Zeo-Karb", a sulfonated coal product of the Permutit Co., and the effluent titrated with standard base. Within the limits of experimental error, the results of the analysis showed the compound to be the mono-hydrochloride.

Table I

Calc. equivs. (for mono-HCl)	-----	6.43×10^{-4}
Determined	-----	6.25 "
		6.30 "
Average	-----	6.28 "

EXPERIMENTAL RESULTS (cont.)

Determination of pK.

According to Brode and others (39, p. 61;45,46,47), it is possible to determine both pK_a and pK_b of a compound from information of the type just presented: absorption spectra for the compound in buffered solutions of varying pH values.

The following curves were obtained by plotting against pH the molar extinction coefficients of the second (higher wavelength) maximum of the absorption spectra at various pH's. The pK is equal to the pH at which the molar extinction coefficient is midway between its upper and lower limits.

The pK values may also be obtained by calculation from the same general information (48):

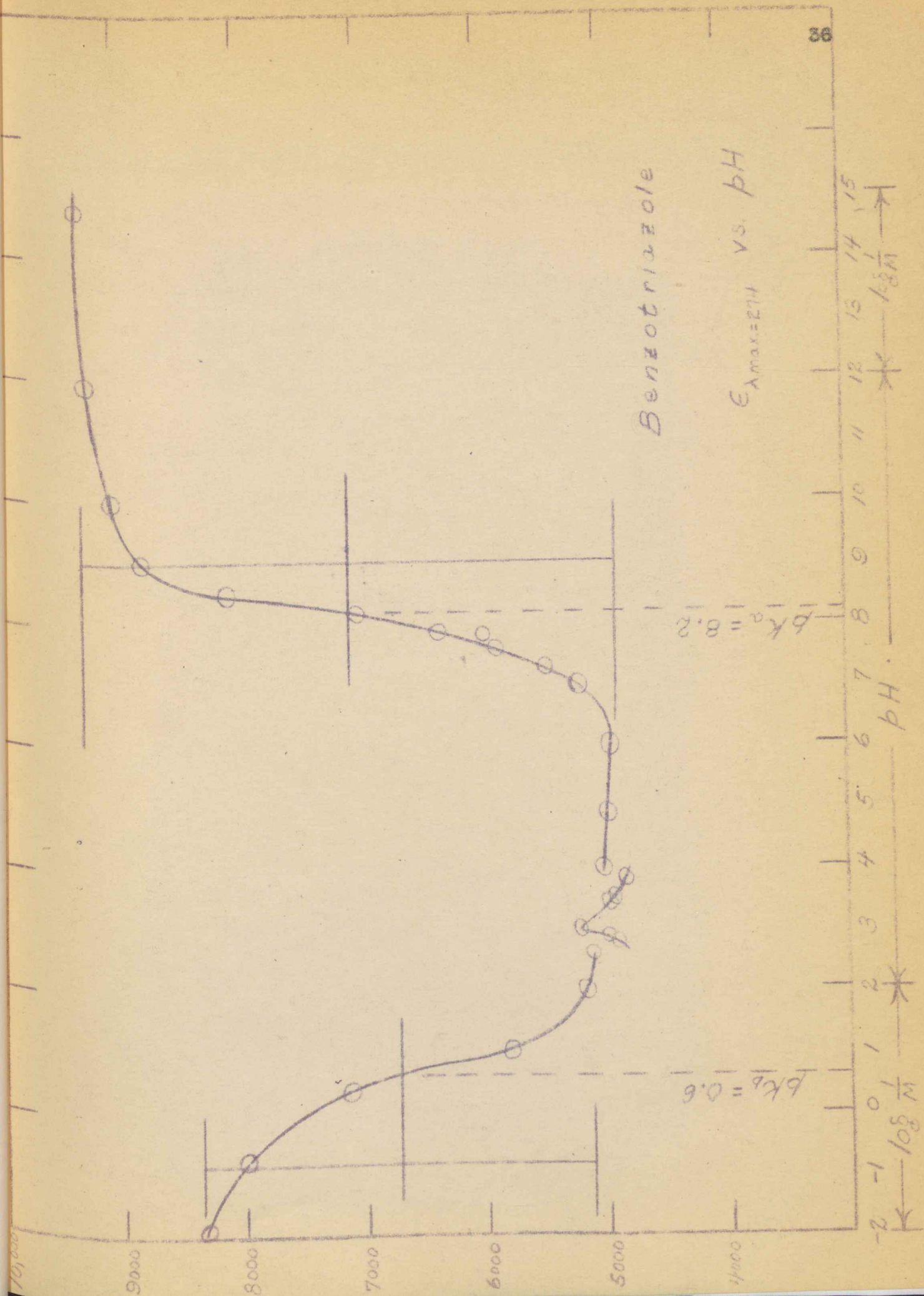
$$pK = pH - \log (\alpha / 1 - \alpha)$$

where $\alpha = (\epsilon_a - \epsilon_m) / (\epsilon_i - \epsilon_m)$. The subscripts m, i, and a refer respectively to the molar extinction coefficients at a given wavelength of the unionized or molecular form of the compound, the ionized form, and a mixture of the two.

