

THE STUDY OF HYDROGEN BONDING IN SUBSTITUTED
BENZOIC ACIDS
BY ULTRAVIOLET ABSORPTION SPECTRA

CENTRE FOR NEWFOUNDLAND STUDIES

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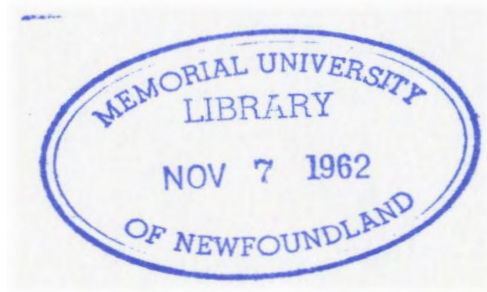
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THE STUDY OF HYDROGEN BONDING IN SUBSTITUTED
BENZOIC ACIDS
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A THESIS

by

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of the requirements for the degree
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ABSTRACT

The known dependence on solute concentration of the ultraviolet absorption spectrum of benzoic acid is re-examined semi-quantitatively and a critical concentration, above which the intensity of absorption becomes independent of concentration, is found to be exhibited by this acid and its substituted analogues, and is taken as a measure of the relative strengths of the dimeric hydrogen bonds. The critical concentration is found to be unaffected by the addition of small amounts of ether to obtain solution of the acid in cyclohexane.

The critical concentrations of a number of substituted benzoic acids are determined and the resulting conclusions as to the relative strengths of the dimeric bonds are interpreted in terms of mesomeric and inductive effects and current theories of hydrogen bonding. To explain the observed spectral effects in the m-substituted acids, it is necessary to postulate an electromeric interaction which differs from the usual inductive effect. The proposed effect is referred to as an I_e effect.

The data show that o-methoxybenzoic acid forms a stronger intramolecular bond than does o-fluorobenzoic acid, suggesting that intramolecular hydrogen bonds of this type are not predominantly electrostatic in nature.

Experimental methods for the spectral examination of concentrated solutions are also described.

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PREFACE

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I INTRODUCTION

The existence of the hydrogen bond, in which the hydrogen is bonded to two atoms, has been realized for some time. Although this apparent bivalency of the hydrogen atom in some environments had previously been proposed to account for the weakness of trimethylammonium hydroxide as a base (52), and the decrease in the combining power of the hydroxyl substituent when in the o-position to a carbonyl group in some aromatic compounds (59), it was Latimer and Rodebush (50) who first introduced the term hydrogen bonding and realized its frequent occurrence.

At the present time the wealth of evidence is such that it can be assumed with confidence that there exists, under certain conditions, in addition to the "normal" chemical bond between an atom and hydrogen, an attractive force between this hydrogen and a second atom and that this force is of sufficient magnitude to permit investigation of the phenomenon.

It has also been recognized that the hydrogen bond is a specific interaction between the - X — H bond in one molecule and the Y atom of another molecule. However, in addition to this type of intermolecular interaction, an intra-molecular bond of similar type, but confined to an interaction between atoms of the same molecule is also known. A widely occurring bond of the latter type is the chelate¹ ring formation exhibited by some o-substituted aromatic compounds, (39,49; see for specific examples 9,20,21,67).

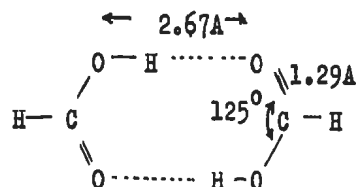
1 This nomenclature was introduced in 1920 by Morgan and Drew (53).

The large amount of data which has been accumulated up to the present time has taken a variety of forms as a multiplicity of phenomena has been ascribed to hydrogen bonding². One of the earliest reported investigations of what was later realized to be a hydrogen-bonded system, was made long before the underlying principles of the interaction were understood. In 1891 Nernst (56) postulated the existence of dimers of benzoic acid to account for the distribution of the acid between benzene and water when in the mixed solvent. Hendrixson (35), by similar studies, obtained a value of 8.7 kcal. per mole for ΔH_{12}^S for benzoic acid in wet benzene. It was not however until more recent years that these and other similar data could be interpreted in the light of hydrogen bonding theory. When the existence of such a bond was realized, this previously random data, combined with the results of some new studies, formed what might be termed the classical investigations of hydrogen bonding, from which in the early 1930's a reasonably consistent picture began to emerge. Most of this older data dealt with the more physical aspects of hydrogen bonded systems - anomalous molecular weight, elevated boiling points, and the like. These features of the early work have been reviewed, for example, by Lassetre (49), and more recently by Davies (22).

Since it became apparent, even from the earliest investigations, that the hydrogen bond of the type O—H...O was one of the most frequently occurring variety, it is not surprising that one of the first systems to be subjected to an

2 Two recent publications (34,61) provide detailed discussion of the latest results of a wide variety of experimental work and many new and important theoretical considerations, as well as a detailed treatment of the general subject.

intensive investigation was the carboxylic acids. Pauling and Brockway (58), determined the structure of formic acid, in the dimeric form, by electron diffraction to be as shown in Structure I. The distance for the O—H...O bond is



Structure I

smaller than would be expected from a consideration of the van der Waal's radius of the oxygen atom, 1.40 Å. Even if the two oxygens were in contact, the interatomic distance would be 2.80 Å. Thus the intervening hydrogen occupies "no space" but pulls the oxygens closer together. It was thus postulated that a bond existed between the hydroxyl hydrogen of one molecule and the carbonyl oxygen of the other. This effect was found to be even more pronounced in oxalic acid dihydrate where the distance between the oxygens was observed to be as small as 2.52 Å (64).

This study has additional significance in that this elucidation of structure enabled the strength of the hydrogen bonds in these acids to be determined from the heats of dissociation and similar data (cf. 49).

An extremely important discovery, which has led to an excellent method for the detection of the presence of a hydrogen bond, was made by Wulf and collaborators (36), who


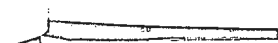
found that when hydrogen was involved in this type of bond it exhibited certain anomalous behaviour in its infrared spectrum. The absence of the characteristic hydroxyl absorption was found to be an excellent criterion for the presence of a hydrogen bond.

This method of investigation has found wide use and examples of applications of the method to the study of various hydrogen bonded systems are numerous. These data are covered in several reviews (e.g. 22,68), and in the more recent publication of Kellner (45). Of particular interest are those investigations which have dealt with the well known dimer formation in benzoic acid and its derivatives (8,12,13,23,24,33,43).

By contrast with the infrared data on hydrogen bonding in general, investigations of the phenomenon by ultraviolet spectroscopy are much less extensive. Shifts in the absorption bands of certain compounds were first reported by Scheibe et al. (65). These shifts, which occur on changing the solvent, and which have been ascribed to hydrogen bonding between solute and solvent molecules, have been investigated by a number of workers (3,4,11,12,48,55,69), but their detailed interpretation is still being developed (see, for example 10, 60).

Hydrogen bonding has also been mentioned as a possible cause of certain anomalous spectra in the light absorption studies of Forbes and co-workers (26,27,28,29).



The dependence on concentration of solute molecules of the ultraviolet spectra of some compounds has been reported also, (7,37,46,47). In particular the concentration



dependence of the electronic absorption spectra of benzoic acid and its derivatives has been reported (31,70). Ungnade and Lamb (70) investigated the absorption band of benzoic acid at 280 m μ , but found no significant effects, due to changes in solute concentration, on the absorption intensities. More recently, Forbes and Templeton (32) found that both change of solvent and change of solute concentration affected the intensities and wavelength of the B-band³ of benzoic acid and its substituted analogues.

The purpose of the present investigation is to continue this latter study on a semi-quantitative basis.

³ The band nomenclature follows that of Moser and Kohlenberg (54).



II EXPERIMENTAL

A. GENERAL

The ultraviolet absorption data were determined with a Unicam SP 500 spectrophotometer. Fused silica cells of path length 100, 20, 10, 5, 2, and 1 millimetres were used for the benzoic acids, while for the diphenyl spectra, demountable sealed cells with silica windows, of path length 0.5 millimetres were used in addition.

The infrared data were determined with a Unicam SP 100 spectrophotometer using a sodium chloride prism, diffraction grating, and a double monochromator system. The cells were 0.5 millimetre path length with potassium bromide windows and the light source was a Nernst Glower.

