THE ULTRA VIOLET ABSORPTION SPECTRA

OF PARA-SUBSTITUTED DERIVATIVES

OF BIPHENYL

A THESIS

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by

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Date Approved by Chairman _____ *March 16, 1951* _____

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

CHAPTER I

PURPOSE OF THIS INVESTIGATION

THE ULTRA VIOLET ABSORPTION SPECTRA

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CHAPTER I

INTRODUCTION

The purposes of this investigation are as follows:

1. To prepare in a state of purity a series of biphenyl derivatives where substitution has taken place in the para position such as 4-aminobiphenyl or where the substitution has been effected in both the para and para-prime position such as 4-nitro-4'-aminobiphenyl.

2. To observe the ultra violet absorption spectra of each compound noting especially the effect of solvent and pH upon the spectrum.

3. To attempt to correlate the spectra of these derivatives of biphenyl with the corresponding derivatives of benzene.

CHAPTER II

INTRODUCTORY DISCUSSION

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INTRODUCTORY DISCUSSION

The fraction of the light transmitted by a given thickness of solution decreases expenentially with increasing concentration of solute, or the density increases linearly with the concentration. Combining the effects of concentration and thickness, one has according to the Beer-Lambert law[1] for monchromatic light:

$$I = I_e^{-\epsilon od} \tag{1}$$

where c is the concentration in moles per liter, d is the thickness in centimeters, and ϵ is the molar extinction coefficient, a characteristic of the solute, independent of the concentration but depending on the solvent and temperature.

Experimental results are usually reported in terms of the molar extinction coefficient, defined by the relation

$$\log I_o / I = \epsilon od \tag{2}$$

or:

$$\epsilon = \frac{\log I_o / I}{od} \tag{3}$$

the concentration being expressed in moles per liter and d in centimeters.

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[1]A. Weissberger, <u>Physical Methods of Organic Chemistry</u>. Interscience Publishers Inc., N.Y. (1946) p 772-776.

Deviations from the Beer-Lambert law indicate molecular interactions such as those causing association, dissociation, complex formation or change in solvation.

In plotting the intensity of absorption as ordinate against wavelength or wave number as abscissa, the molar extinction coefficient is the best function to represent the intensity, as it is independent of concentration and thickness. If the range of the molar extinction is very great the logarithm of the quantity is plotted against wavelength.

It frequently happens that compounds existing in equilibrium have overlapping absorption bands, their curves of extinction coefficient _versus_ wavelength intersecting at λ i. If two such compounds, each obeying the Beer-Lambert law, are in equilibrium, then, at constant temperature and constant total molar concentration and constant thickness of layer, the density-wave-length curves of all equilibrium mixtures will intersect at the fixed wavelength λ i [2]. This fixed wavelength of intersection has been called the _isobestic_ point and is a criterion for the existence of two compounds in equilibrium.

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[2] F. Weigert, _Ber_, __49__, 1525 (1916).

CHAPTER III

SURVEY OF THE LITERATURE UPON THE ULTRA VIOLET

ABSORPTION SPECTRA OF BIPHENYL AND RELATED

COMPOUNDS

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SURVEY OF THE LITERATURE UPON THE ULTRA VIOLET

ABSORPTION SPECTRA OF BIPHENYL AND RELATED

COMPOUNDS

Pickett, Walter and Prince[3] found that the ultra violet
absorption spectra of biphenyl which was substituted in such a
manner as to restrict the inter-rotation between the two benzene
rings at their junction differed markedly from the spectra of a
biphenyl derivative without restricted coplanarity.

All of the compounds used in the present work are of the
para-substituted type and the position of such groups is not
expected to affect the normal coplanarity of the biphenyl molecule.

The degree of interaction between the substituted group
and the basic ring structure of biphenyl comes to light in the
work of O'Shaughnessy and Redebush and others.[4,5] These workers
conclude that halogen, methyl or NH_3 exhibit very little
electronic interaction with the benzene ring while hydroxy,
methoxyl, amino and carboxy groups show a marked increase in
interaction with the benzene ring. The unsaturated groups show
the most reaction.

[3]L. W. Pickett, G. F. Walter and H. Prince. J. Am. Chem.
Soc. 68, 2296-9 (1936) .

[4]M. T. O'Shaughnessey and W. H. Redebush, J. Am. Chem. Soc. 62,
2906-11 (1940).

[5]M. Pesterner and E. Mayer, Monatsh 70, 104-12 (1937).

An extensive study of the spectra of simple, unsaturated compounds of mono and para disubstituted benzene derivatives was made by Doub and Vandenbelt[6]. These works are very complete and show the effects of substituted groups, various acidic and basic solutions in water on the spectra.

Later, Doub and Vandenbelt[7] made a study of the meta and ortho disubstituted benzene derivatives and concluded that as in the case of the para disubstituted compounds substitution with like electronic groups has quantitatively less displacement on the spectrum than with groups of complementary character (i.e. with ortho-para versus meta directing).

In biphenyl two unsaturated groups may have the effect of adding two more double bonds to the conjugated system and favoring the formation of ionic structure relative to ortho and para groups. Meta substituted groups can not contribute effectively to the polarity of the molecule as a whole because a conjugated structure requires a double bond between the carbon atoms linking the chain. the effect of groups in the ortho position is to hinder the natural coplanarity of the molecule and also to interfere with the rotation of the two rings. Thus the absorption power of the molecule is reduced.

[6]Doub and Vandenbelt. J. Am. Chem. Soc. 69, 2714-23 (1947).
[7]Doub and Vandenbelt. J. Am. Chem. Soc. 71, 2414-20 (1949).

A ooplanar struoture is necessary for the development of the typical biphenyl absorption spectrum. Jones[8] infers that conjugated aromatic chromophores contribute additively to the total absorption when prevented from acquiring a ooplanar configuration.

Williamson and Rodebush[9] carried out a series of experiments on ortho, para and meta substituted biphenyls and found that departure from coplanarity increased with increase in the size of the group present in the ortho position. Some of the substituted groups were hydroxy, methyl, amino, nitro, methoxyl and methyl-carboxy.

The problem of steric hinderance was encountered by Friedel, Orohin and Reggell[10] and this effect is discussed for biphenyl and the 2-methyl, 2-methoxy and 2-hydroxy derivatives of biphenyl.

Albert Londen[11] calculated the allowable electronic transitions of the biphenyl molecule as taking place in the spectrum at 2400, 1900, 1500 and 1400 A. Experimental results for biphenyl dissolved in 95 per cent ethyl alcohol shows an absorption maxima at 2480 A.

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[8] R. N. Jones, J. Am. Chem. Soc. 63, 1658-61 (1941).

[9] B. Williamson and W. D. Rodebush, J. Am. Chem. Soc. 63, 3018-25 (1941).

[10] R. A. Friedel, M. Orohin, L. Reggell (U.S. Bureau of Mines) J. Am. Chem. Soc. 70, 199-204 (1948).

[11] A. Londen (Cath. Univ. of Amer., Washington, D.C.) J. Chem. Phys. 13, 396-428 (1948).

In theory the energy levels of biphenyl are calculated by the
Heitler-London-Heisenberg method. This method considers the
change of the energy spectra of two phenyl molecules brought
about by the formation of a biphenyl molecule. The assumption
is that the spectrum of phenyl and benzene are identical.

That the coplanarity of the biphenyl molecule can be
influenced by solvent or state is reported by Merkel and Wiegand.[12]
Planar molecules yield well-defined and very steep absorption
curves in a specific region but absorption bands of non-planar
molecules are broad and weak. Thus, biphenyl which is planar in
the crystal state is found to be non-planar in hexane solution
as well as in the vapour state. Conclusions from ultra violet
absorption measurements agree with these from X-ray spectra and
dipole measurements. In water and alcohol the absorption spectra
shows the normal steep bands. All the curves obtained in this
work are of the steep variety showing that little interference
with the coplanarity existed when ethyl alcohol, chloroform or
acid and basic solutions in water were used.

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[12] E. Merkel and C. Weigand. C.A. 43, (1949). .

CHAPTER IV

PREPARATION OF BIPHENYL DERIVATIVES

Preparation of 4-Nitrobiphenyl (I)

Ten grams (0.06 moles) of biphenyl was slowly added to
10 ml of 10% fuming nitric acid. A violent reaction took place
with the evolution of heat and oxides of nitrogen. The mixture
was further heated for 30 minutes at just below the boiling point.
On cooling a crystal mass formed. This was washed with water to
removed the nitric acid and followed with a rinse of cold alcohol.
The final product was recrystallized twice from ethyl alcohol and
weighed 3.8 grams with a m.p. of $113°$(corr.). The recorded m.p.
is $113-114°$.[13]

Preparation of 4-Nitro-4'-nitrobiphenyl (II)

The method of Gill and Turner[14] was used with slight
modification. Eighty grams (0.53 moles) of biphenyl was slowly
added to 1820 grams of nitric acid (d = 1.42) and the mixture
stirred vigorously. To this was also added 40 ml of fuming
nitric acid (10%) fuming). The temperature was raised to $50°$
and held there for two hours. The reaction mixture was then
allowed to cool to room temperature. The bulky precipitate was
washed thoroughly with distilled water by decantation and filtered. Next,

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[13]Lange, N.A., Handbook of Chemistry, 4th Edition
Sandusky: Handbook Publishers Inc., (1941) p. 434.

[14]Gill and Turner, J. Chem. Soc. 494 (1929).

the precipitate was washed with cold alcohol to remove most of
the water and finally cold ether was used to rinse the precipi-
tate before filtering and drying. The m.p. was 235-236° (corr.)
with a yield of 29% while the recorded m.p. is 233-237°.[15]

Preparation of 4-Nitro-4'-aminobiphenyl (III) or
(4'-Nitroxenylamine)

A trial run following the method of Sherwood and Calvin[15]
produced no product. Another method, similar in many respects
was used[16].

Ten grams (0.04 moles) of (II) was weighed. In another
beaker ten grams of $Na_2S.9H_2O$ were dissolved in 250 ml water
and three grams of sulfur was added. (II) was first ground in
50 ml of acetone and this mixture was slowly added to the stirred
reduction mixture and the total heating time was five minutes.
A yellow-orange precipitate forms and this was filtered.

A revision in the procedure was made at this time. The
precipitate was transferred to a beaker containing 150 ml of
concentrated HCl and the mixture was heated to boiling. The
mixture was filtered hot and to the filtrate was added just
enough NH_4OH to neutralize the acid and to precipitate the compound.

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[15]Sherwood and Calvin, J.Am. Chem. Soc., 64, 1350-3 (1942).
[16]Guglialmelli and Franco, CA 24, 3235   .

The solid was washed thoroughly with water and recrystallized twice from alcohol to give bright orange needles with a m.p. of 199-201° (corr.). The yield was 17% with a recorded m.p. of 203.5-204° (corr.) as found by Sherwood and Calvin[15].

Preparation of 4-Methylbiphenyl (IV) or
(4-Phenyl Toluol)

One mole (107 grams) of para-toluidine was dissolved in 185 ml. of HCl (d= 1.2) the solution cooled by ice and diazotized by adding a slight excess of sodium nitrite (70 grams) dissolved in water. The temperature was kept low by adding a minimum of ice.