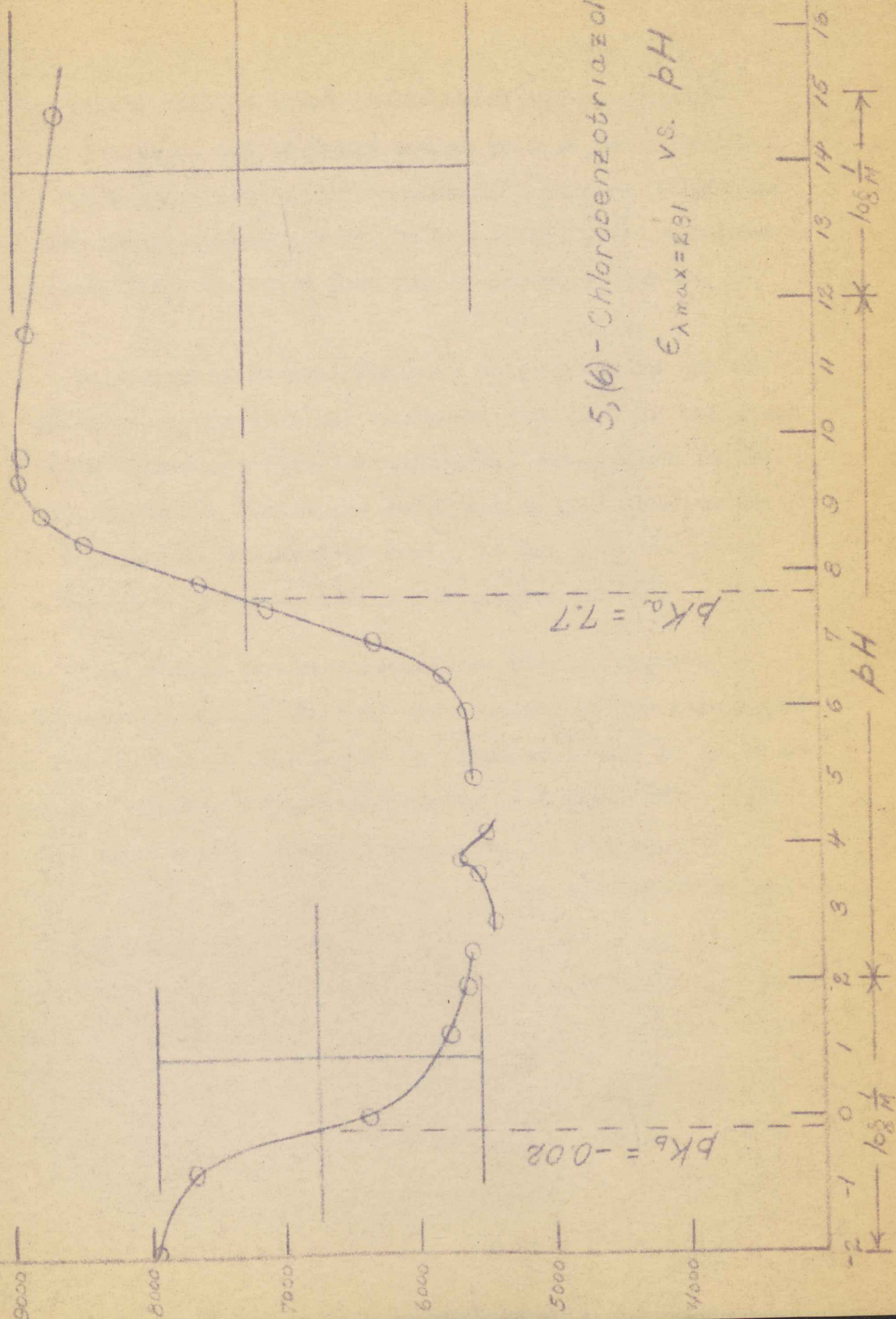
The calculated pK_a of benzotriazole agrees nicely with the graphically determined value; but for reasons which thusfar have escaped detection, the calculated values of pK_b of benzotriazole and both pK's for the chloro-derivative do not agree with the graphically determined values.

Benzotriazole

$\epsilon_{\lambda \text{ max}} = 274$ vs. pH



5, (6) - Chlorobenzotriazole

 $\epsilon_{\lambda \max} = 291$ vs. pH

EXPERIMENTAL RESULTS (cont.)

The reader will no doubt wonder about the apparently anomalous points in the pH range 2-4 on both of the preceding curves. While the author is at as much of a loss as the reader to explain the apparent anomaly, he has investigated the following possibilities and ruled them out as probable causes:

1. Experimental error- Numerous determinations and re-determinations in the pH range concerned were run. In all cases there was no doubt but what the apparently out-of-line points were real. Since the deviations could not be justified on any readily conceivable theoretical basis, it was felt that they must be caused by some extraneous but unknown factor.

2. Time change due to oxidation or similar causes- A buffered aqueous sample (pH 2.8) was examined at the wavelength of the second maximum (274 m μ .) on successive days in order to determine if density varied appreciably with time. After four days, the total change (density decrease) was not at all significant compared to the deviation of the apparently anomalous points from the smooth curve.

EXPERIMENTAL RESULTS (cont.)