The cyclohexane used was Fisher certified reagent, spectroanalysed; ether was Eastman white label, spectrograde; and the carbon tetrachloride was Eastman spectrograde.

All of the compounds were obtainable commercially, and were purified by recrystallization and/or sublimation and carefully dried. Elemental analysis proved the absence of any appreciable amounts of water of crystallization of the benzoic acids. For example *p*-toluic acid analysed for C, 70.7% \pm 0.1% as against C, calculated, 70.6%.

The physical constants of the compounds used in this work are recorded in Table I.

TABLE I

A. Physical Constants of Benzoic Acids

Substituent	<u>Melting Point</u>	
	Published Value (38)	Observed Value
none	122° C.	120.6° - 121.5° C.
<u>o</u> -methyl-	103.7°(104-5)	102.0° - 103.1°
<u>m</u> -methyl-	108.75°(109-112)	107.0° - 108.7°
<u>p</u> -methyl-	179.6°	177.4° - 178.3°
<u>o</u> -hydroxy-	159°	158.2° - 158.8°
<u>m</u> -hydroxy-	201.3°(199-200)	200.0° - 201.0°
<u>p</u> -hydroxy-	213° (214.5-5.5)	214.1° - 214.5°
<u>o</u> -methoxy-	98° (100-1)	98.1° - 99.5°
<u>m</u> -methoxy-	107-8°	105.7° - 107.1°
<u>p</u> -methoxy-	184.2°	183.4° - 183.9°
<u>o</u> -fluoro-	122°	120.9° - 121.7°
<u>m</u> -fluoro-	124°	123.2° - 123.8°
<u>p</u> -fluoro-	182°(184-6)	183.0° - 184.3°

B. Physical Constants of Diphenyl

Diphenyl	69-71°	68.0° - 68.2°
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The molecular extinction coefficient, ϵ , is defined by

$$\epsilon = \frac{\text{Log}(I_0/I)}{c \cdot l} \quad (1)$$

where I_0 and I are the intensities of the incident light and the transmitted light respectively, c is the concentration in moles/litre, and l is the cell length in centimetres.

By careful manipulation, the maximum extinction coefficient values were measured with a precision estimated at $\pm 2\%$ or better, and the general reproducibility of these values was well within this margin. In the diagrams presented this reproducibility is indicated by vertical lines as shown in Figure I.



Figure I. Method of experimental error representation. The point represents the observed value and the vertical lines, the extent of the experimental error.

The instrumental error in wavelength values was estimated to be $\pm 0.5\%$ and the instrument was calibrated at intervals against a didymium filter, assuring accuracy of the absolute values of the reported wavelengths.

For each of the acids investigated a complete B-band was determined at least in duplicate and the concentration dependence of the ϵ_{max} values was obtained by determining the spectra of solutions of varying concentrations, in the region $\pm 5 \text{ m}\mu$ of the observed B-band maximum.

Factors for the correction of slight differences in cell absorption were not used, but the spectrum of each solution was determined twice, reversing the cells for the second examination. The reported ϵ_{max} values were calculated from the mean of these two observations.

B. METHOD OF EXTENSION OF THE CONCENTRATION RANGE

The standard technique in the determination of ultraviolet spectra; that is the use of two cells, one containing pure solvent and the other, the substance under investigation in solution; introduces certain limitations since the solute concentration must be chosen so that the optical density is within the optimum range of 0.3 to 0.7. Outside this range the readings are unreliable due to reflectance phenomena below the minimum of 0.3 and fluorescence phenomena above the maximum of 0.7.

Since many of the acids studied in this investigation required examination of their concentrated solutions, it was suggested (72) that a method of extending the concentration range was to use progressively more concentrated solutions in the solvent cell in place of pure solvent.

To investigate this possible solution to the problem, diphenyl, which does not exhibit appreciable concentration dependence in the investigated concentration range, was used as a reference compound. Figure II shows the B-band of diphenyl in cyclohexane solution at two different concentrations. The spectrum of the solution of concentration 0.628×10^{-4} moles/litre was determined in two ways - (a) using pure cyclohexane in the solvent cell and (b) using a solution of diphenyl in cyclohexane ($C = 0.314 \times 10^{-4}$ moles/litre) in the solvent cell. In (b), the ϵ_{\max} values were determined by equation (1), p. 8, using $c = 0.314 \times 10^{-4}$ moles/litre, i.e., the difference in the solute concentrations in the solvent and solution cells.

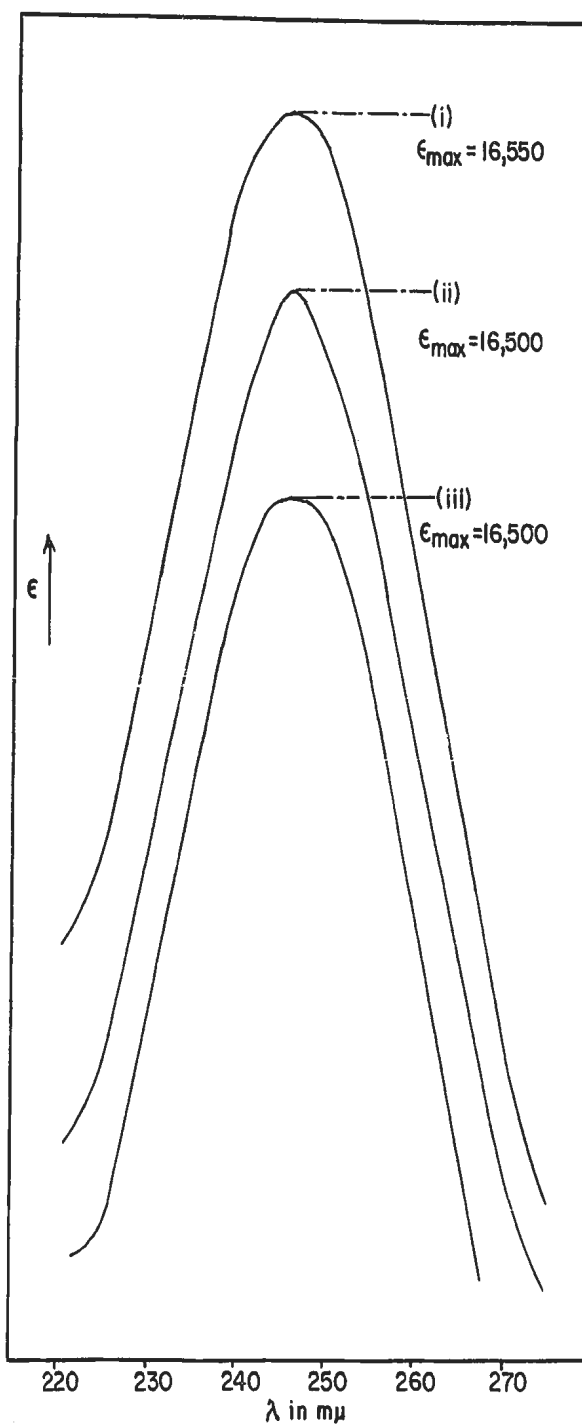


Fig. II The B-band of diphenyl in cyclohexane (bands shifted vertically for clarity)

(i) Diphenyl in cyclohexane ($0.628M$) vs. cyclohexane cell length 5 mm.

(ii) Diphenyl in cyclohexane ($0.628M$) vs. diphenyl in cyclohexane ($0.314M$) - cell length 10 mm.

(iii) Diphenyl in cyclohexane ($0.314M$) vs. cyclohexane cell length 10 mm.

Concentrations given are $\times 10^{-4}$ in moles per litre.

The figure shows that employing a solution in the solvent cell, although altering the band shape slightly, introduces no appreciable error in the value of ϵ_{\max} .

Further confirmation that the method introduces no appreciable error is obtained from Figure III which gives a plot, for diphenyl in cyclohexane, of ϵ_{\max} against log concentration⁴. The figure shows that a straight line relation is maintained by the ϵ_{\max} values whether determined by using pure cyclohexane in the solvent cell, or a solution of diphenyl in cyclohexane in that cell.