This solution was then added with vigorous agitation to a mixture of 275 ml of 40% solution of sodium hydroxide, 600 cc benzene and sufficient ice to keep the temperature below 5°. After one hour of stirring ice was no longer added and the temperature of the mixture was allowed to rise to room temperature. Stirring was continued for three hours.

The mixture, in two layers, was separated. The top, benzene layer, was saved and solid CaCl₂ was added to removed any water in the layer. The benzene was carefully removed by distillation at reduced pressure. When most of the benzene had been distilled, the

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[15]Ibid.

pressure on the system was reduced to 20 mm. The fraction coming

over at 145-153°C was a mass of golden brown flakes and weighed

30 grams. On recrystallization from alcohol, the crystals were

white, flat plates which melted at 48-49° (corr.). The yield is

18% using this method of Gomberg and Pernert[17] who recorded the

m.p. as 47-48°.

Preparation of 4-Nitro-4'-methylbiphenyl (V)

Fifteen grams of (IV) were dissolved according to Gomberg

and Pernert[17] in 100 ml of glacial acetic acid and this was

slowly added to a stirred mixture of 150 ml of HNO_3 (d = 1.42)

and 100 ml of glacial acetic acid. The reaction was allowed to

proceed for 24 hours at room temperature. A yellow precipitate

was formed and this was filtered, washed with water and recrystal-

lized from a small amount of alcohol. The compound melted sharply

at 140° (corr.) and was obtained in a 38% yield. Grieve and Hey[18]

recorded the m.p. as 140-141°.

Preparation of 4-Nitro-4'-carboxybiphenyl (VI)

A solution was made of two grams of (V) dissolved in 60 cc

of warm glacial acetic acid.[18] This solution was slowly added

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[17]Gomberg and Pernert. J. Am. Chem. Sec. 48, 1380 (1926).

[18]Grieve and Hey. J. Chem. Soo. 971 (1933).

to another solution of four grams of chromium trioxide dissolved in 60 cc of glacial acetic acid and the combined mixture was heated on the steam bath for ten hours.

On dilution with water, a white precipitate was formed. The precipitate was washed with a 5% solution of acetic acid to remove the chromium salt, filtered and recrystallized from acetic acid. The colorless crystals melted at 343-346° (corr.) and a yield of 60% was obtained. Grieve and Hey[18] recorded the m.p. as 338-340°.

Preparation of 4-Hydroxybiphenyl (VII) or
(p-Phenyl Phenol)

The method of Bell and Kenyon[19] is used in this preparation with the starting material being 4-aminobiphenyl. The 4-aminobiphenyl was obtained from the Eastman Kodak Company and recrystallized twice from ethyl alcohol before using. The melting point of the starting material was 50-52°. During the final hydrolysis with steam a light yellow oil was formed. On cooling the dried, separated oil solidified. This crude solid was recrystallized twice from 95% alcohol and had a m.p. of 162-164° (corr.). The yield was 40% and the recorded m.p. is 165°[20].

[18] Ibid .

[19] Bell and Kenyon. J. Chem. Soc. 3048 (1926)

[20] Hodgman, C.D., Handbook of Chemistry and Physics, Cleveland: Chemical Rubber Publishing Co., (1946) p.979.

Preparation of 4-Nitro-4'-Hydroxybiphenyl (VIII)

The following mixture was made according to Gilman and Blatt[21] : 1.7 grams of (III), 2.8 ml. water, 2.05 ml. concentrated sulfuric acid and 5 grams of ice. To the above mixture at $0 - 5^{o}$ a solution of 0.65 grams of sodium nitrite dissolved in 1.55 ml. water was slowly added with stirring and until there was a permanent color to starch-iodide paper. A thick paste forms and this was stirred constantly.

In another beaker, 9.3 ml. of concentrated sulfuric acid was added to 10.7 ml. of water and the temperature of this mixture was maintained at 160° with the aid of a metal bath while the diazotized amine was slowly added over a 50-minute period. The reaction mixture was filtered and the crude compound weighed 1.2 grams. The precipitate is recrystallized from ethyl alcohol using a small amount of activated carbon to clarify the alcohol solution. The precipitate is orange-yellow and melted at $198-199^{o}$ (corr.). An overall yield of 70% was obtained and the recorded m.p. by Angeletti is $200-201^{o}$.[22]

[21]Gilman and Blatt, Organic Synthesis, Vol. I, John Wiley and Sons, New York, (1948) p. 404.

[22]Angeletti, C.A. 21, 579 (1927).

Preparation of 4-Carboxybiphenyl (IX) or

(4-Phenyl Benzoic acid)

The same procedure was used as in the making of (VI)[17] and the compound obtained melts at 218-220° (corr.) with a 60% yield. The recorded m.p. was 219-224°.[20] The starting material was purified (IV).

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[17]Ibid.

[20]Ibid., p.979.

CHAPTER V

THE U. V. SPECTROPHOTOMETER

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THE U. V. SPECTROPHOTOMETER

A Beckman Ultra Violet Quartz Spectrophotometer Model DU,
serial number 1089 was used in all the measurements. For a
light source, a hydrogen discharge tube is used for extension
of the short-wave limit to 2200 A. [22A]

With this instrument, the point by point method was used
to insure high accuracy and good reproducibility. During the
main runs, readings were taken every 5 mu. To accurately locate
the absorption maxima, readings were taken every 1 mu.

Quartz cell 119315, $d = 1.001$ cm was used for the blank
and cell 11905, $d = 1.000$ was reserved for the dissolved sample.
The solvents used were chloroform, 95% ethyl alcohol and various
concentrations of base, acid and buffered solutions in distilled
water.

The general procedure followed was to weigh accurately
the required amount of solid compound and dissolve it in a known
quantity of solvent. By making a test run in the Beckman
spectrophotometer one could judge whether the concentration of
the solution was sufficient to give a reading within the range
of 20 to 80% transmission.

[22A] G. Harrison, R. Lord and J. Loofbourow, *Practical
Spectroscopy*, Prentice-Hall Inc., N.Y. (1948) p. 400-402.

At times the concentration of the solution was increased or decreased during a run to permit a more accurate investigation of an area which had transmitted outside of the most desirable range. To calculate the extinction coefficient, the new concentration must also be known.

In compounding some of the samples, a weighed amount of solid was dissolved in a specific volume of solvent, such as 95% alcohol. Then, a small portion of this solution (1/2 to 2 cc) is diluted to a larger volume of 100 cc with the proper solvent. In this manner, one could carefully pipette out a definite vol. of sample containing almost the same exact weight of solute each time. The blank for this particular run, would have added to it the same amount of "original" solvent.

The knob for adjusting sensitivity was set so as to obtain the smallest slit-width possible for all wavelengths. In order to obtain readings below 230 mu the check switch was set at 0.1 instead of the normal setting at 1.0. This reduces the sensitivity of the instrument.

For each reading, the following data was recorded: the wavelength in millimicroms, the slit width in millimeters, and the density reading.

CHAPTER VI

DISCUSSION

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The nomenclature of Doub and Vendenbelt[6] for derivatives
of benzene is used to identify the various bands. The most intense
bands are usually designated as the first primary bands while those
bands occuring at shorter wavelengths and with less intensity are
referred to as the second primary bands. Low intensity bands at
longer wavelength than the first primary bands are called secondary
bands.

To show how the various bands of biphenyl shift upon
substitution, a composite plot is given in figure 1. The ultra
violet absorption spectra of mono and para- disubstituted biphenyl
derivatives are arranged to show the progression of the bands. A
smooth sequence is formed, thus, confirming the identification and
interrelationship of the bands.

Gillam and Hey[23] have determined the ultra violet absorption
spectra of the para-polyphenyls in chloroform. If the square of
the wavelength of the first absorption band of these compounds is
plotted versus the number of phenyl nuclei, a smooth curve results.[24]
The first absorption band (at 254 m.u.) of benzene does not fall
upon this curve. Gillam and Hey suggested that the 197 m.u. band of

[6]Ibid.

[23]A.E. Gillam and D.D. Hey, J. Chem. Soc. 1170 (1939).

[24]G.E.K. Branch and M. Calvin, The Theory of Organic Chemistry
(Prentice-Hall,Inc.) (1943) p.167.

benzene should be compared with the first absorption band of the para-polyphenyls. Wheland [25] suggested that the more intense absorption of benzene at shorter wavelengths should be used in this comparison, but he did not further identify this band. Doub and Vandenbelt[6,7] have identified the 203.5 m.u. line of benzene in water as solvent with the first primary absorption band of the derivatives of benzene. That this identification is correct is confirmed by the fact that the plot of this wavelength places benzene upon the above mentioned curve of the para-polyphenyls. Thus, the interrelationship of the first primary absorption bands of these compounds is established. The weak absorption of benzene at 254 m.u. is classified as the secondary absorption band while the still more intense absorption at 183.5 m.u. is designated as the second primary absorption band by Doub and Vandenbelt.[6,7]

The discussion of the absorption spectra of biphenyl and its para-substituted derivatives shall be largely united to a discussion of the first primary absorption band.

The secondary absorption band of biphenyl and of most of its derivatives is not be be found, presumably because it is hidden by the more intense primary band. The second primary

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[25] G.W. Wheland, *The Theory of Resonance*, John Wiley & Sons.,N.Y. (1945) p. 151.

[6,7] *Ibid.*

absorption band of biphenyl and of certain of its derivatives apparently occurs at wavelengths which are too short to be measured accurately by the Beckman Spectrophotometer used in this work.

No satisfactory quantitative theory exists for predicting the absorption spectrum of derivatives of benzene or of biphenyl. It would, however, seem possible that a relationship should exist between the absorption spectrum of _para_-substituted derivatives of biphenyl and the corresponding derivatives of benzene.

In figure 2 the spectra of biphenyl derivatives are compared with the corresponding benzene derivatives with respect to the location of the first primary absorption band. In this figure the wavelength of the biphenyl derivative minus that of biphenyl (i.e.△λ) is plotted _versus_ the wavelength of the benzene derivative minus that of benzene (i.e.△λ) the points fall approximately upon a smooth curve of initial slope of unity.

The equation of the portion of figure 2 which is represented by the straight (dotted) line is

$$\left(\lambda_B - \lambda_{B^\circ} \right) = \left(\lambda_D - \lambda_{D^\circ} \right) \qquad (I)$$

or

$$\triangle \lambda_B = \triangle \lambda_D$$

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[6]_Ibid._

where :

$\lambda_B^\circ =$ wavelength of first primary band of benzene

$\lambda_B =$ " " " " " " the substituted benzene

$\lambda_D^\circ =$ wavelength of first primary band of biphenyl

$\lambda_D =$ " " " " " " the substituted biphenyl

and where λ_D and λ_B apply to the same substituted groups.

This equation fits closely the data for the monosubstituted derivatives of benzene versus the corresponding mono-para-substituted derivatives of biphenyl. It fits fairly closely to the data for the para- derivatives of benzene versus the para-para prime derivatives of biphenyl which have two meta directing groups or one meta directing and one weak para directing group. This relationship does not apply to the case of para disubstituted compounds containing a strongly meta directing and a strongly para directing group.