3. Presence of an impurity in the sample- Since the "wiggle" has been found to occur in the curves for both the parent compound and its chloro-derivative, it seems improbable that the impurity possibility is the responsible factor. This fact alone, however, cannot rule out entirely the possibility, for the same type of impurity is likely to be present in both compounds.

4. Interaction with the buffer solution- The only other readily apparent possibility lies in the buffer solutions used (Sørensen's glycine - hydrochloric acid buffer was used in the region now considered). That is, it is conceivable that the "wiggle" resulted from some peculiarity in the behavior of the buffer.

To test this possibility, a potentiometric titration of the glycine solution component of the buffer was run. Nothing of any interest showed up in the potentiometric titration curve in the pH region concerned.

As was pointed out previously, however, absorption spectra afford a more sensitive measure of structural changes than do potentiometric titration curves, and therefore the above cannot be considered as conclusive proof. Future work is planned in order to examine this point further.

DISCUSSION

An initial analysis of the absorption spectra reveals four basic types: the spectra characteristic of strongly acidic solutions, mildly acidic solutions (pH 0-3), neutral solutions (pH 3-8), and basic solutions.

It seemed logical to assume the existence of the following structural modifications of the parent compound to account for the four basic spectral types: the anion (XXVII - XXXV), in basic solutions; the normal molecule (I - XI), in neutral solutions; a mono-hydrochloride (XII - XVII), in mildly acidic solutions; and a di-hydrochloride (XVIII - XXVI), in strongly acidic solutions. (The Roman numerals refer to the table of resonance structures in the appendix). As will be shown presently, it indeed appears that these structures represent the significant link in the correlation of the spectra with molecular structure.

In order to test in part the validity of the above assumption, the hydrochloride of benzotriazole was prepared and analyzed to determine the number of molecules of HCl associated with each molecule of benzotriazole. The results of the analysis, as previously noted, support the claim to the existence of a mono-hydrochloride.

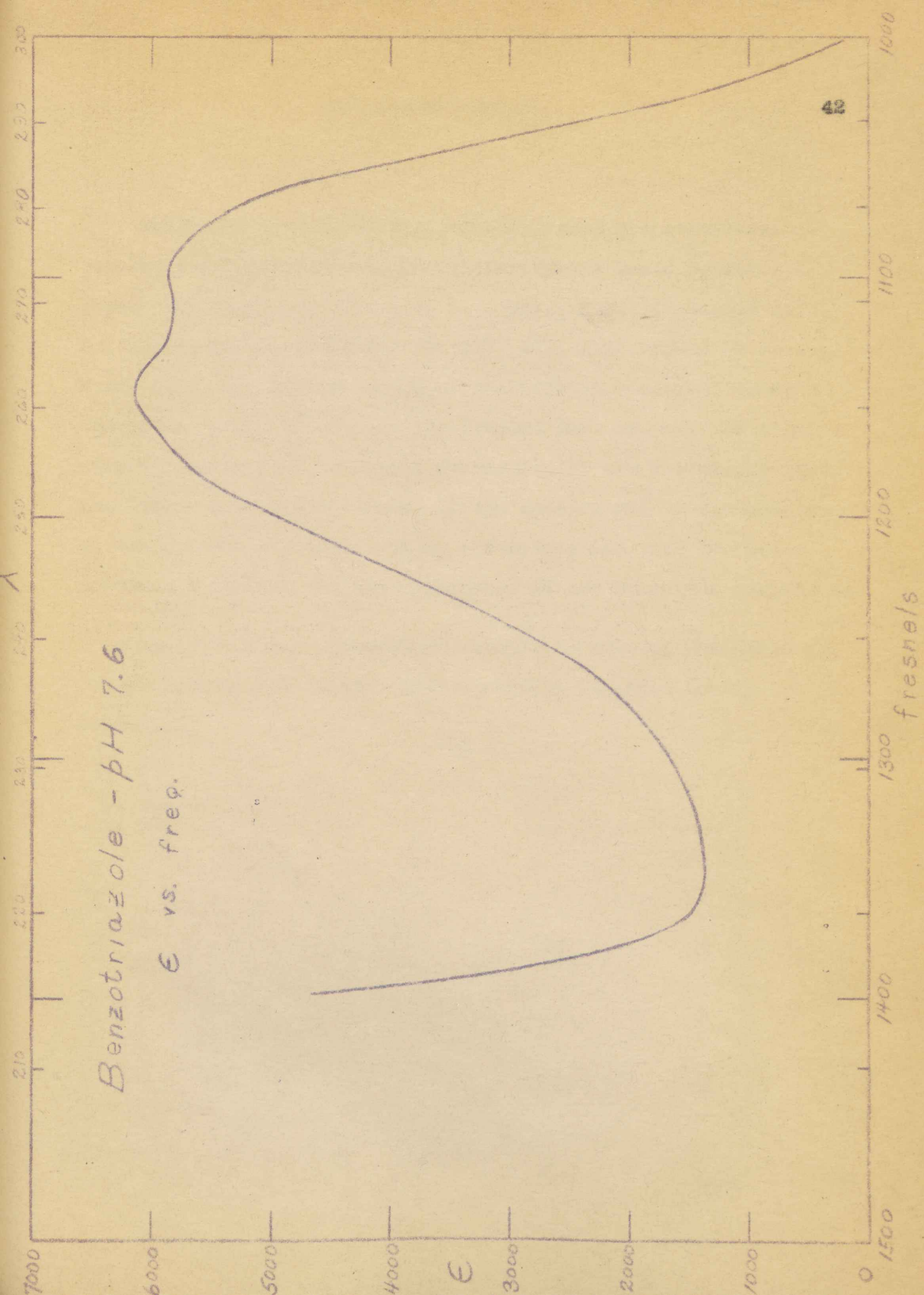
DISCUSSION (cont.)