In general it was found that this method could be used to obtain the spectrum of three solutions, of concentration C , $2C$, and $3C$, using the same path length cell throughout - a difference in concentration between the solutions in the two cells being maintained at a constant value, C .

This method has the distinct advantage of allowing the study of concentrated solutions using only the standard fused silica cells. The only alternative procedure is to use cells of very narrow and accurately known path lengths which are neither convenient to work with nor readily available. Further, the method overcomes the difficulty that some solutions of intermediate concentrations require unobtainable path-length cells to yield optical density values in the required range, since by choosing an appropriate concentration difference between solvent and solution cells, the spectra of solutions of any intermediate concentration may be obtained.

⁴ In this and subsequent figures the concentration is plotted on a \log_{10} scale to avoid compression of the points obtained at low concentrations.

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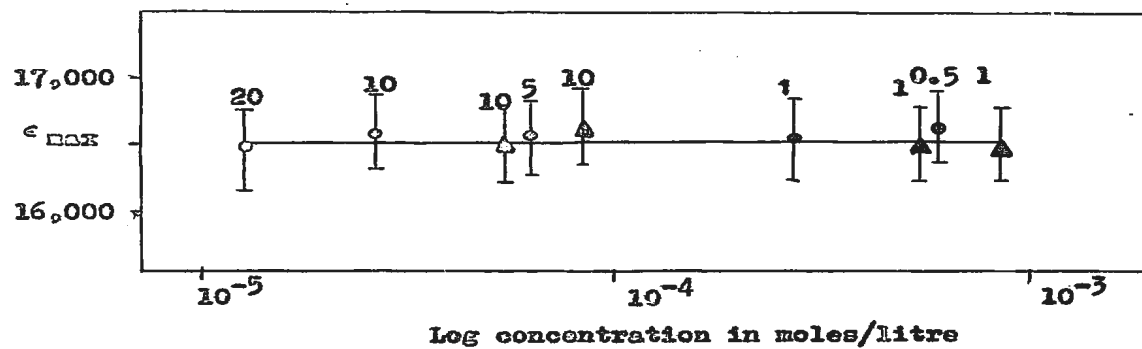


Fig. III Plot of ϵ_{MAX} vs. log concentration for diphenyl in cyclohexane. The number above each point is the cell length in mm. Values obtained using pure cyclohexane in the solvent cell are given as ●, while those obtained with a solution of diphenyl in cyclohexane in the solvent cell are shown as ▲.

III THE ULTRAVIOLET ABSORPTION SPECTRUM
OF BENZOIC ACID

A. GENERAL

The ultraviolet absorption spectrum of benzoic acid in cyclohexane solution at different concentrations is presented in Figure IV. The figure shows that an increase in the solute concentration causes a corresponding increase in the molecular extinction coefficient and a bathochromic shift in the wavelength of maximal absorption of the B-band. It is also apparent from the figure that the shape of the B-band remains essentially the same at the three different concentrations. Very similar curves, which also exhibit this latter behaviour, were obtained for all the substituted benzoic acids studied in this investigation. Thus the intensities of the maximal absorption can be taken as a measure of the actual absorption by the substances.

Changes in the wavelength and intensities of the C-band maxima under these conditions, if any, are too minute to be discerned⁵ and the present investigation is confined to a study of the behaviour of the B-band maxima.

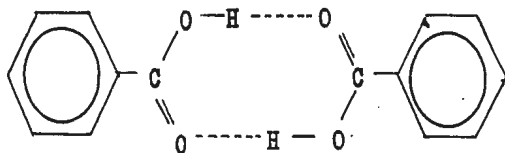
The observed dependence on concentration, proposed by Forbes and Templeton (32) as a solute-solute interaction, is ascribed to dimer formation. In addition to the evidence already mentioned for the existence of benzoic acid dimers in general (cf. p.2 et seq.), the hypothesis is supported by some other evidence.

The absorption spectrum of a number of other

⁵ Slight variations have been reported (41) on large changes in solute concentration.

molecules, investigated in a concentration range similar to that studied here, do not show any concentration dependence. In particular, the concentration dependence practically disappears for the methyl benzoate (32,70) B-band ⁶. This indicates that the hydroxyl group is necessary for the occurrence of the phenomenon.

It appears highly probable that the concentration dependence which is observed for benzoic acid is related to the formation of dimers as shown in Structure II,

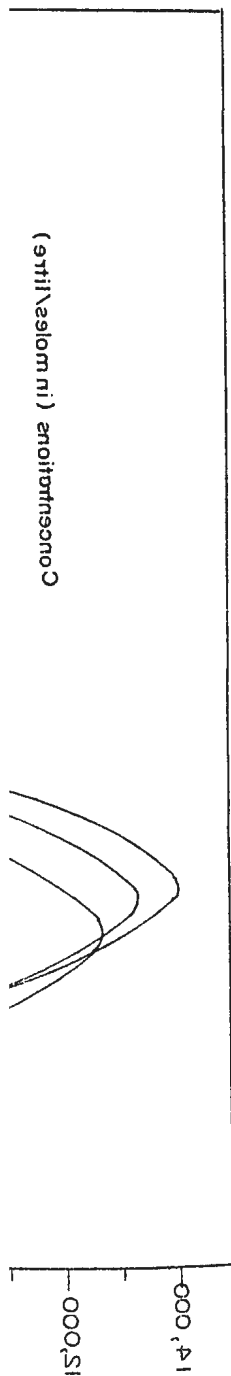


Structure II

which has been observed at concentrations similar to those of the present investigation (5,41,43).

It was also found that addition of ether to the solution of benzoic acid in cyclohexane caused a decrease in the concentration dependence and that the decrease became more pronounced with increasing percentages of ether. (cf. Fig. VII). Since such addition introduces the possibility of a competitive mode of hydrogen bonding, i.e. between solute and solvent molecules (cf. Structure III), the decreased concentration dependence indirectly suggests solute - solute hydrogen bonding in the absence of ether and consequently indirectly supports the hypothesis. Similar indirect support is obtained from the spectra of salicylic

⁶ The C-band variations reported for benzoic acid (cf. Footnote 5, p.13) disappear in the case of methyl benzoate (41).



acid in cyclohexane solution which shows a decreased concentration dependence, which is ascribed to another competitive mode of hydrogen bond formation, viz. intramolecular bonding as shown in Structure VI, p.55.

Figure V shows that it is possible to obtain a plot of ϵ_{\max} against concentration and that such a plot enables a determination of a concentration at which the ϵ_{\max} values become essentially independent of concentration. It is proposed to refer to this concentration as the critical concentration. Its position in this and subsequent figures is indicated by vertical arrows.

Since it is apparent that the observed variation in intensity and wavelength of the B-band maxima is very probably due to dimerization of the acid through intermolecular hydrogen bonding, it follows that any significant change in this observed concentration dependence is due to some change in the monomer-dimer equilibrium.

It is proposed that the critical maximal concentration represents the concentration above which the particular acid exists primarily in the dimeric form. That is, above this concentration the principal absorbing species is the dimerized benzoic acid molecule and that changes in its concentration which occur on increasing the total acid concentration, cf. Fig. VI p.19, are too small to alter the ϵ_{\max} value outside the limits of experimental error. This hypothesis is supported by an application of the mass action law in the following manner.