Equation (I) states that if a given group, or combination of groups, shifts the absorption spectrum of benzene toward the visible region by a certain number of millimicrons, this group, or combination of groups, alters the absorption spectrum of biphenyl in the same direction and to the very same extent.

Equation (I) may be transposed to read as follows:

$$\left(\lambda_D - \lambda_B \right) = \left(\lambda_D^\circ - \lambda_B^\circ \right) \cong \text{constant} \cong 44 \text{ mu} \quad (II)$$

When applied to the monosubstituted compounds, this
equation states that the biphenyl compound and the corresponding
phenyl compound differ in wavelength by an approximately constant
amount. The extent of deviation from constancy is shown in Table 1.
Expressed in other words, equation II shows that replacement of
the para-hydrogen of a mono-substituted benzene derivative by a
phenyl group has the effect of shifting the wavelength of
absorption by about 44 m.u. towards longer wavelengths. Quali-
tatively, this effect was to be predicted since it is general
experience that increasing the length of a conjugated system
results in absorption of light at longer wavelengths.

For the portion of the curve of figure 2 which does not
follow equation I, the $\Delta\lambda$ values of benzene derivatives are
nearly without exception larger than the $\Delta\lambda$ values of biphenyl
derivatives. This difference is probably due in part to the
fact that for biphenyl replacement of the para - hydrogens with
chromophoric and/or auxochromic groups results in a smaller
fractional increase in size of the conjugated system (i.e. to a
smaller fractional increase in the length of the oscillator and
in the number of π electrons) than is true in the case of benzene.
In the case of the diphenyl polyenes, $C_6H_5 (CH{=}CH)_n C_6H_5$, a
plot of the square of the wavelength of absorption _versus_ the
number of units (n) in the polyenic chain gives a straight line.[24]

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[24]_Ibid_. p.164.

This means that $d\lambda/dn$ varies inversely with the square root of

n+k, where k is a constant.

A factor of probably greater importance for the p,p'-

disubstituted derivatives of biphenyl is that the para groups

are further apart than in the corresponding derivatives of

benzene such that the effect of one group upon the other has

to be relayed through two benzenoid nuclei rather than one,

as well as through the bond joining the benzene nuclei. This

effect is of special importance when the two groups are of

opposite electronic type, i.e. electron donar and electron

acceptor groups. Such is the case with the amino and nitro groups.

The $\Delta\lambda_B$ value of p-nitroaniline is 177.5 while that of aniline is

26.5 and that of nitrobenzene 65.0; clearly here a combination

of two groups of different types upon the benzene nucleus gives

a marked displacement in the wavelength of absorption. This

seems to be attributable to electronic interaction of the groups

across the ring with resultant lessening of the constraint

upon the electrons responsible for the absorption of light. In

the case of 4-nitro-4'-aminobiphenyl, on the other hand, $\Delta\lambda_D$

is only 122; moreover, this compound absorbs at shorter wave-

length than p-nitroaniline, the corresponding maxima being 370

and 381 mu respectively.

That the interaction of groups is smaller in this

biphenyl compound than in p-nitroaniline is confirmed by

The acidity constants of the corresponding ammonium salts. Thus, K_a of 4-nitro-4'-aminobiphenyl is 7.3×10^{-5} as determined in the present work while the K_a of p-nitroaniline is recorded as 7.8×10^{-2} [26] and as 7.7×10^{-3} [27]. The K_a value of aniline is given as 1.8×10^{-5} [27] therefore introduction of a p-nitrophenyl group into the para position of aniline does somewhat increase the acidity constant of this amine.

The same general relationship seems to exist for the 4-nitro-4'-hydroxybiphenyl anion compared to the anion of p-nitrophenol. These two derivatives of biphenyl were the only compounds examined which absorbed at shorter wavelengths than the corresponding benzenoid compounds.

A third factor contributing toward variation from linearity as expressed by equation (I) is that it was not possible in all cases to measure the absorption spectra in identical media. Thus, the amines and carboxylic acids had to be determined in solutions containing appreciable concentrations of excess acid or base, while certain of the other compounds were so difficultly soluble in water as to necessitate the use of alcohol as solvent. In the cases which were checked, the maximum variation of wavelength of absorption with change in medium was 10 mu.

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[26]L.P. Hammett, Physical Organic Chemistry, McGraw-Hill, N.Y., (1940) p. 266.

[27]R.Q. Brewster, Organic Chemistry, Prentice-Hall, Inc., N.Y., (1948) p. 574.

CHAPTER VII

DISCUSSION OF RESULTS

CHAPTER VII

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The results of the various point by point readings are
plotted in the same manner previously described e.g. the
logarithm of the extinction coefficient versus wavelength. A
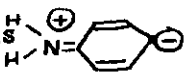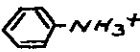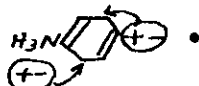series of curves is obtained.

Relationship of the U.V. Absorption Spectra of Biphenyl
with 4-Aminobiphenyl and 4-Methylbiphenyl.

In figure 3 is seen the strong similarity between the
spectra of biphenyl and HCl solution of 4-aminobiphenyl and
4-methylbiphenyl. The maxima of three curves fall within
the range of 248-250 mu.

This strong similarity between the three absorption
curves show first, that the methyl group contributes little
to the ease in which the electronic transitions of the
biphenyl molecule take place though the absorption maximum
does occur at a somewhat longer wavelength. Second, the
formation of the amine salt affects the absorption of light
since the main resonating structure is the biphenyl configuration
excluding the amine salt portion. Therefore, in the latter case
4-aminobiphenyl in 0.1N HCl has a UV spectra which closely
resembles that of biphenyl though absorption occurs with lower
intensity.

In the region below 220 mu, curves take an upward trend
and it seems that another set of maxima, the second primary
band, is present if one could penetrate this region.

Concerning the benzene molecule, several workers have
observed similar effects of the acid media on the spectra of
aniline and of the small effect of the methyl group, in toluene
on the spectra also.

Kumler and Strait[28] state that the absorption of light
is determined chiefly by the contributions of the forms
In acid these forms are excluded because the ion
already has four bonds attached to the nitrogen and this is the
maximum possible. Hence, the only resonance possible to account
for the absorption of light is within the ring itself .

4-Nitrobiphenyl Spectra Compared with 4-Nitro-4'-Methylbiphenyl
and 4-Nitro-4'-Aminobiphenyl in Concentrated Acid Solution,and
4,4'-Dinitrobiphenyl.

The absorption maxima of the four compounds in figure 4 are
similar in position and fall within 11 mu of each other. In the
case of 4-nitro-4'-methylbiphenyl we see that the 4-methyl group
shifts the maximum of 4-nitrobiphenyl from 307 to 318 mu while the
4-methyl group shifts the maximum of biphenyl from 248 to 254 mu.
Again, the effect of the amine group in concentrated HCl (0.1N)

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[28] W. Kumler and L. Strait, J. Am. Chem. Soc.,65, 2349 (1943).

is lost since the spectrum of 4-nitro-4'-aminobiphenyl in 0.1N HCl

has a maxima at 307 mu, the same position as the maximum of

4-nitrobiphenyl, although at lower intensity. The second primary

band of biphenyl which was mentioned above has been shifted

into the observable region of the ultra violet in the case of

4-nitro-4'-methylbiphenyl. It is also seen from figure 4 that

the spectra of 4-nitrobiphenyl and 4,4'-dinitrobiphenyl are

quite similar in both the position of the maximum and extinction

coefficient. This fact is confirmed by the work of Williamson

and Rodebush[9] who found that the maximum of the primary band of

4,4'-dinitrobiphenyl, in alcohol, was located at 305 mu with an $\in$

of 24,000. Adams and Russell[29] found that the primary band

maximum of 4-nitrobiphenyl was located at 307 mu and with an $\in$

of 25,900. In the present work the primary band of 4,4'-dinitro-

biphenyl was found at 305 mu with an $\in$ of 23,900, while the

primary band of 4-nitrobiphenyl was located at 307 mu with an $\in$

of 21,000.

4-Aminobiphenyl

Figure 5 concerns the molecule of 4-aminobiphenyl and

shows the shift in absorption maxima towards the longer wave-

lengths as the basicity of the solvent is increased. The total

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[9]Ibid.

[29]Adams and Russell, J. Chem. Soc., 202-6 (1930).

shift is 27 mu as the compound in 0.1N HCl has a maximum at

248 mu and in 0.1N NaOH a maximum at 275 mu. An isobestic

point is found in the region of 260 mu.

The two pure forms of the 4-aminobiphenyl, e.g., the

free amine and the amine cation BH,⁺ each have a characteristic

absorption which is constant for a series of solutions. If

the absorption curves of the mixtures did not pass through

the isobestic point then it is indicative of the presence of

more than two forms or reaction products, the influence of a

medium or salt effect upon specific absorption, or other causes

of deviation from Beer's law. In our study it is found

that a solution of the compound which is 1×10^{-4} normal in

HCl shows approximately 50% ionization and a maximum at 260 mu.

Williamson and Rodebush[9] investigated a series of

para disubstituted biphenyl derivatives where both groups

were the same. They found that 4-4'-diaminobiphenyl in

ethyl alcohol had a maximum at 285 mu as compared to 280 mu

for 4-aminobiphenyl in the present work. We see that the

disubstituted biphenyl derivative is very similar in the

position of its maximum although the extinction coefficient

is 23,000 units to 8,000 units for the monosubstituted amino-

biphenyl. Adams and Russell[29] record the maximum of

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[9]Ibid.

[29]Ibid.

aminobiphenyl as 280 mu in ethanol.

4-Nitro-4'-Aminobiphenyl

The isobestic point found for 4-nitro-4'-aminobiphenyl is in close agreement with that of Sherwood and Calvin[15] who found this point at 330 mu as compared with 335 mu found in the present work. Sherwood and Calvin used alcohol as their solvent while we used water in making the basic and acid solutions. The isobestic point also has an extinction co-efficient of 8500 which is very similar in magnitude to the 8600 found by Sherwood and Calvin. These investigators record only the portion of the spectra from 300 mu to 480 mu while in figure 6 is given the spectra from 220 mu. In this figure at 270 mu is located another isobestio point as well as a second maximum at 374 mu. These same authors found K_a for 4-nitro-4'-aminobiphenyl to be $10x10^{-4}$. In comparison we found an average value of $0.91x10^{-4}$ for K_a.

An ionization of 50% occurs in the solvent which is $1x10^{-4}N$ in HCl since this curve falls midway between the solutions which were highly concentrated in acid and in base. As the solvent is changed from 0.1N HCl to $1x10^{-3}$ NaOH the maximum shifts from 307 mu to 374 mu.

In comparing the spectral shift of 1-nitro-4-aminobenzene with 4-nitro-4-aminobiphenyl as the acidity of the solvent is

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[15] Ibid.

varied, we find that the maximum is displaced 177 mu in the first
case as compared with 122mu for the biphenyl derivative.