The next step in the correlation of the spectra with molecular structure was to determine the significance of the two maxima in the absorption spectra. Two possibilities exist: the maxima are harmonics of a fundamental frequency characteristic of a single chromophore, or they are characteristic of two separate chromophores.

Although it was found impracticable to resolve the absorption spectra into partial absorption bands (49), it was possible to analyze an ϵ vs. frequency curve and determine with some degree of certainty that the two maxima are not harmonics of a fundamental frequency (see following curve). The peaks of the partials are probably slightly farther apart than the peaks of the envelope, but it appears nonetheless quite probable that a single fundamental frequency is not involved. The conclusion then is that two separate chromophores are involved.

Benzotriazole - pH 7.6

ϵ vs. freq.



DISCUSSION (cont.)

Reference to some of the possible resonance structures of benzotriazole (see appendix) discloses three basic structural types: the benzenoid (e.g.; I, XII, XVII, XXVII), quinoid (XIV, XX, XXIX), and semi-quinoid (V, XIV, XXI, XXX). Since it is well known (see, e.g., 5) that quinone and related compounds exhibit absorption peaks at greater wavelengths than benzene and other simple compounds of benzenoid structure, it was postulated that the longer wavelength maximum of the spectra was characteristic of the quinoid and semi-quinoid structures and that the lower wavelength maximum was characteristic of the benzenoid structures.

With the above assumptions in mind, a logical theoretical correlation of the spectra with structure is quite easily developed.

DISCUSSION (cont.)

In order to avoid undue confusion in the presentation, the following theory of correlation will be discussed for the four spectral types individually.

1. Strongly Acidic Solutions- Reference to the table of resonance structures shows that in strongly acidic solutions the principle resonance contributors are of the quinoid and semi-quinoid type. Furthermore, since resonance occurs between several equivalent structure-pairs (XXI,XXII;XXIII,XXIV, etc.), it is expected that such resonance should be of relatively great importance. Therefore it would seem highly probable that the spectra of strongly acidic solutions should show a strong peak at the higher (274 mmu.) wavelength. Experimental evidence bears this out.

2. Basic Solutions- Upon referring to the table of resonance structures, it is evident that resonance of the anion is analogous and essentially equivalent to resonance of the di-hydrochloride cation. Therefore the same theoretical treatment accorded to the strongly acidic solution category will also apply in this case. On this basis, then, the spectra of the two types should be similar. The experimental evidence is in full accord with this postulation.

DISCUSSION (cont.)

3. Mildly Acidic Solutions- The appearance of two maxima in the spectra of mildly acidic solutions suggests as previously noted, that two separate chromophores are involved. It has also been suggested that these two chromophores are represented by the benzenoid and quinoid or semi-quinoid type of resonance structures.

Reference to the table of resonance structures indeed shows that for mildly acidic solutions the molecule can resonate with several structures of the three basic types.

For purposes of elucidation of the situation which exists in the case of neutral solutions, the assumption is made that the contributions of the benzenoid and quinoid or semi-quinoid structures to the true state of the molecule in mildly acidic solutions are approximately equal. (The spectra indicate that the benzenoid contribution is slightly greater than the quinoid or semi-quinoid; the first maximum is slightly greater than the second). This assumption is justified in part at least by modern resonance theory (22, p. 16), which tells us that usually the structure with the greatest number of bonds is the most stable.

DISCUSSION (cont.)

Referring again to the table of resonance structures, it is seen that of the six structures postulated for mildly acidic solutions, XII, XIII, and XIV are probably the most stable, for each of these structures contains four double bonds whereas the rest contain only three. Since XII and XIII are benzenoid in character and XIV quinoid, it would appear that the above assumption is reasonably accurate, for approximately half of the resonance contributors are benzenoid in character and the other half quinoid or semi-quinoid; (as a matter of fact, the resonance treatment indicates that the benzenoid contribution is slightly greater than the quinoid or semi-quinoid; and this is precisely the conclusion drawn from the absorption spectra).

4. Neutral Solutions- Since the spectra of neutral solutions are similar to those of mildly acidic solutions, it is to be expected that the structural situation might be nearly the same in both cases.

Assuming this to be the case, and bearing in mind the previous assumption, it is possible to predict the relative contributions of the basic structural types in neutral solutions. As it turns out, this gives us a great advantage, for the majority of the resonance structures postulated for neutral solutions (the quinoid and semi-quinoid structures) are charge-separated structures. (Knowledge of the relative contributions of such structures is generally quite uncertain).