The association constant of benzoic acid has been determined by several methods. In benzene solution, a value

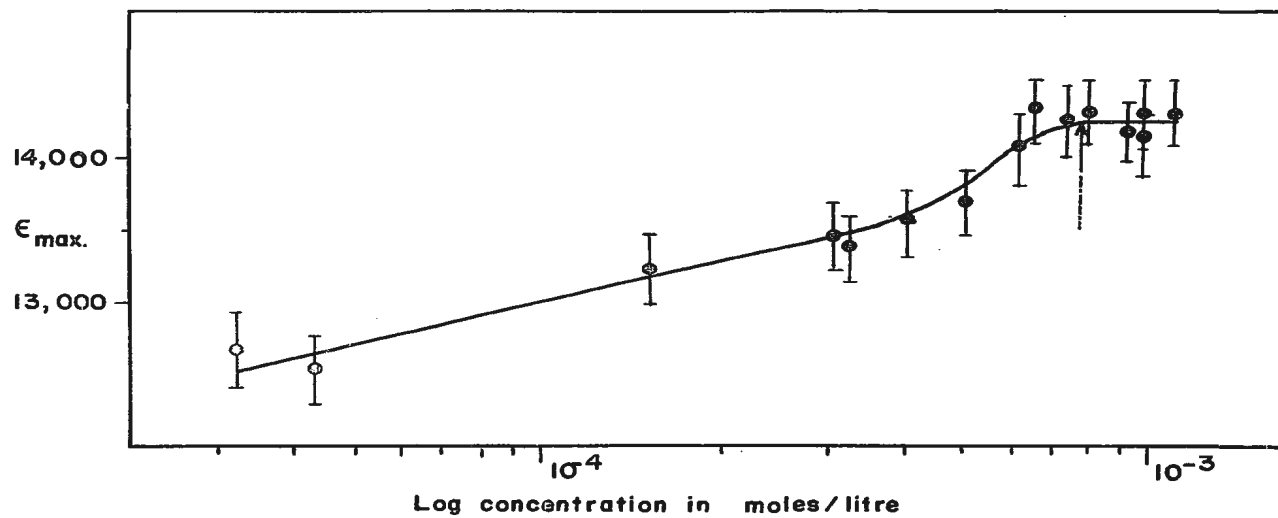


Fig. V Plot of maximal absorption against solute concentration for benzoic acid.

of $K = 1.5 \times 10^4$ at 5.4°C . was obtained by cryoscopic measurements (6). The value of $K = 1.5 \times 10^4$ in CCl_4 solution at room temperature has been reported from an investigation of infrared data (24). From ultraviolet data, a value of $K = 1.76 \times 10^4$ was obtained (41) in n -hexane at room temperature. An approximate value of K , the association constant, from the spectral data, was taken as 1.6×10^4 .

Defining K by the relation

$$K = [D] / [M]^2 \quad (2)$$

and expressing $[D]$, the dimer concentration, in terms of $[M]$, the concentration of monomer, and $[C]$, the total acid concentration, as

$$[D] = \frac{[C] - [M]}{2} \quad (3)$$

substitution of this expression in equation (2) yields, on insertion of the approximate K value, a quadratic equation of the form

$$3.2 \times 10^4 [M]^2 + [M] - [C] = 0 \quad (4)$$

which can then be solved for various values of $[C]$. From the $[M]$ values calculated in this manner, the percentage of the total acid concentration in the dimerized form was determined for values of $[C]$ from 10^{-2} to 10^{-6} moles/litre. The results are plotted in Figure VI, along with the spectral curve for benzoic acid on the same concentration scale.

From the form of the theoretical curve, the hypothesis is supported in that the curve indicates:

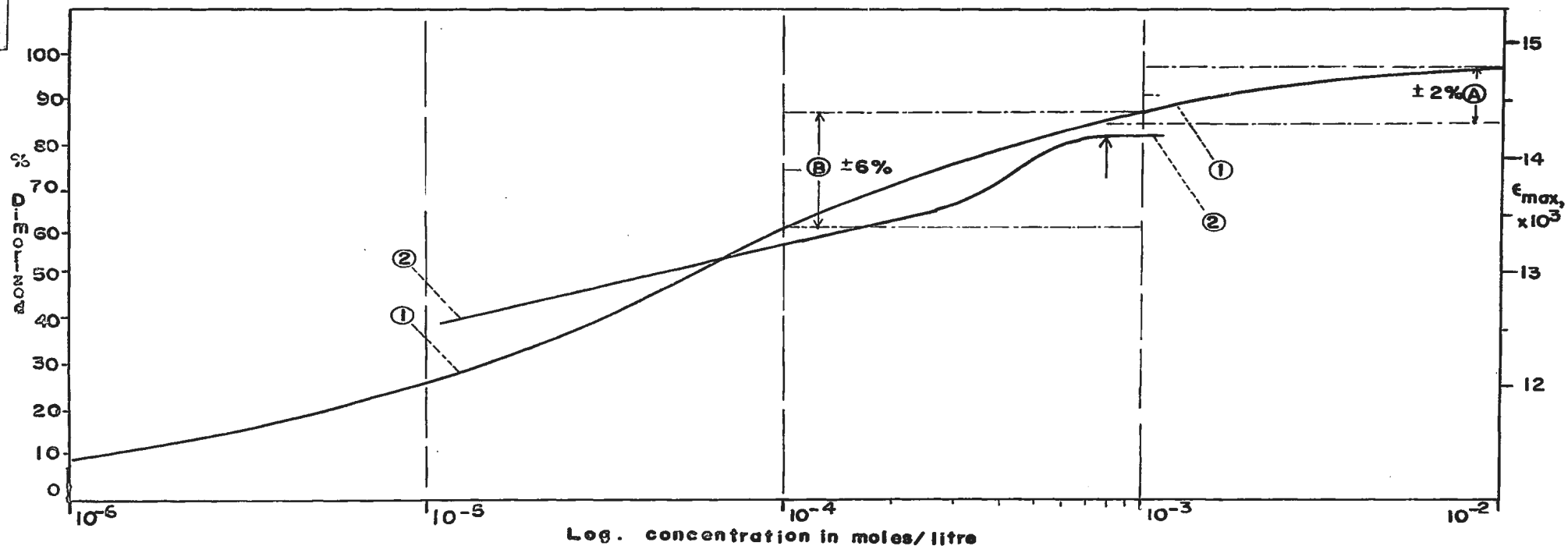


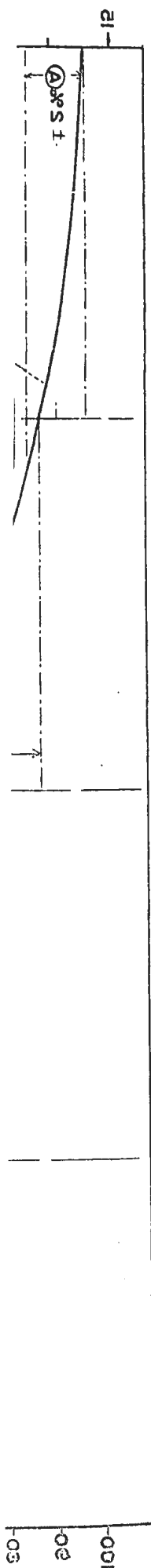
Fig. VI A plot of (1) calculated percentage of the total acid concentration in the dimerized form (theoretical curve) and (2) ultraviolet extinction coefficient, ϵ_{\max} , (experimental curve) against log concentration for benzoic acid. Theoretical values were calculated from $K = [D] / [M]^2$ assuming $K = \text{ca. } 1.6 \times 10^4$ (cf. p.18).

(a) at the critical concentration and above, the acid does exist predominantly in the dimerized form, ca. 82%.

(b) although the experimental data do not follow the theoretical plot exactly, an examination of the two curves in the areas marked A and B in the figure shows that the behaviour of the experimental curve might be expected. In the concentration range 10^{-3} to 10^{-2} moles/litre (A in the figure) the theoretical values fall within $\pm 2\%$ on the ϵ_{\max} scale - the experimental error of the present investigation. Thus the method would not be expected to discern the change in dimer concentration, when the total acid concentration varies from 10^{-3} to 10^{-2} moles/litre. It is also instructive to note that the theoretical curve deviates from the $\pm 2\%$ range of ϵ_{\max} values just at the critical concentration. On the other hand, in the concentration range 10^{-4} to 10^{-3} moles/litre (B in the figure) the spread of percentage dimerized values is $\pm 6\%$ - outside the limits of experimental error. Consequently the observed alteration of the ϵ_{\max} values in this range is anticipated.

A further implication of this theoretical approach is that it should be possible to obtain from the spectra of solutions in the concentration range ca. 10^{-7} - 10^{-5} moles/litre a critical minimal concentration, below which the solutions would be predominantly monomer. However, this range is below the concentration of the most dilute solution which can be examined using these techniques⁷. The fact that this point

⁷ The limit in 10 cm. cells is ca. 5×10^{-5} moles/litre. At this and lower concentrations background absorption by the solvent becomes serious.



is inaccessible precludes application of the standard relations to the spectral data for the acids investigated, to determine their association constants. This is elucidated below.