4-Carboxybiphenyl

The primary band of this compound is shifted from 265 mu
to 275 mu when the solvent is changed from 0.01N NaOH to 0.1N HCl.
Broad maxima are evidenced at both these points. An isobestic
point is seen at 260 mu and another at 290 mu on figure 7. In
comparing this shift with that experienced by benzoic acid,
the latter's primary band maximum is shifted 6 mu towards the
visible region, from 224 to 230 mu in going from basic to
acid media.

Williamson and Rodebush[9] found that 4-4'-dicarboxy-
biphenyl in alcohol had a maximum occuring at 280 mu with an
extinction coefficient of 30,000. With 4-carboxybiphenyl a
comparable maximum for a neutral solution is found to occur
at 275 mu with an extinction coefficient of 10,000.

4-Nitro-4'-Carboxybiphenyl

In figure 8 is shown the effect of base on the spectrum
of the compound. The maximum of the first primary band is
shifted from 302 mu to 314 mu going from a solution which is
1.0N HCl to one which is 0.1N NaOH, respectively. This 12 mu

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[9] Ibid.

shift might appear small when compared to the 59 mu shift of
the first primary band in 4-nitro-4'-aminobiphenyl. However,
when compared with the ultra violet absorption spectral of
p-nitrobenzoic acid the shift is in close agreement, since
p-nitrobenzoic acid shifts 10 mu towards the visible region
going from 264.5 mu to 274 mu when the solution is changed
from 0.1N HCl to 1.0N NaOH. Note the inverse direction of
shift with 4-carboxybiphenyl and benzoic acid upon change of pH.

4-Hydroxybiphenyl

This compound's ultra violet absorption spectrum is
unusual in the fact that two complete bands are seen in
figure 9, one the first primary band falling at 255 mu, and
the other, the secondary band, at 380 mu. The shift in the
first primary band goes from 255 mu in a neutral solvent to
275 mu in 1.0N base. The secondary band is shifted from
380 mu to 430 mu.

Isobestic points occur at 265, 325 and a third at
395 mu. Williamson and Rodebush[9] found that the primary
band maximum of 4,4'-dihydroxybiphenyl in alcohol lies at
265 mu, while in this thesis the maximum for an alcoholic
solution of 4-hydroxybiphenyl was found also to occur at
265 mu. The extinction coefficient of the former compound
is 22,400 as compared to 19,400 for the latter.

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[9] Ibid.

4-Nitro-4'-Hydroxybiphenyl

The ultra violet absorption spectra for this compound in 0.01N NaOH and in 1.0N HCl is shown in figure 10. In the acid solution the primary band maximum is at 340 mu and at 232 mu there is evident the maximum of the second primary band. This second primary band is completely shown, which is not the case with the same band for 4-nitro-4'-amino-biphenyl in HCl solution as shown in figure 6.

In the basic solution the primary band maximum is shifted to 402 mu while in 4-nitro-4'-aminobiphenyl, in base, the shift is only to 374 mu.

Isobestic points for the absorption spectra 4-nitro-4'-hydroxybiphenyl are found at 218, 242, 288 and 366 mu. For 4-nitro-4'-aminobiphenyl the isobestic points fall at 270 and 332 mu.

CHAPTER VIII

SUMMARY

SUMMARY

The ultra violet absorption spectra of para-substituted derivatives of biphenyl were investigated for the following compounds: biphenyl (I), 4-aminobiphenyl (II), 4-methylbiphenyl (III), 4-hydroxybiphenyl (IV), 4-carboxybiphenyl (V), 4-nitrobiphenyl (VI). 4,4'-dinitrobiphenyl (VII), 4-nitro-4'-aminobiphenyl (VIII), 4-nitro-4'-carboxybiphenyl (IX), 4-nitro-4'-methylbiphenyl (X), and 4-nitro-4'-hydroxybiphenyl (XI). These compounds were made using published methods of preparation, but in some cases the method was slightly revised to increase the yield.

The acidic and the basic compounds (II, IV, V, VIII, IX and XI) were run in both acidic and basic solvents in order to determine the ionization constants of these compounds and to note especially the effect of pH upon the spectra. Ethyl alcohol, 95%, was used as the solvent for the non-ionic compounds, (I, III, VI, VII and X).

The location of the first primary band was established for biphenyl and the para monosubstituted and para disubstituted derivatives of biphenyl and it was clearly shown that this band is shifted toward longer wavelengths by chromophoric and auxochromic groups. When the derivatives were arranged to show the progression of the bands, a smooth sequence was obtained, thus, confirming the identification and relationship of the bands.

The spectra of these derivatives of biphenyl were correlated with the corresponding derivatives of benzene. For the para monosubstituted derivatives of biphenyl, it was shown that the replacement of the para hydrogen of a monosubstituted benzene derivative by a phenyl group has the effect of shifting the wavelength of absorption by about 44 mu towards longer wavelengths. For the disubstituted derivatives of biphenyl this relationship is approximated by only the 4-4'-dinitrobiphenyl, 4-nitro-4-amino-biphenyl cation, 4-nitro-4'-carboxybiphenyl anion, and 4-nitro-4'-carboxybiphenyl.

The compounds II and VII in acidic media were shown to have spectras strikingly similar to I and VI, respectively, since the NH_3 group does not stabilize the excited electronic states of the molecules.

Another factor of importance is that two groups of the opposite electronic type, (e.i. electron donor and electron acceptor groups) give a marked displacement in the wavelength of absorption of the biphenyl derivative as compared to a derivative with groups of similar electronic type. This seems to be attributable to electronic interaction of the groups across the biphenyl ring with resultant reduction of the constraint upon the electrons responsible for the absorption of light.

From the ultra violet absorption data, the following average values for Ka (the ionization constant as an acid) were obtained: 9.1×10^{-5} for (II), 3.5×10^{-8} for (IV), 4.8×10^{-6} for (V) and 0.91×10^{-4} for (VIII).

APPENDIX I

TABLES

TABLE I

COMPOUND	1st Primary Bands		Deviation	
	λ_D (mμ)	λ_B (mμ)	$\lambda_D - \lambda_B$	$(\lambda_D - \lambda_B - 44.0)$
Biphenyl	248a	203.5	44.5	0.5
4-Aminobiphenyl cation	248	203.0	45.0	1.0
4-Methylbiphenyl	254a	206.5	47.5	3.5
4-Hydroxybiphenyl	255	210.5	44.5	0.6
4-Carboxybiphenyl anion	265	224.0	41.0	-3.0
4-Carboxybiphenyl	275	230.0	45.0	1.0
4-Aminobiphenyl	275	230.0	45.0	1.0
4-Hydroxybiphenyl anion	275	235.-	40.0	-4.0
4-Nitrobiphenyl	315	268.5	46.5	2.5
4,4'-Dinitrobiphenyl	305a	266.0	39.0	-5.0
4-Nitro-4'-Amino biphenyl cation	304	258.0	46.0	-2.0
4-Nitro-4'-Carboxybiphenyl	302	264.5	37.5	-6.5
4-Nitro-4'-Carboxy-biphenyl anion	315	274.0	41.0	-3.0
4-Nitro-4'-Methylbiphenyl	318a	285.0	33.0	-11.0
4-Nitro-4'-Amionbiphenyl	374	381.0	- 7.0	-51.0
4-Nitro-4'-Hydroxy-biphenyl anion	402	402.5	- 0.5	-44.5
4-Nitro-4'-Hydroxy-biphenyl	340	317.5	22.5	-21.5

a) The absorption spectrum of the biphenyl compound was run in
95% alcohol rather than in water.

TABLE II

Compound	Solvent	1st Pri. Band		Sec. Band		$\Delta\lambda$ $\lambda_1 - 248$	2nd Pri. Band	
		$\lambda_1 (m\mu)$	$\epsilon \times 10^{-3}$	$\lambda_3 (m\mu)$	$\epsilon \times 10^{-3}$		$\lambda_2 (m\mu)$	$\epsilon \times 10^{-3}$
Biphenyl	95% ETOH	248	17.0			0		
4-Aminobiphenyl	95% ETOH	280	8.0					
	0.1N NaOH	275	9.0			27.0		
	1.0N HCl	248	8.6			0.0		
	0.1N HCl	248	8.6					
	1×10^{-3}HCl	248	8.6					
	1×10^{-4}HCl	260	6.8					
	CHCl$_3$	279						
	1.0N KOH in 95% ETOH	285	8.9					
4-Methylbiphenyl	95% ETOH	254	22.6			6.0		
4-Hydroxybiphenyl	0.1N NaOH	275	19.0	440	2.9	27.0		
	0.01N NaOH	273	17.5	440	2.9			
	0.01N NaHCO$_3$	265	17.0	440	2.1			
	0.01N HCl	255	19.5	375	1.9	7.0		
	95% ETOH	255	19.4	377	1.9			
4-Carboxybiphenyl	1.2N NaOH	265	10.0			17.0		
	0.01N NaOH	265	8.5					
	0.01N HCl	275	10.4	315	1.5	27.0		
	0.1N HCl	275	12.5	315	2.1			
4-Nitrobiphenyl	95% ETOH	307	21.0			59.0		
	H$_2$O	315	20.5				223	17.1
	CHCl$_3$	307						
4,4'-Dinitro-biphenyl	95% ETOH	305	23.9			57.0		
	CHCl$_3$	306						

TABLE II (continued)

Compound	Solvent	$\lambda_1 (m\mu)$	$\epsilon \times 10^{-3}$	$\lambda_2 (m\mu)$	$\epsilon \times 10^{-3}$	$\dfrac{\Delta \lambda}{\lambda_1 - 248}$
4-Nitro-4'-Amino biphenyl	0.1N HCl	305	15.1	225	11.5	57.0
	0.01N HCl	304	15.2	220	12.6	
	1x10⁻⁴HCl	365	9.9	245	10.1	
	H_2O	365	12.1	245	11.9	
	10⁻³NaOH	374	15.2	250	13.0	126.0
	$CHCl_3$	365	10.5	250	11.0	
	1.0N KOH in ETOH	380	15.5	250	15.0	
	0.1N HCl in ETOH	300	15.7			
4-Nitro-4'-Carboxy biphenyl	1.0N NaOH	315	19.4	230	15.5	67.0
	1x10⁻³NaOH	312	16.5	235	13.3	
	0.1N NaOH	314	16.9	230	13.6	
	0.01N NaHCO₃	312	13.7			
	1.0N HCl	302	13.3			54.0
	1.0N HCl in ETOH	315	17.0			
	1.0N KOH in ETOH	325	25.6			
4-Nitro-4'-Methyl biphenyl	ETOH	318	18.5	225	15.0	70.0
	$CHCl_3$	319		225		
4-Nitro-4'-Hydroxy biphenyl	0.01N NaOH	402	25.3			154.0
	0.10N NaOH	400	26.4			
	1.0N HCl	340	23.6	232	19.0	92.0