DISCUSSION (cont.)

By analogy, then, with the situation in mildly acidic solutions, it appears that the relative contributions of the benzenoid and quinoid or semi-quinoid structures to the true state of the molecule in neutral solutions are approximately equal. That is, the contribution of the charge-separated structures appears to be approximately equal to that of the non-charge-separated structures.

DISCUSSION (cont.)

In the light of the foregoing theoretical discussion, the spectra of 5,(6)-chlorobenzotriazole may be explained relative to the spectra of the parent compound. That is, the differences between the spectra of the two compounds may be related to the differences between the various resonance structures of the two. It was felt that if such an explanation proved successful, it would substantiate in part the original theory developed for the parent compound.

Three effects of the chlorine substitution must be considered: the inductive effect, the weighting effect, and the resonance effect. In the case of the first of these, it appears that those structures bearing a negative formal charge on the carbon atom attached to the chlorine atom will be stabilized relative to the analogous structures of the unsubstituted compound, and that those structures bearing a positive formal charge in the same position will be less stable. The corresponding effects as evidenced spectrally will be increased absorption accompanying stabilization and decreased absorption accompanying decreased stability.

In the case of the second effect, it is generally observed that the weighting of a resonator leads to both batho- and hyperchromic spectral shifts. This effect will apply in all cases, independently of the other two.

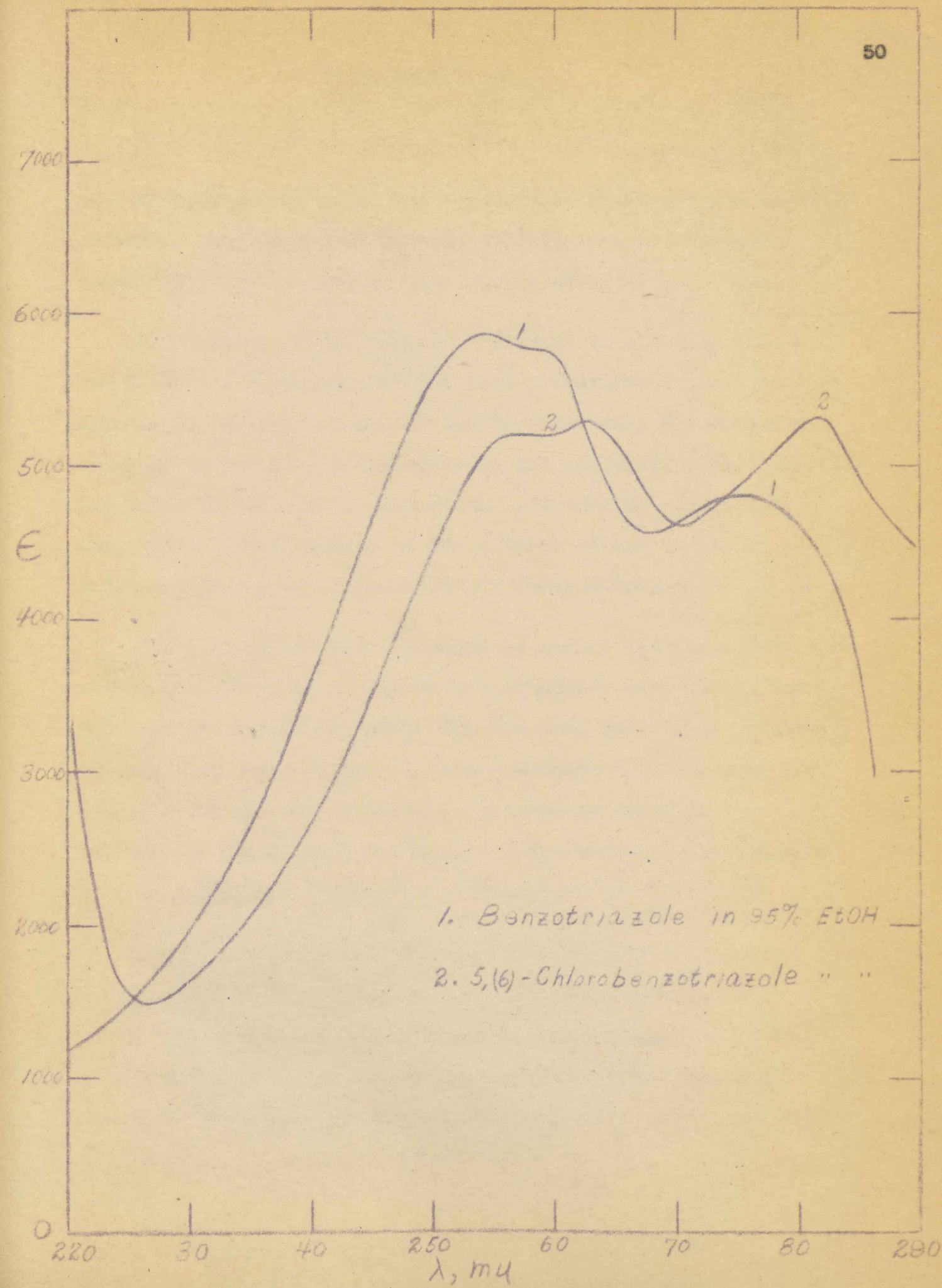
DISCUSSION (cont.)