The observed extinction coefficient, ϵ_0 , at a total acid concentration, $[C]$; is related to the ϵ value, ϵ_M , due to absorption by monomer species of concentration $[B]$; and to the ϵ value, ϵ_D , due to absorption by molecules of concentration $[B]^2$, existing as part of the benzoic acid dimer; by the relation,

$$\epsilon_0[C] = \epsilon_M[B] + \epsilon_D[B]^2 \quad (5)$$

To make the necessary calculations, values must be assumed for ϵ_D and ϵ_M . These may be obtained from that part of the spectral curve where absorption is predominantly by dimer and monomer species respectively. That is, from the straight line above the critical concentration a value of ϵ_D may be obtained (assuming $[B]^2 \gg [B]$); similarly the ϵ_M value could be obtained from points below the critical minimal concentration, if such were available, (assuming in this case that $[B] \gg [B]^2$). Using the relation,

$$[C] = [B] + [B]^2 \quad (6)$$

values for $[B]$ and $[B]^2$ can be determined from equation (5) and equation (6) for a value of $[C]$ and hence, since the dimer concentration, $[D] = \frac{1}{2}[B]^2$, the K value may then be calculated from equation (2). However the fact that the critical minimal concentration is unobtainable prevents the

application of this method. In the present case of benzoic acid, however, these equations are applied approximately to illustrate that the method and, in particular, the ultra-violet absorption data yield a value of K which is of the same order as that obtained from other investigations.

Assuming that the concentration dependence curve is approximately symmetrical and taking a concentration of 0.6×10^{-4} moles/litre as the mid-point (where from Figure VI, $[B] = [B']$) and where the errors will thus be at a minimum in the values of ϵ_D and ϵ_M ; a value of 12,200 was obtained for ϵ_M .

Applying the method outlined above a value of $K = 1.2 \times 10^4$ was calculated as compared with the known value of 1.6×10^4 (cf. p. 18). This calculation was made in the case of the reference acid to offer support for the general arguments concerning the observed concentration dependence, but there is obviously little value in making similar calculations of K for the other acids since,

(a) the value of K should be known in the first instance to enable the determination of the mid-point of the concentration dependence curves, and

(b) in the case of the acids with dimeric bonds very much stronger than benzoic acid (cf. Section IV) even this mid-point is outside the investigated range, and

(c) the differences in the association constants of the acids will in most cases be of such small order that the errors introduced by the number of assumptions necessary to the calculations will render conclusions based on their relative values unreliable.

It is proposed therefore to use the critical concentrations, since the rigorous mathematical treatment of these data, while providing support for the arguments in general, is not, on the basis of the above considerations, justified.

From the preceding general argument in this section, it also follows that the value of the critical concentration is semi-quantitatively related to the dissociation constant and thus to the strength of the hydrogen bond, whence the general hypothesis that the lower the value of the critical concentration, the stronger will be the dimeric hydrogen bond.

In this investigation the concentration dependences and hence the critical concentrations for a number of substituted benzoic acids were determined and the results interpreted in the light of the above hypothesis and current theories of hydrogen bonding.

At the outset, however, it was found that a number of these acids were not sufficiently soluble in cyclohexane to permit the determination of their concentration dependence in that solvent. This difficulty was overcome by the addition of small amounts of ether to obtain solution. This modification evidently made it necessary to investigate the effects of such addition.

B. THE EFFECT OF ADDITION OF ETHER

Figure VII shows the observed changes in ϵ_{\max} with changes in solute concentration for benzoic acid in cyclohexane-ether mixtures as solvent.

The figure shows that in ether solution there is no concentration dependence, while in cyclohexane solution containing 5% of ether, a dependence on concentration is observed. In solutions of intermediate percentages of ether, the acid exhibits intermediate concentration dependences.

The data in Figures VIII and IX show the concentration dependence of *p*-toluic acid and *p*-hydroxybenzoic acid respectively, and also show that these acids exhibit a behaviour similar to that of the reference acid, benzoic. The significance of the relative values of the critical concentrations for the three acids will be discussed later.

The most striking observation concerning these data is that for all of the acids, the critical concentration, characteristic of each acid, occurs at essentially the same concentration irrespective of whether a small amount of ether has been added to the solution or not.

Thus under the conditions of the present investigation, the concentration dependence may be determined either in cyclohexane or in cyclohexane solution containing small amounts of ether without altering the position of the critical concentration.

Some further implications of these data may be discussed at this point. For the acids studied in ether-cyclohexane mixtures, the dimeric hydrogen bond is stronger than

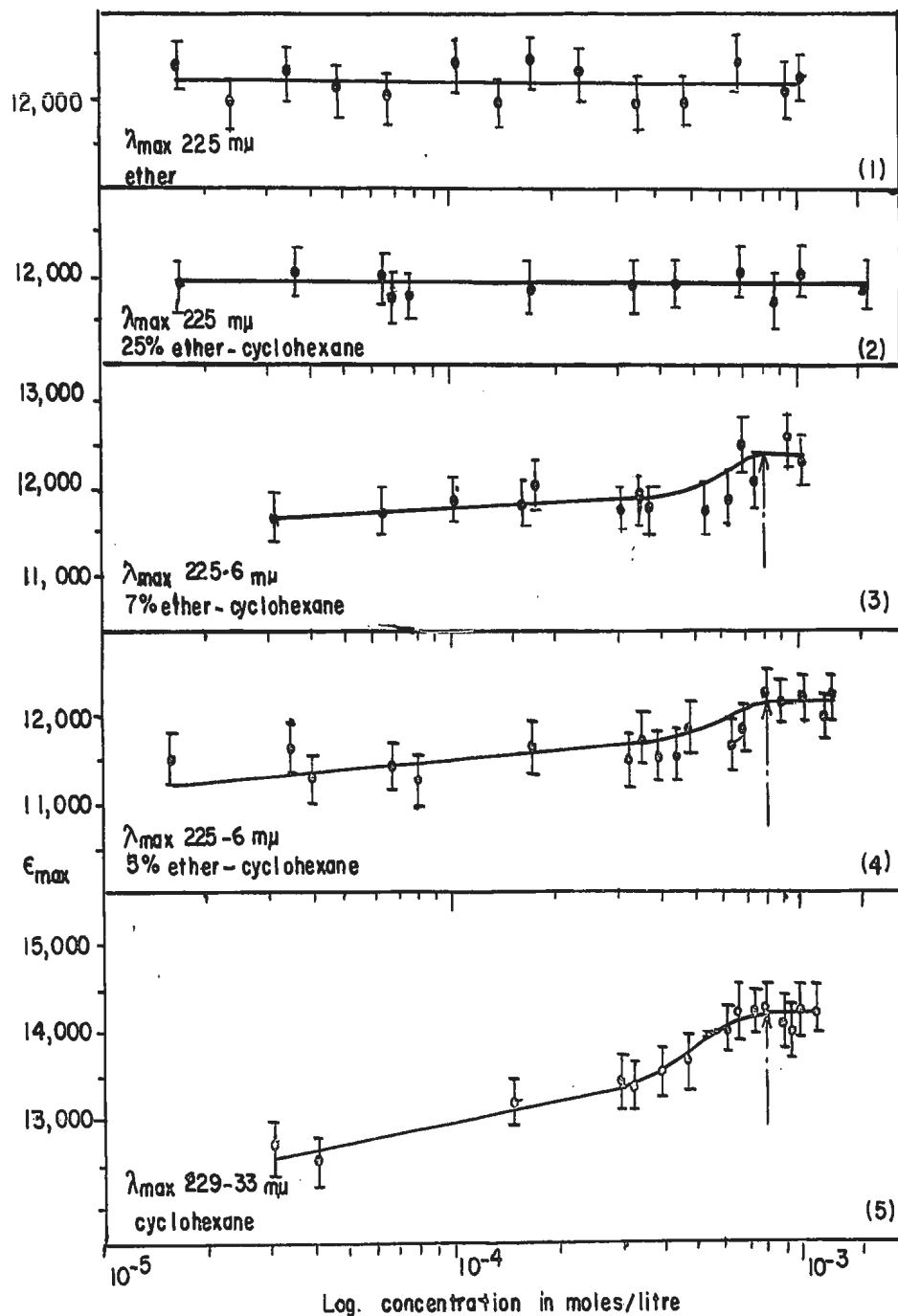


Fig. VII The variation of ϵ_{\max} on changing the concentration of acid for benzoic acid in (1) ether solution (2) cyclohexane solution containing 25% ether, (3) cyclohexane solution containing 7% ether, (4) cyclohexane solution containing 5% ether, and (5) cyclohexane solution.