TABLE III

Acid Ionization Constants

Compound	λ mu	Ka	Ka(Benzene derivative)	
4-Aminobiphenyl	244	11×10^{-5}		
	280	7.2×10^{-5}		
	average value	9.1×10^{-5}	1.85×10^{-5}	[27]
4-Hydroxybiphenyl	280	0.70×10^{-8}		
	344	6.30×10^{-8}		
	average value	3.50×10^{-8}	1.3×10^{-10}	[13]
4-Carboxybiphenyl	270	4.40×10^{-6}		
	280	5.20×10^{-6}		
	average value	4.80×10^{-6}	6.6×10^{-5}	[13]
4-Nitro-4'-Aminobiphenyl	300	7.26×10^{-5}		
	360	11.0×10^{-5}	0.77×10^{-2}	[27]
	average value	9.1×10^{-5}	7.8×10^{-2}	[26]

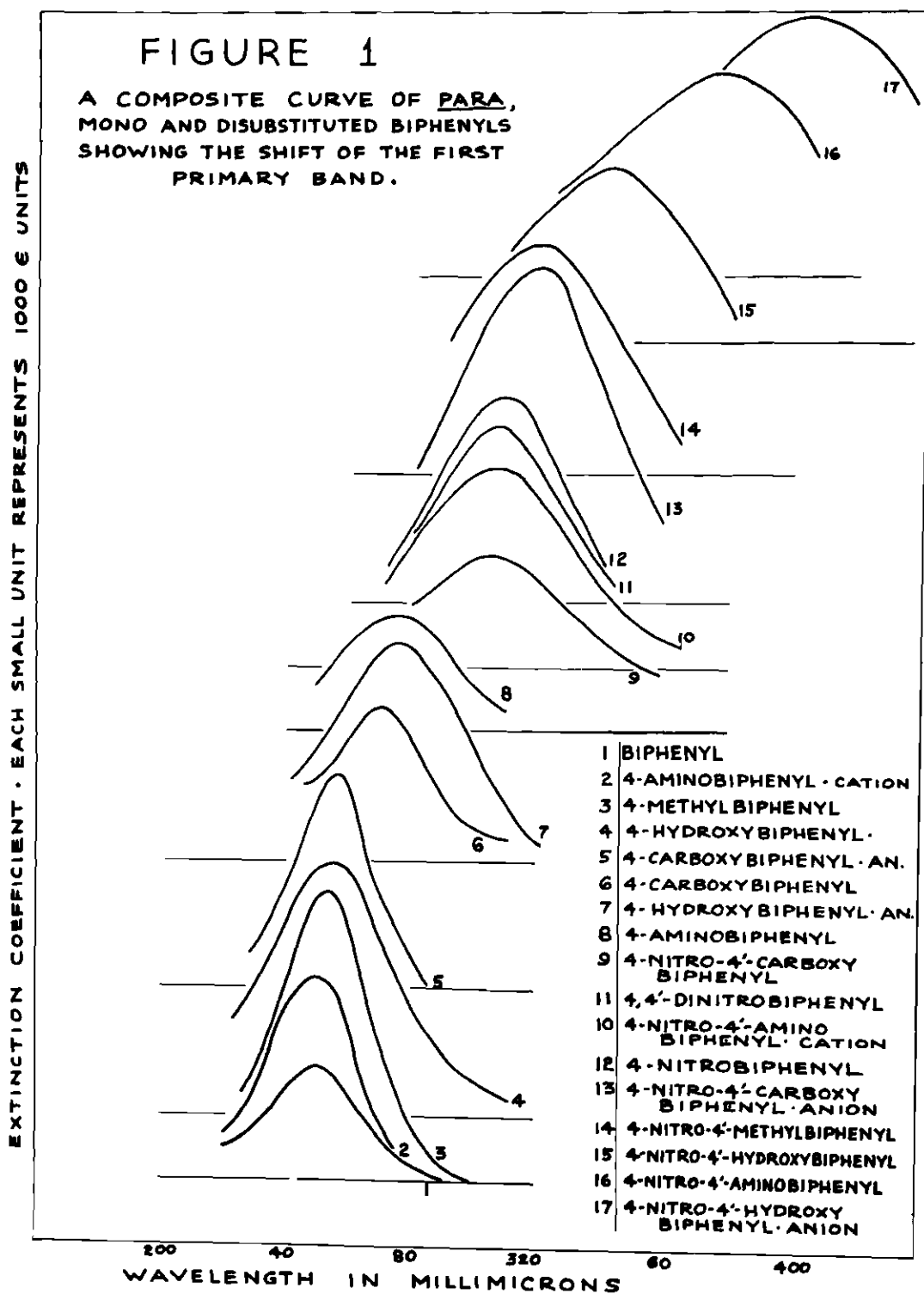[13] Lange, N.A., Ibid, p.1218.

[26] Hammett, L.P., Ibid, p.266.
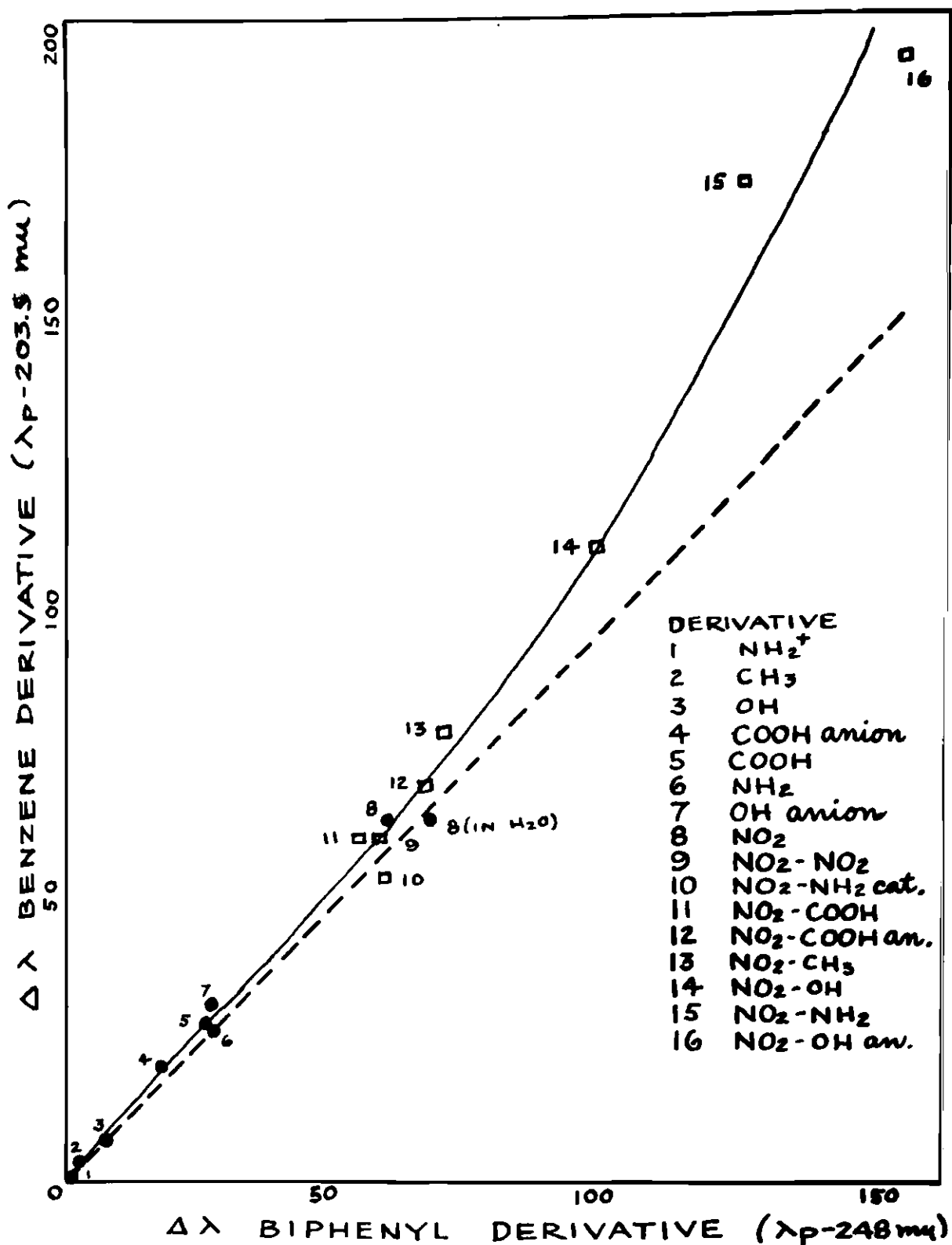
[27] Brewster, R.Q., Ibid, p.574.

APPENDIX II

CURVES

FIGURE 1

A COMPOSITE CURVE OF PARA,
MONO AND DISUBSTITUTED BIPHENYLS
SHOWING THE SHIFT OF THE FIRST
PRIMARY BAND.

EXTINCTION COEFFICIENT · EACH SMALL UNIT REPRESENTS 1000 ∈ UNITS

1	BIPHENYL
2	4-AMINOBIPHENYL · CATION
3	4-METHYLBIPHENYL
4	4-HYDROXYBIPHENYL ·
5	4-CARBOXYBIPHENYL · AN.
6	4-CARBOXYBIPHENYL
7	4-HYDROXYBIPHENYL · AN.
8	4-AMINOBIPHENYL
9	4-NITRO-4'-CARBOXY BIPHENYL
11	4,4'-DINITROBIPHENYL
10	4-NITRO-4'-AMINO BIPHENYL · CATION
12	4-NITROBIPHENYL
13	4-NITRO-4'-CARBOXY BIPHENYL · ANION
14	4-NITRO-4'-METHYLBIPHENYL
15	4-NITRO-4'-HYDROXYBIPHENYL
16	4-NITRO-4'-AMINOBIPHENYL
17	4-NITRO-4'-HYDROXY BIPHENYL · ANION