The net result of the third effect will be the same as that of the first: resonance stabilization will produce greater absorption and vice versa.

As in the previous presentation, the individual spectral categories will be discussed separately.

1. Neutral Solutions- The only readily apparent observation that can be made in the case of neutral solutions is that either structure VII or VIII will be stabilized by the inductive effect of the chlorine. Combined with the weighting effect, this should and does lead to both batho- and hyperchromic shifts of the spectra relative to those of the parent compound in neutral solutions. (See curve on next page as representative of this situation in neutral solution). (See also discussion under mildly acidic solutions category for the relative importance of the inductive and weighting effects).

2. Mildly Acidic Solutions- The inductive situation in the case of mildly acidic solutions is similar to that in the case of neutral solutions, but in an opposite direction. Furthermore, since the spectral shifts relative to the parent compound are similar in both cases, it is inferred that the inductive effect is of little consequence relative to the weighting effect.



DISCUSSION (cont.)

3. Strongly Acidic and Basic Solutions- Since the same general situation is encountered in both strongly acidic and basic solutions, the two will be discussed together.

The spectra of the chloro-derivative in strongly acidic and basic solutions exhibit the same bathochromic shift as the spectra in neutral and mildly acidic solutions, but suffer a decrease in the absorption maximum. The weighting effect explains the bathochromic shift, but not the decrease in absorption. Apparently, then, another of the effects of the chlorine substitution becomes significant in these solutions.

The only effect not discussed as yet is the resonance effect. In itself it is apparently of little importance, for the chlorine cannot resonate with the ring (this fact becomes evident when one attempts to draw resonance structures of the molecule wherein the chlorine is allowed to enter in the resonance). Apparently, however, the resonance of the molecule is more subtly effected by the presence of the chlorine.

The relatively great stabilization of benzotriazole in strongly acidic and basic solutions has been attributed to resonance between several equivalent structure-pairs. If in some way, however, the equivalence of these structure-pairs should be destroyed, it would be expected that the resonance stabilization would be decreased.

DISCUSSION (cont.)

The chlorine atom on the ring has just this effect; the equivalence of such structures as XXI, XXII; XXX, XXXI is destroyed by the presence of the chlorine. It is therefore not surprising that the absorption of the chloro-derivative in strongly acidic and basic solutions is less intense than that of the parent compound in the same solutions.

SUMMARY

The ultraviolet absorption spectra of benzotriazole and 5,(6)-chlorobenzotriazole have been determined in ethanol and iso-octane solutions as well as in numerous buffered aqueous solutions of varying pH. In addition thereto, an attempt has been made to correlate the spectra on a theoretical basis with the molecular structures of the compounds.

An analysis of the hydrochloride of benzotriazole has been performed, the pK values of both compounds have been determined, the solvent effect on the spectra has been determined, and potentiometric titration curves of the compounds have been discussed.

The work reported herein is the first in a series of studies on the ultraviolet absorption of several structurally similar compounds. Future work is planned wherein a like study will be made of such compounds as benzimidazole, indole, and indene.

It is hoped that some insight into the structural behavior of these and related compounds will be gained through these studies, and that the final results will place us somewhat closer to our ultimate goal of a better and more complete understanding of the fundamental principles underlying the exact nature of color and the absorption of radiant energy in general.

APPENDIX

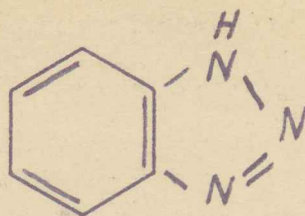
Resonance Structures of Benzotriazole:

The normal structure of benzotriazole has been established by Krollpfeiffer, Pötz, and Rosenberg (44) as structure I, next page.

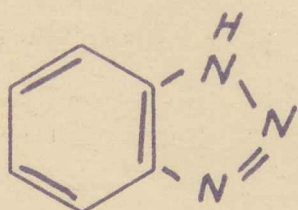
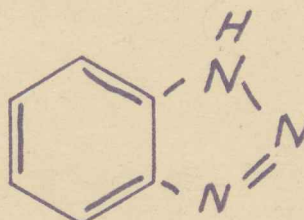
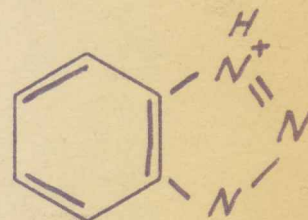
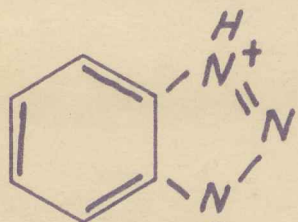
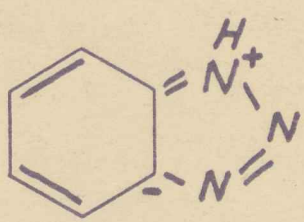
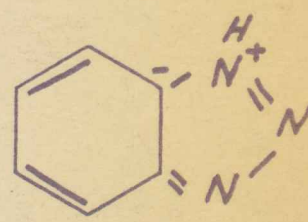
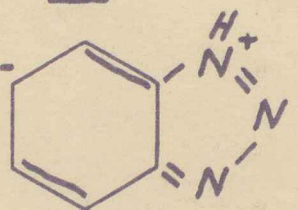
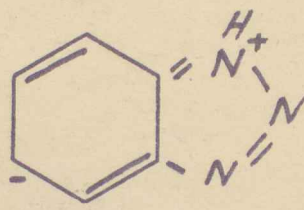
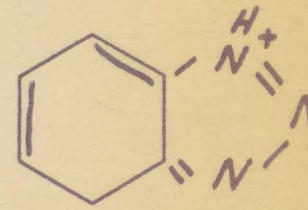
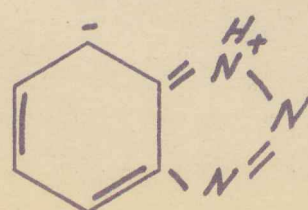
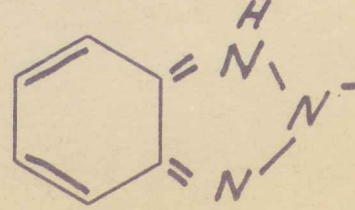
In the following tables, resonance hybrids of I and related structures in neutral, acidic, and basic solutions are presented.