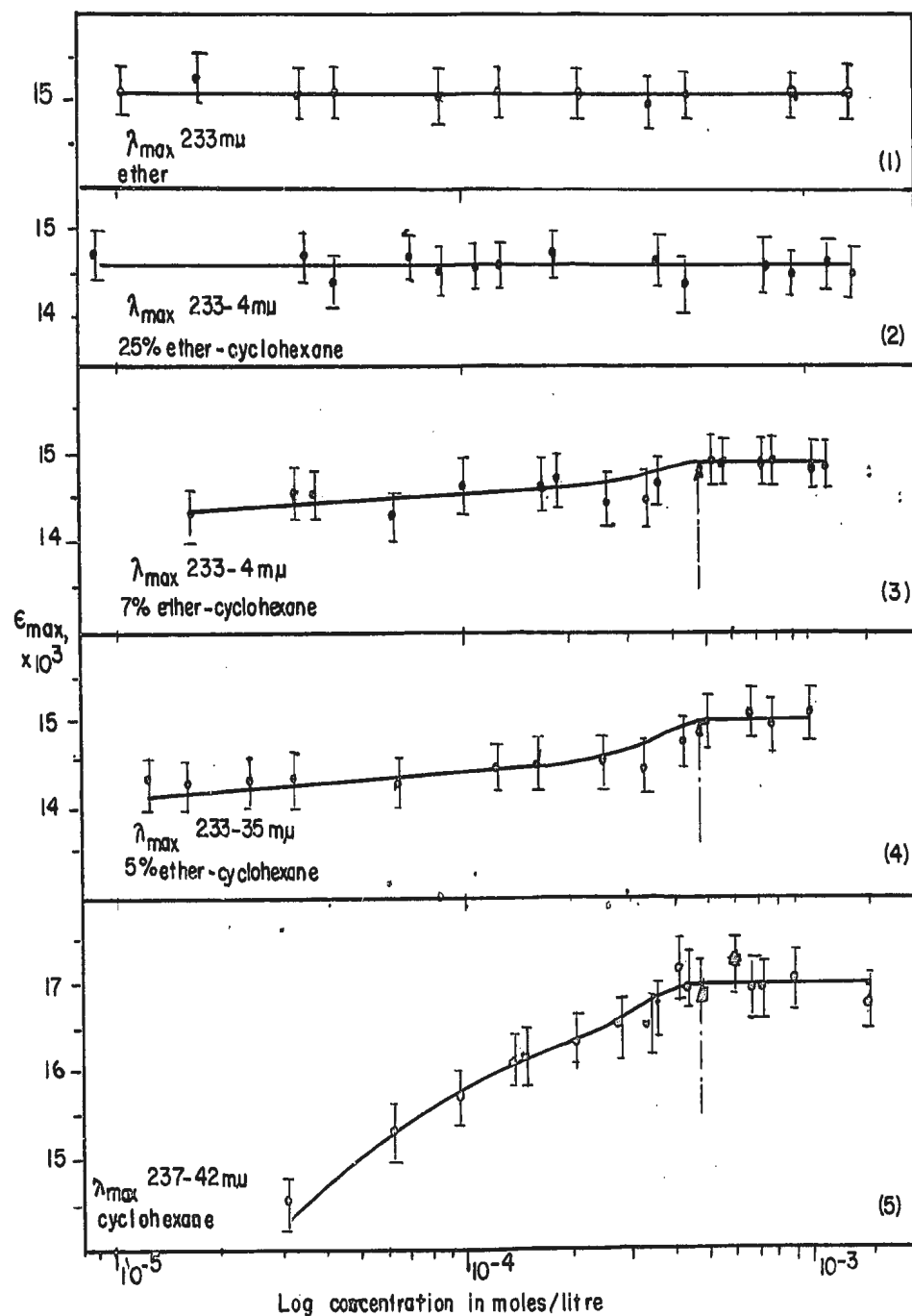


Fig. VIII The variation of ϵ_{\max} on changing the concentration of acid for p-toluic acid in (1) ether solution, (2) cyclohexane solution containing 25% ether, (3) cyclohexane solution containing 7% ether, (4) cyclohexane solution containing 5% ether, and (5) cyclohexane solution.

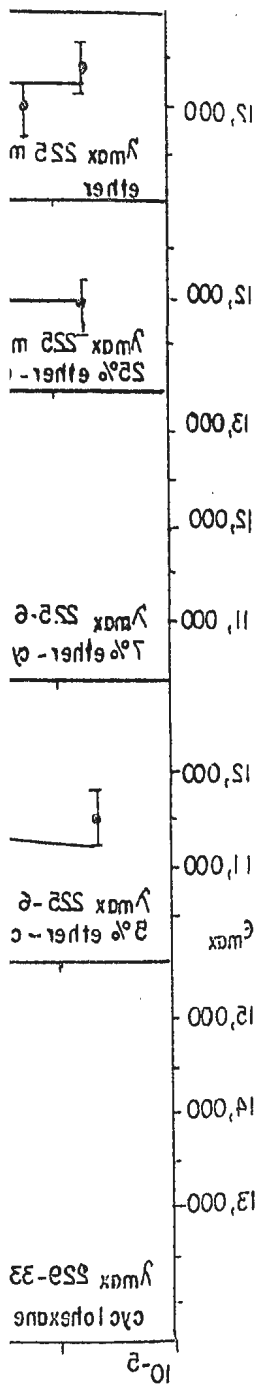


Fig. VII The variation of ϵ_{\max} on changing the concentration of acid for p-toluic acid in (1) ether solution, (2) cyclohexane solution containing 25% ether, (3) cyclohexane solution containing 7% ether, and (4) cyclohexane solution containing 5% ether.