WAVELENGTH IN MILLIMICRONS

FIGURE 2 DISPLACEMENT OF SIMILAR
DERIVATIVES OF BIPHENYL versus BENZENE
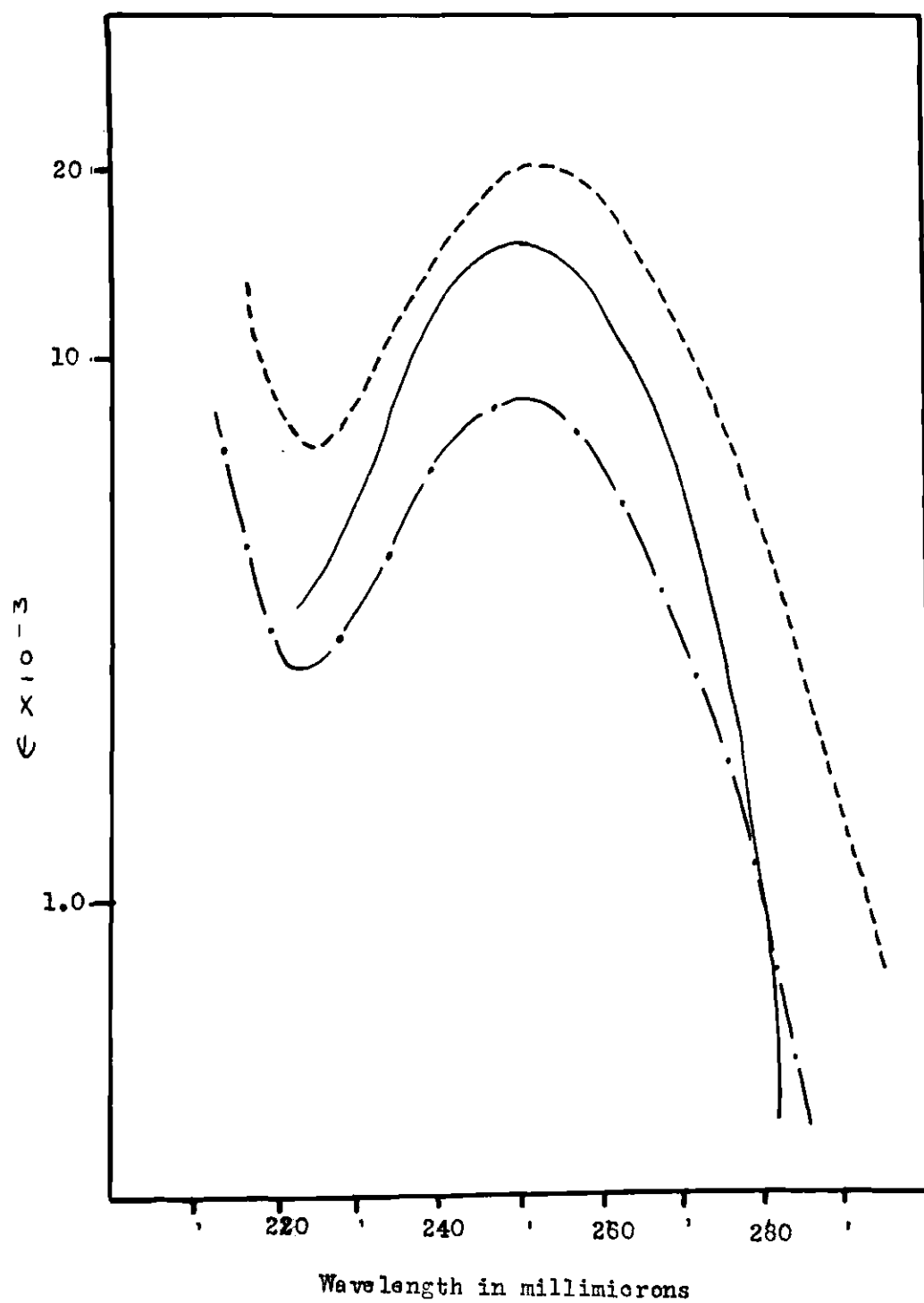
Fig. 3.—A comparison of the first primary bands of Biphenyl, 4-Methylbiphenyl and 4-Aminobiphenyl cation. ------------, 4-Methylbiphenyl; —————————— , Biphenyl; ——•——•—— , 4-Aminobiphenyl cation.
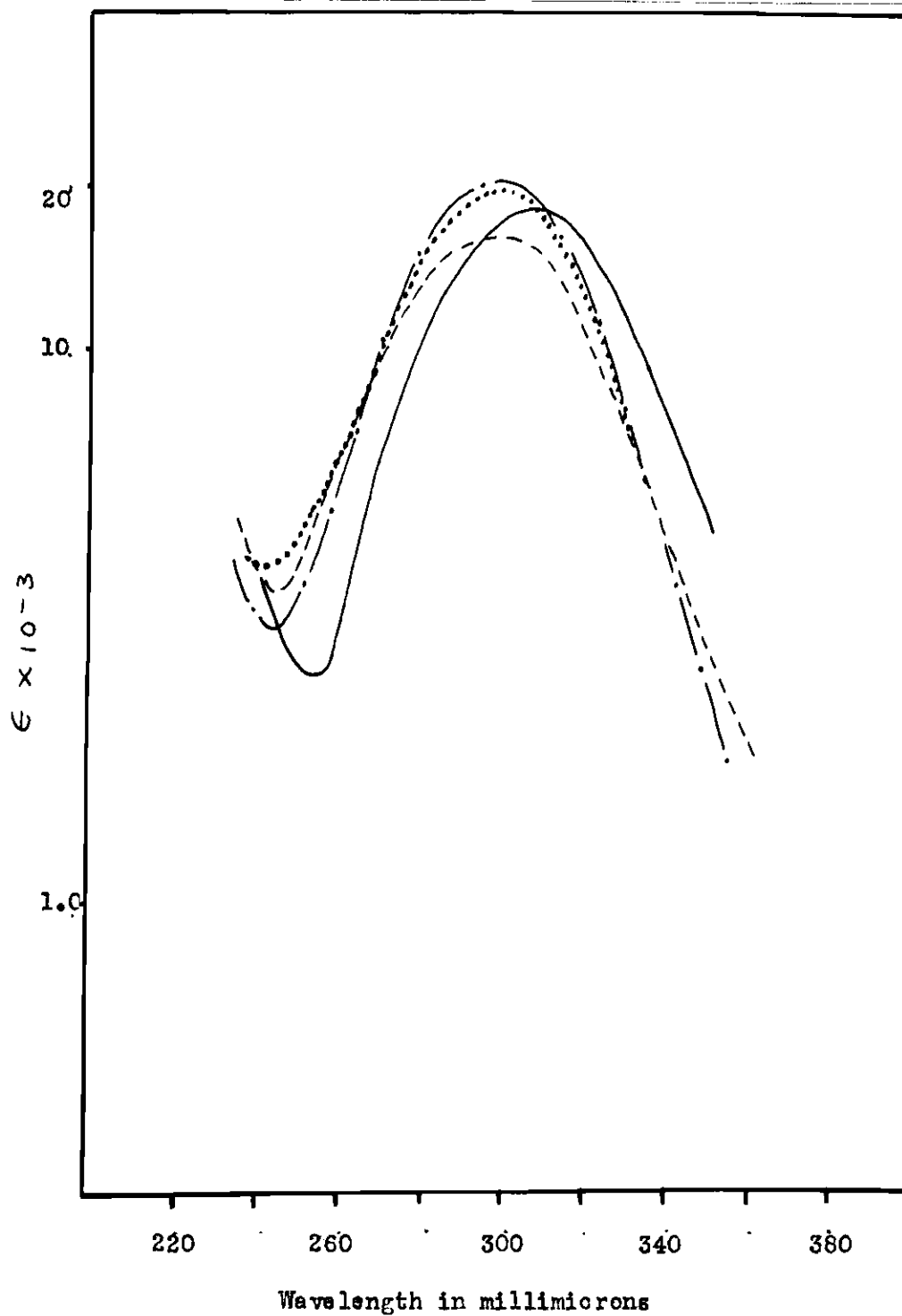
Wavelength in millimicrons

Fig. 4.-The 4-Nitrobiphenyl Spectra Compared with 4-Nitro-
4'-Methylbiphenyl, 4-Nitro-4'-Aminobiphenyl cation and 4,4'-Di-
nitrobiphenyl. --------, 4-Nitrobiphenyl; ———— , 4-Nitro-4'-Methyl-
biphenyl; •••••••, 4,4'-Dinitrobiphenyl; —•—•—•, 4-Nitro-4'-
Aminobiphenyl.