The configurations chosen for the mono-hydrochloride (MA-1) and the di-hydrochloride (SA-1) are those most favored by resonance.

Resonance Structures of Benzotriazole

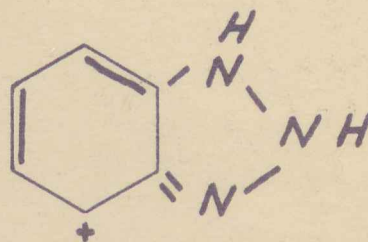
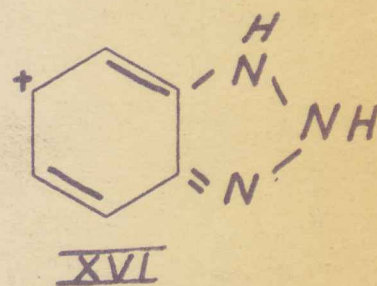
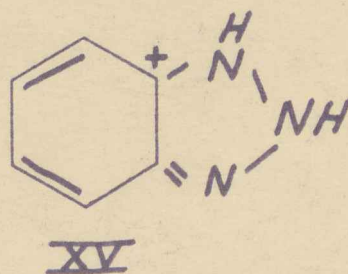
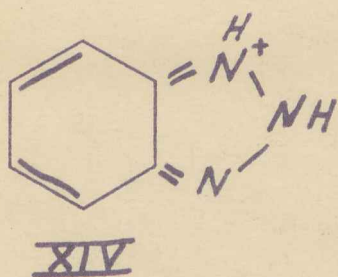
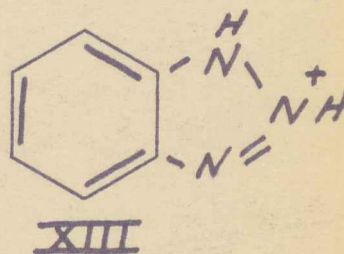
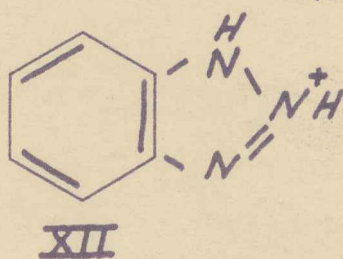
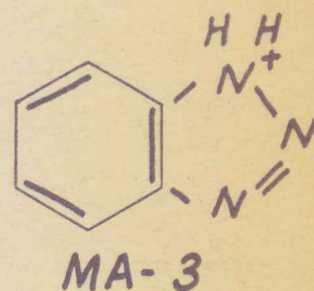
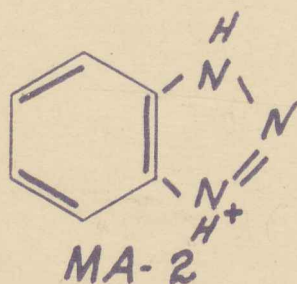
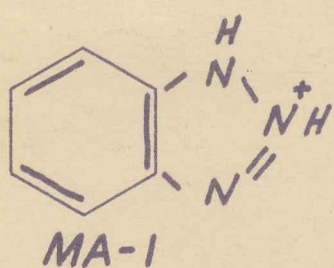
**I**