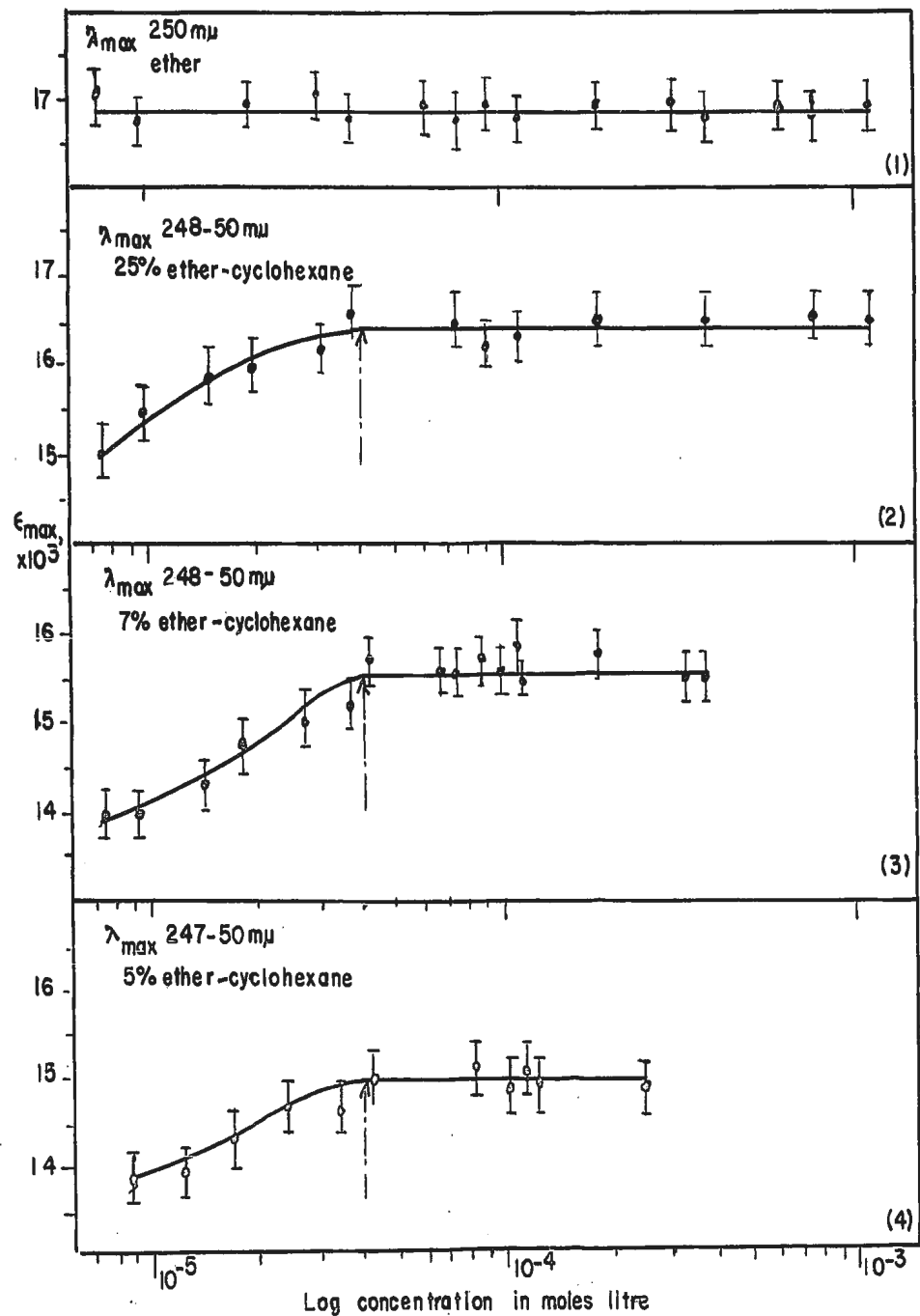


Fig. IX The variation of ϵ_{max} on changing the solute concentration for p-hydroxybenzoic acid in (1) ether solution, (2) cyclohexane solution containing 25% ether, (3) cyclohexane solution containing 7% ether, and (4) cyclohexane solution containing 5% ether.

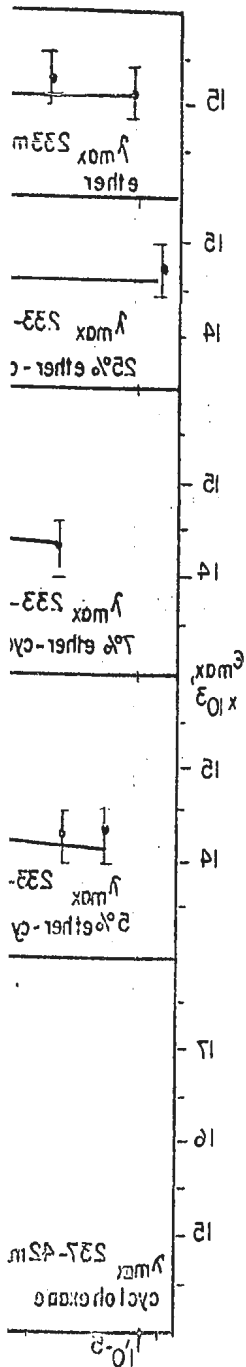
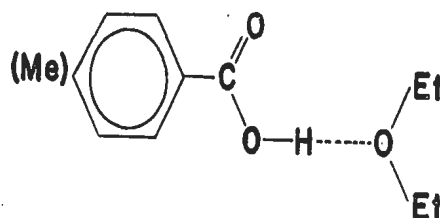
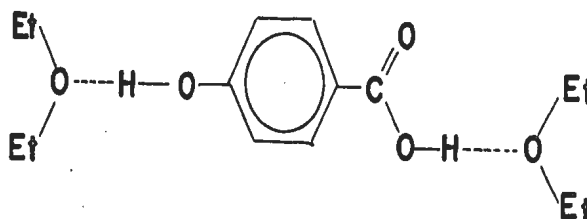


Fig. IX
 a
 b
 c
 d

any competing intermolecular bond between benzoic acid and ether molecules. That is, dimerization as shown by Structure II (p.15), would be the preferred process over formation of solute-solvent species of Structures III or IV.



Structure III



Structure IV

If this were not so, no concentration dependence would be observed since the large excess of ether, compared with benzoic acid (e.g. 5% ether as against 10^{-4} - 10^{-3} moles/litre of benzoic acid) would preclude any possibility of the benzoic acid dimerizing to an appreciable extent. However dimerization does occur, as evidenced by the observed concentration dependence, and hence the initial conclusion follows.

On the basis of the general results it seems reasonable to assume that the absence of any concentration dependence in solutions of pure ether and in solutions of large ether concentrations, corresponds to absorption by a single species; and further, from the theoretical curve of Figure VI, it is evident that benzoic acid does exist primarily not

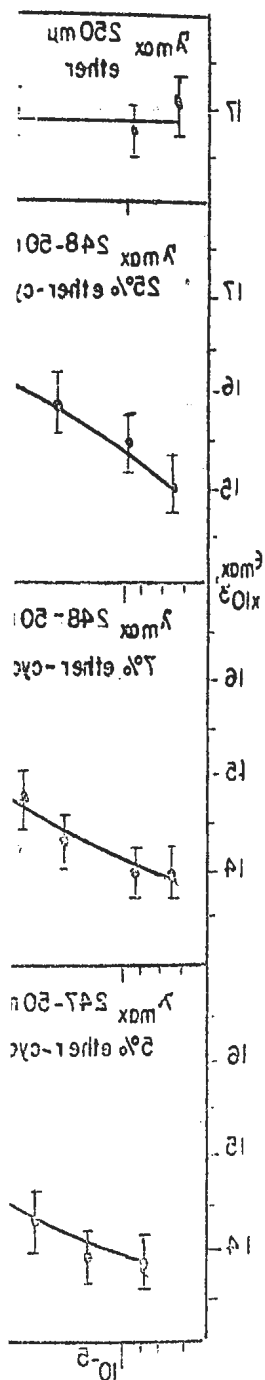


Fig. 1. The concentration dependence of the various parameters.

in the dimeric form below the critical concentration of 8×10^{-4} moles/litre; and thus absorption in solutions of lower concentration can hardly be ascribed to dimer absorption, thus suggesting that the single species absorbing is a monomeric one. This conclusion, however, does not negate that of the previous paragraph, for although the benzoic acid dimeric bond is stronger than the benzoic acid-ether linkage, the latter does exist and will become more important with increasing percentages of ether.

This may be explained on the basis of the assumption that both the intermolecular bonds are not static hydrogen-bonded complexes⁸. This assumption is supported by evidence from nuclear magnetic resonance spectra. While infrared results often yield vibrational bands for both the hydrogen-bonded and non-hydrogen-bonded states (cf. p. 4 and infrared data in Section IV), this is not the case with nuclear magnetic resonance measurements since the latter require that the half-life of each state be larger than the reciprocal of the shift, in frequency units, caused by the hydrogen bond. Since the latter may be of the order of ca. 10^{-2} to 10^{-3} seconds, and further since only one strong signal is usually found, the life of the hydrogen bond in question must be considerably shorter than this value (63). Thus the bond will be undergoing this breaking and reforming

8 The application of this hypothesis to the conditions of the experiment receives indirect support from the work of Coggeshall and Lang (17), who showed the absence of spectral changes for solutions of phenol and aniline at different temperatures (although the temperatures employed were sufficient to destroy any hydrogen bonded complexes) and thus concluded that for these compounds the spectral changes observed on changing from a polar to a non-polar solvent do not depend on static hydrogen bonded complexes.

process, and thus the species which will predominate, and hence which will give rise to the observed spectral effects, will be determined by two factors - (a) the relative strengths of the two bonds, and (b) the probability that the appropriate molecules will be sufficiently proximate to permit bond formation. Applying these conditions to the present system shows that (a) favours the formation of the benzoic acid dimeric bond, since this bond is formed preferentially (cf. p. 28), while (b) will favour the ether-benzoic acid bond in any solution where the ether concentration appreciably exceeds that of the benzoic acid. At low ether concentrations the former of these opposing forces apparently predominates, i.e., the dimer formation is the more important process and a concentration dependence is observed. At high ether concentrations the benzoic acid molecules become so completely surrounded by the solvent ether molecules that factor (b) predominates and thus the benzoic acid-ether bond will become more important and the spectral curve becomes invariable with changing concentration. Thus as the percentage of ether present is increased, the benzoic acid dimer-monomer equilibrium contributes less and less to the observed spectra and the absorption by species of type III (p.28), in the case of benzoic acid and *p*-toluic acid, becomes the dominant influence and causes a shift to shorter wavelengths and decreased intensities, and the disappearance of the concentration dependence. Similarly for *p*-hydroxybenzoic acid predominance of structures of type IV (p.28) on increasing the % ether in solution, causes a shift to longer wavelengths, higher intensities, and a similar obliteration of the dependence on concentration.