Wavelength in millimicrons.
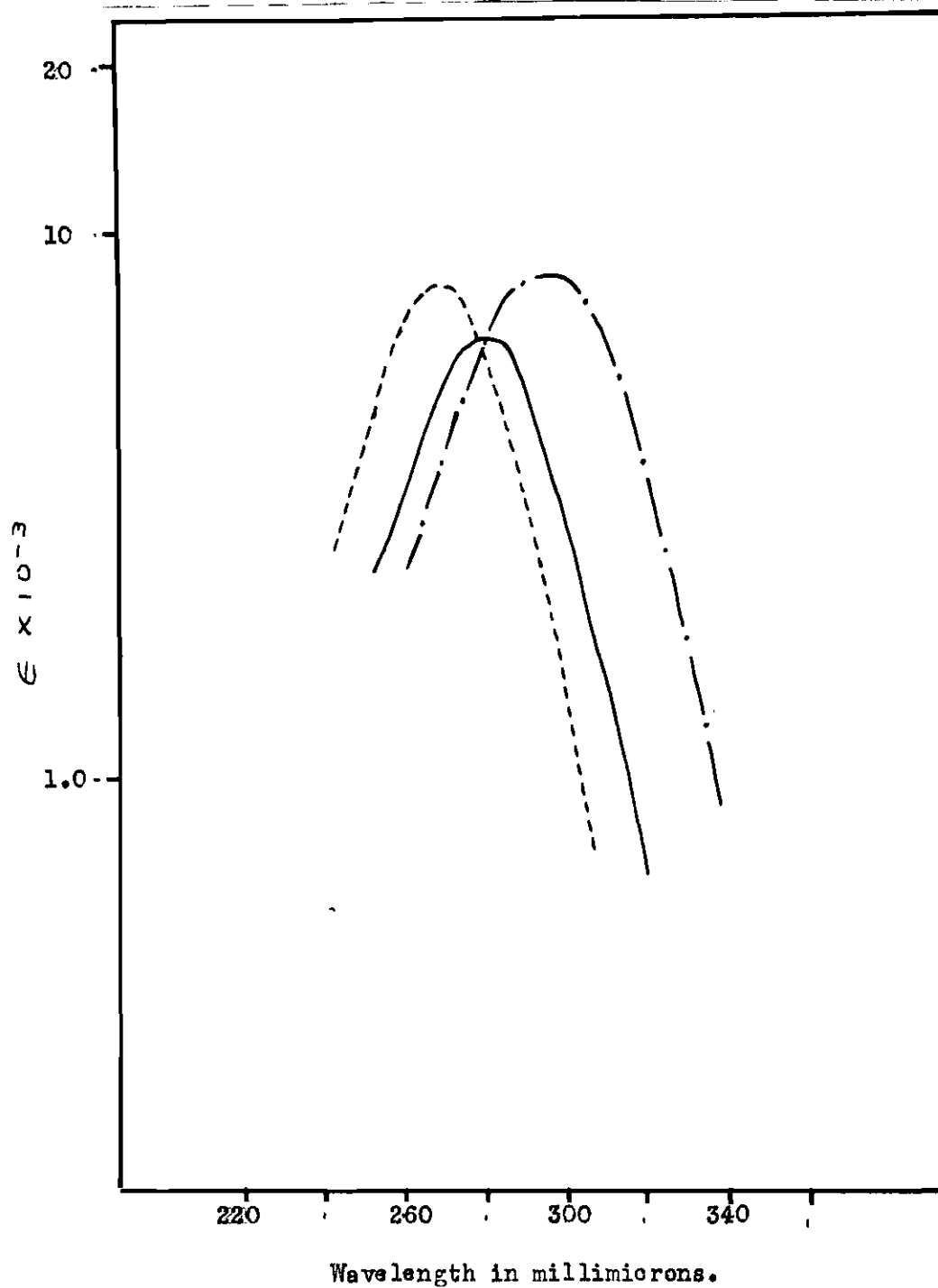
Fig. 5.—The absorption spectra of 4-Aminobiphenyl in various solvents. ----------------, 0.1N HCl; ————————, 1x10⁻³ HCl; —•——•——•—— , 0.1N NaOH.
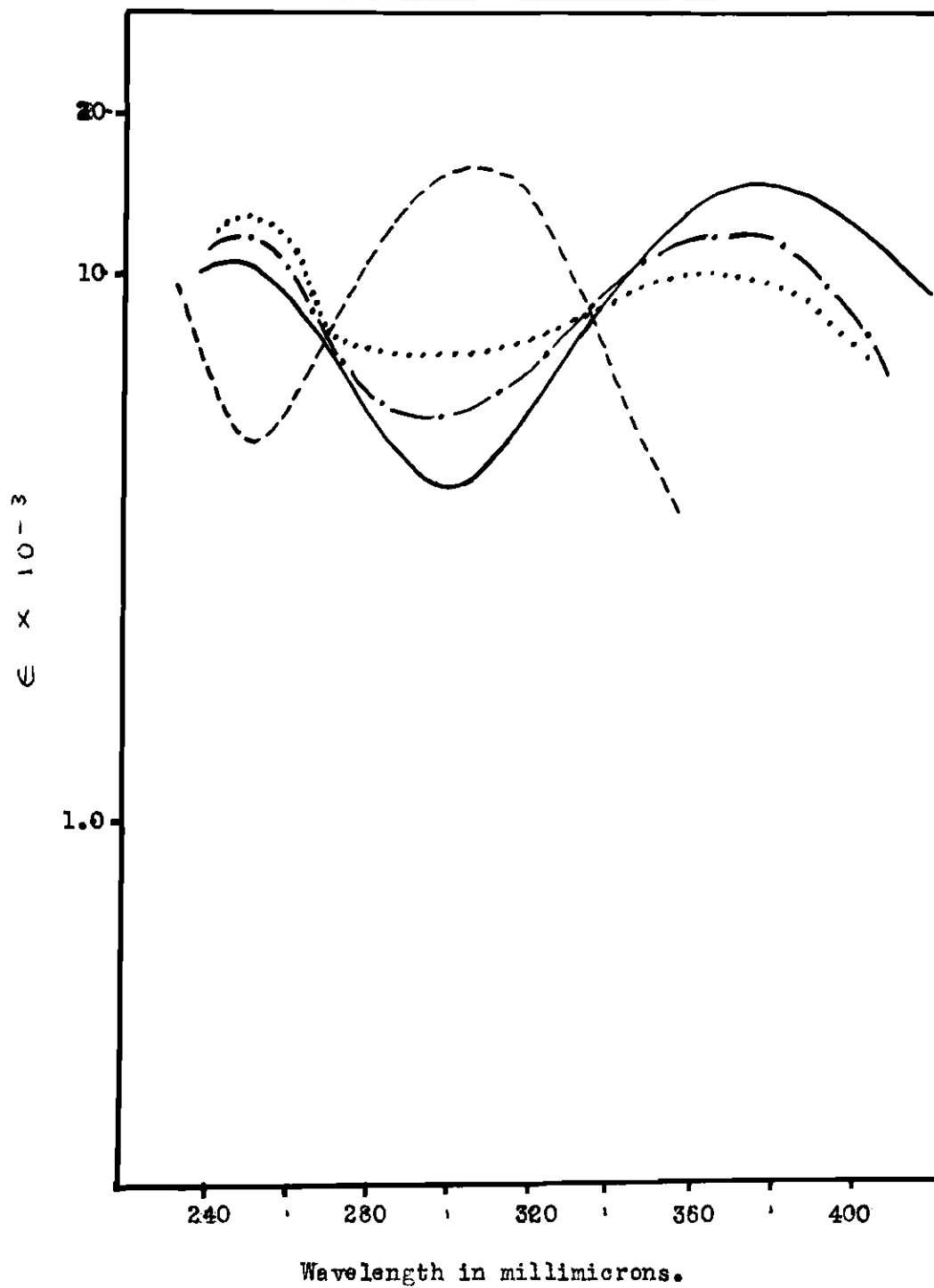
Fig. 6. — 4-Nitro-4'-Aminobiphenyl in various acidic and basic water solutions. ----------------, 0.01N HCl; •••••••••••• , 1x10⁻⁴ HCl; ———•———•——— , water; ————————' 1x10⁻³ NaOH.
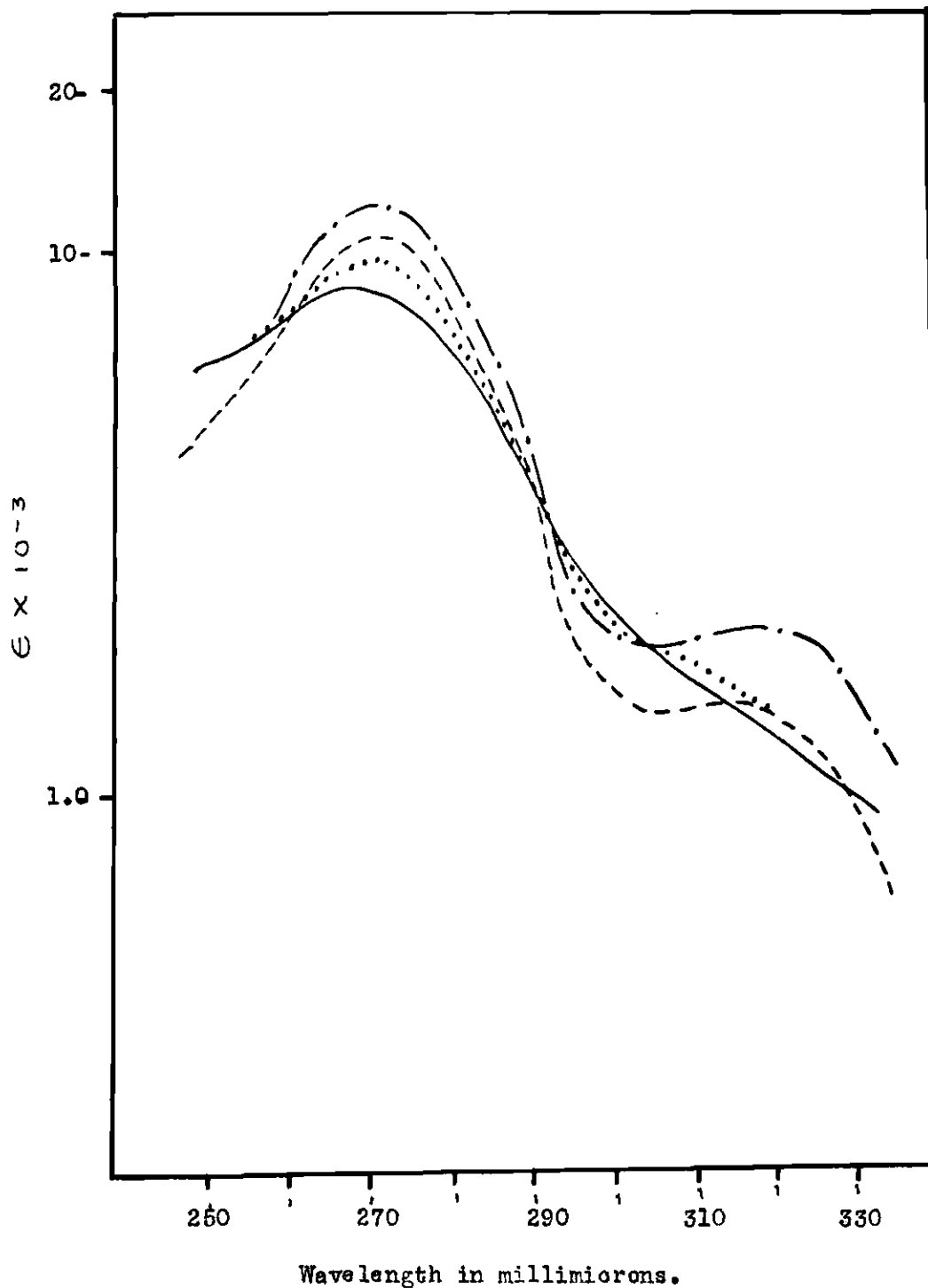
Fig. 7.--4-Carboxybiphenyl in acidic and basic water solutions.
___.___.___.___, 0.1N HCl; -------------------, 0.01N NaOH;
.................., 1x10⁻⁵ HCl; _____, 0.01N HCl.

20 -

10 -

$\in \times 10^{-3}$

1.0 -
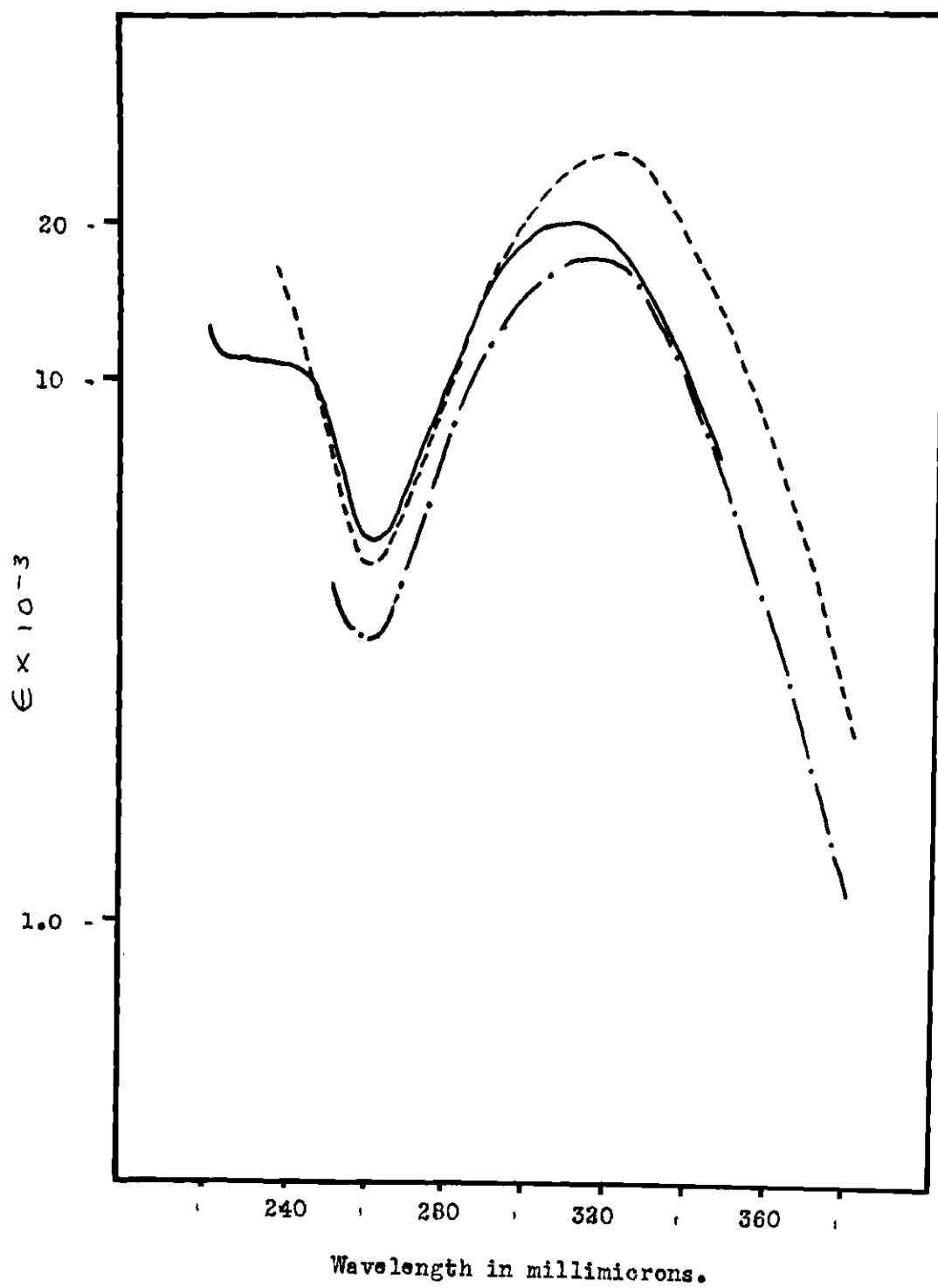
240   280   330   360

Wavelength in millimicrons.