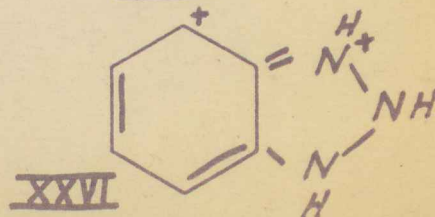
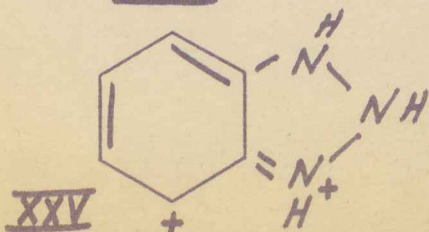
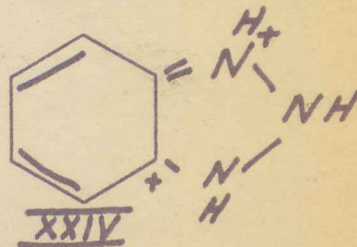
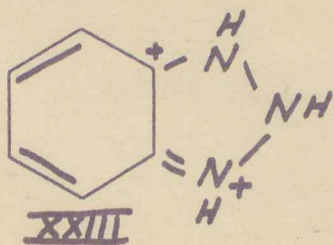
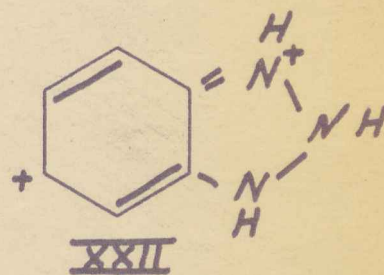
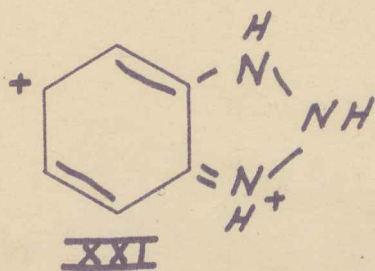
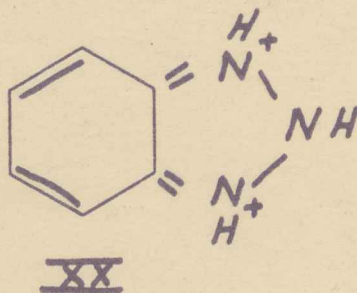
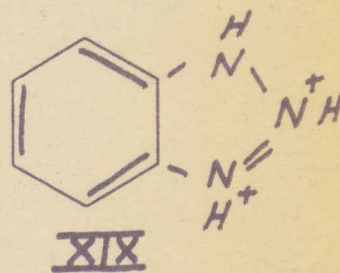
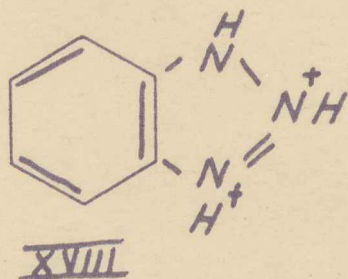
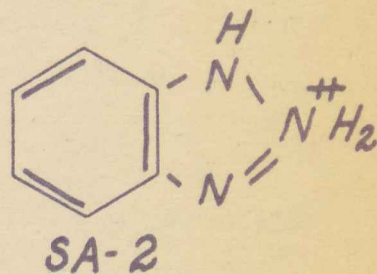
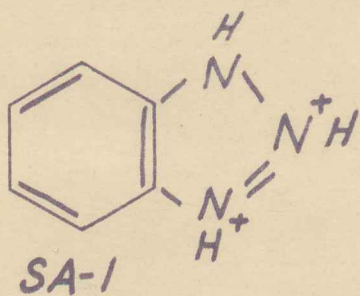
Neutral Solutions:

**I****II****III****IV****V****VI****VII****VIII****IX****X****XI**

(cont.)

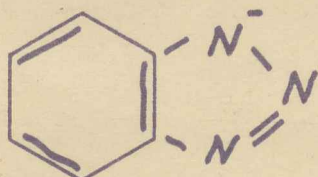
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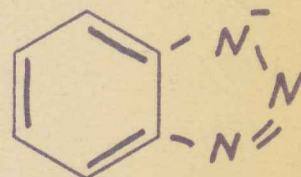
Strongly Acidic Solutions:

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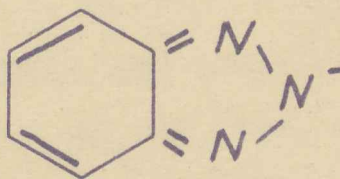
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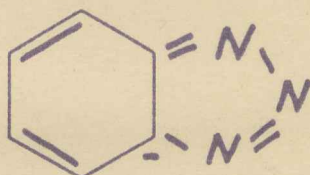
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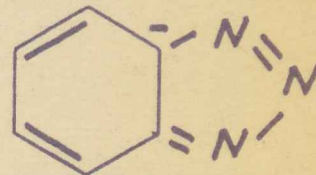
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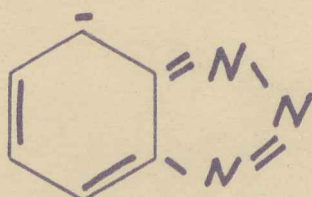
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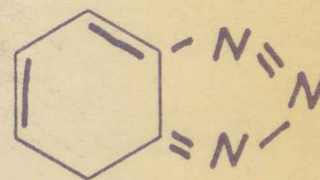
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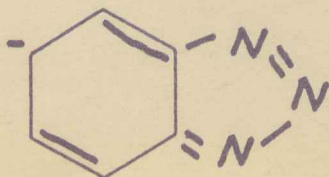
XXXI



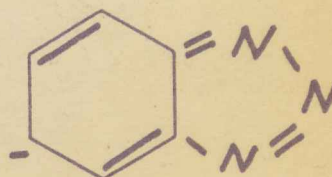
XXXII



XXXIII



XXXIV



XXXV

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