Fig. 8.—4-Nitro-4'-Carboxybiphenyl in various basic and acidic alcohol solutions. ----------, 1.0N KOH; _____, ethanol; —·—·—, 0.1N HCl.

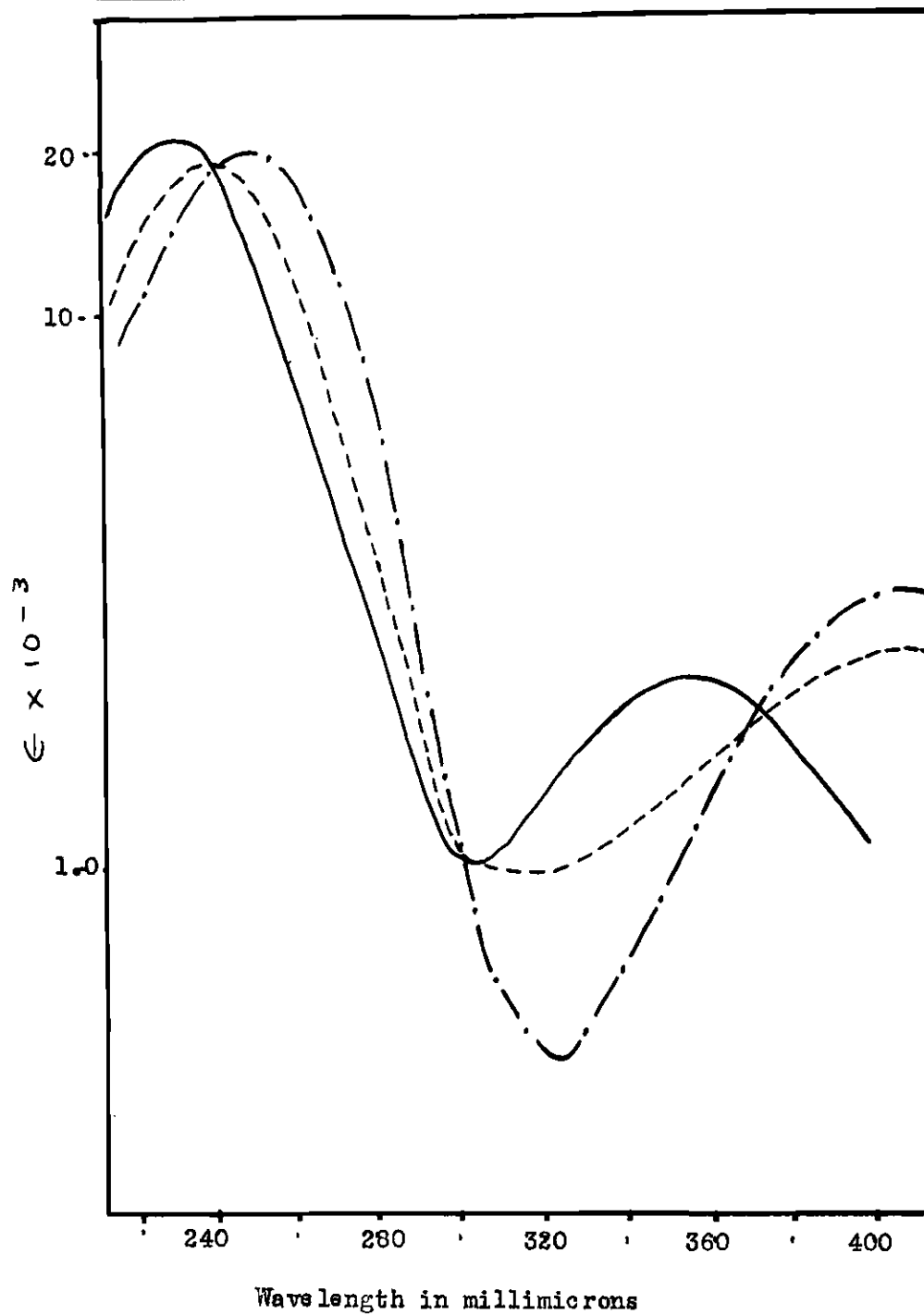Wavelength in millimicrons

Fig. 9.—4-Hydroxybiphenyl in various basic and acidic
water solutions. _____, 0.1N HCl; :----------, 0.01N NaHCO₃;
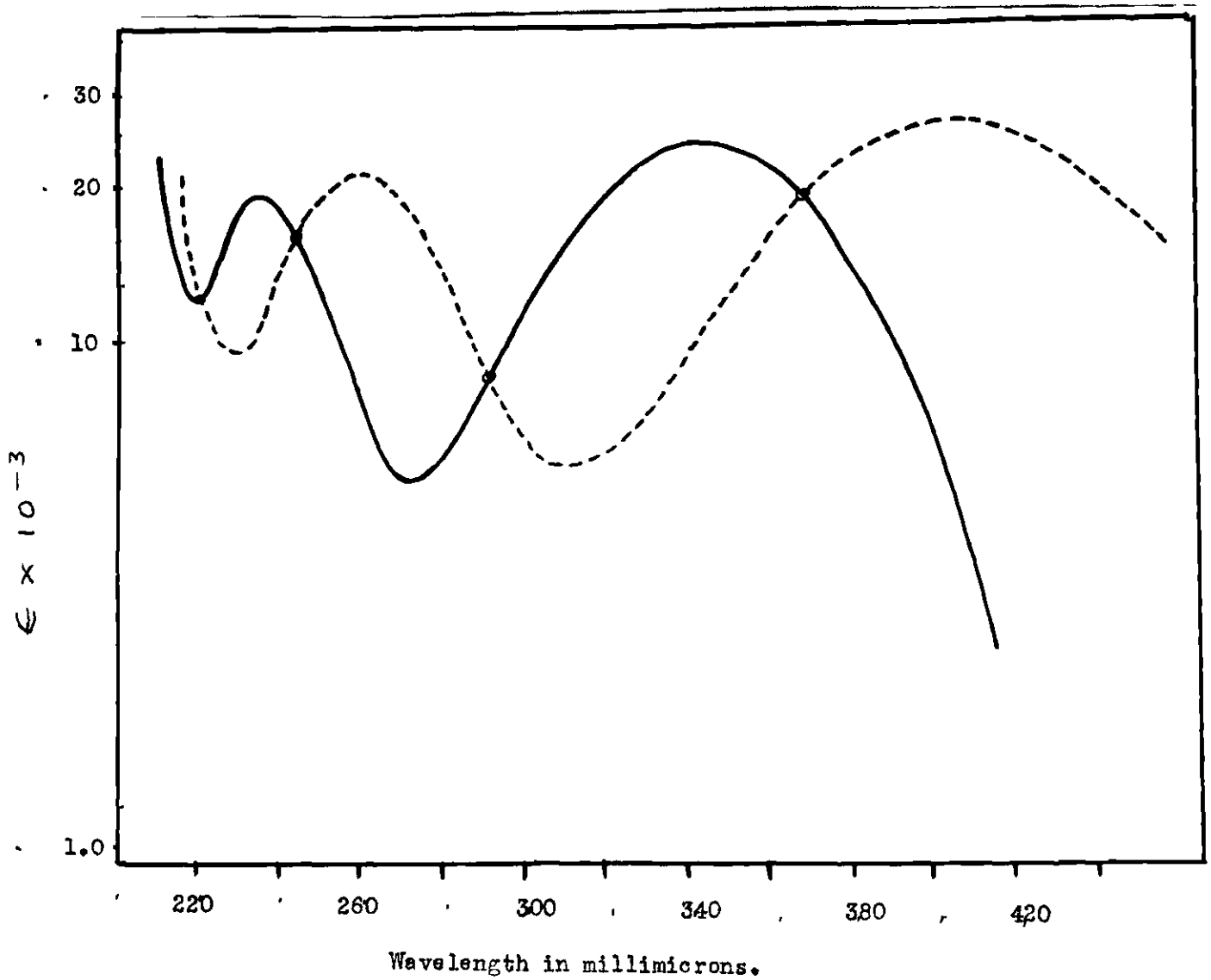—•—•—•—, 0.01N NaOH.

Wavelength in millimicrons.

Fig. 10.—4-Nitro-4'-Hydroxybiphenyl in acidic and basic solutions. ----------------, 0.01N NaOH; ——————————, 1.0N HCl.

APPENDIX III

CALCULATIONS

APPENDIX III

CALCULATIONS

Sample calculation to find the acid ionization constant using pH and the absorption spectra data. From Sherwood and Calvin[36] we have the relationship:

$$\epsilon \text{ apparent} = N_1 \epsilon_1 + N_2 \epsilon_2 \qquad (1)$$

where N_1 is the mole fraction of the compound in one specific form and N_2 is the mole fraction of the compound in the other form.

$$N_2 = 1 - N_1 \qquad (2)$$

From the absorption spectra of 4-nitro-4'-aminobiphenyl in water solution:

$$\epsilon_{ACID} \text{ at } 300 \text{ mu} = 14.8 \times 10^3$$

$$\epsilon_{BASE} \text{ at } 300 \text{ mu} = 4.1 \times 10^3$$

$$\epsilon_{APP} \text{ at } 300 \text{ mu} = 7.3 \times 10^3$$

and the pH at ϵ apparent is 4.5.

From equations (1) and (2):

$$N_1 (4.1) + (1 - N_1)(14.8) = 7.3$$

$$N_1 = 7.5/10.7, \text{ therefore the ratio}$$
$$N_1/N_2 = 2.3$$

at a pH of 4.5. Ionization constant for the acid (Ka) follows from:

$$Ka = (H)(\text{ratio } N_1/N_2) = 10^{-4.5} \times 2.3 = 7.26 \times 10^{-5}$$

for 4-Nitro-4'-aminobiphenyl.

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[36]Ibid.

In table 3 are given other values of the acid ionization
constants calculated by the same method as used on the preceding
page and utilizing only the data from the ultra violet
absorption spectra of the compound.

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