It follows from these arguments that the stronger the intermolecular dimeric bond, the greater will be the concentration of ether necessary to cause the disappearance of the concentration dependence. This is so since a greater ether concentration in the cyclohexane solution will be required to overcome the preferential dimeric bond formation. This phenomenon is, in fact, observed (see below) thus offering support for the discussion above.

For example the stronger dimeric hydrogen bond postulated for p-hydroxybenzoic acid (see p.40) requires more than 25% ether concentration to obscure the concentration dependence (cf. Figure IX) as against the 25% ether which produces the same effect in the spectral curve of the reference acid, benzoic (cf. Figure VII). Similar but even more pronounced behaviour is exhibited by the weaker dimeric bond postulated for salicylic acid (see p.55) whose concentration dependence is almost completely obscured in cyclohexane solutions containing 5% of ether. This is illustrated in Figure X, which gives the actual concentration dependence for this acid in cyclohexane solution and in cyclohexane solution containing 5% of ether.

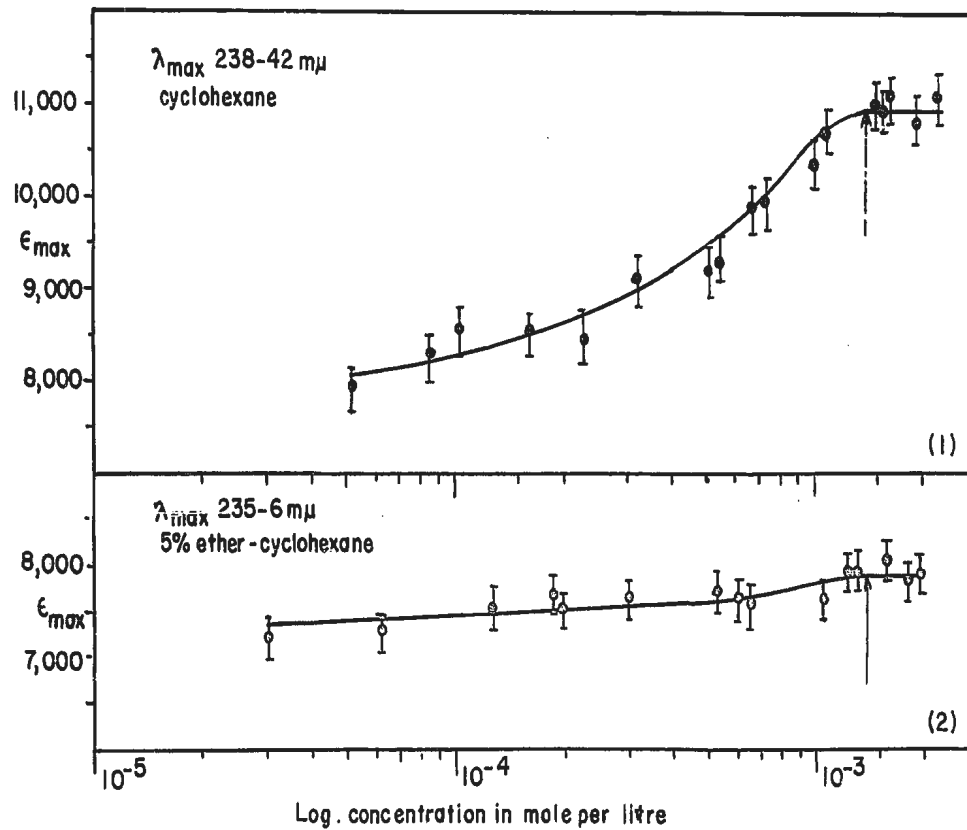


Fig. X The variation of ϵ_{\max} on changing the concentration of acid for salicylic acid in (1) cyclohexane, and (2) cyclohexane solution containing 5% ether.

IV. THE STRENGTH OF THE DIMERIC HYDROGEN

BOND IN SUBSTITUTED BENZOIC ACIDS.

A. INTRODUCTION

The initial investigations described in the previous sections may be summarized at this point as follows:

(a) the spectra of the benzoic acids exhibit a concentration dependence and a critical concentration above which the ϵ_{\max} values become essentially independent of solute concentration.

(b) the critical concentration may be taken as a measure of the relative strengths of the dimeric hydrogen bond in these acids, assuming that the lower the value of this concentration, the stronger will be the intermolecular hydrogen bond.

(c) the position of the critical concentration, and hence conclusions as to the strengths of the bond, are unaffected by the addition of small amounts of ether to the cyclohexane solution.

The critical concentrations for the acids studied in this investigation are listed in Table II and the actual spectral curves are presented in subsequent figures. It is proposed to deal separately with the acids in three divisions, (1) the p-substituted, (2) the m-substituted acids, and (3) the o-substituted acids.

Before detailed consideration is given to the individual cases, a discussion of the general arguments involved is desirable. Considering first the case of the unsubstituted benzoic acid, it is important to note that

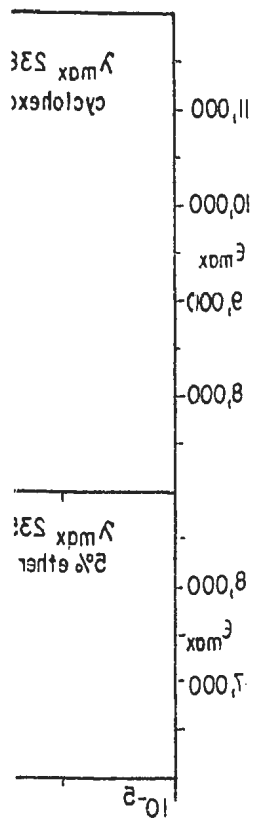


Fig. X
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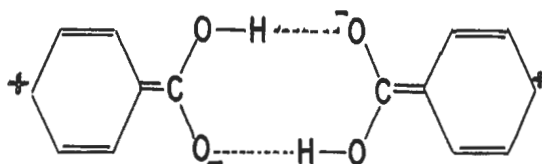
Critical Concentrations for Benzoic Acids
from the Concentration Dependence of their
Ultraviolet Absorption Spectra.

Substituent	Critical Concentration in moles/litre x 10 ⁴	Solvents ^(a)
none	8.0	A,B,C,D,E
p-methyl-	4.7	A,B,C,D,E
p-hydroxy-	0.40	B,C,D,E
p-methoxy-	0.34	B
p-fluoro-	(b)	A
m-methyl-	1.6	A
m-methoxy-	1.4	B
m-hydroxy-	0.12	B
m-fluoro-	(b)	A
o-methyl-	11.0	A
o-hydroxy-	14.0	A,B
o-methoxy-	none	A,B,
o-fluoro-	(b)	A

(a) A, cyclohexane; B, 5% ether-cyclohexane; C, 7% ether-cyclohexane;
D, 25% ether-cyclohexane; E, ether.

(b) Beyond investigated concentration range.

the benzoic acid dimer is reported to be stronger, i.e. more stable, than the dimers of aliphatic acids, such as acetic (1,71). Thus the replacement of a methyl or ethyl group by a phenyl group has the effect of stabilizing the dimer. This increased stabilization may be explained on the basis of a mesomeric interaction. That is, the mesomeric effect of the phenyl group would be expected to increase the electronic charge on the carbonyl oxygen and hence stabilize the dimer relative to the monomer. This mesomeric contribution may be represented by resonance forms of type V.



Structure V

Thus, if the dimeric hydrogen bond is visualized as being stabilized by extended resonance structures in this manner, substituents which are known to have the effect of strengthening such resonance forms, i.e. exhibiting a positive mesomeric effect, should cause an increase in the dimer strength through increased stabilization as visualized by resonance forms of type V. On the other hand, substitution of groups known to have a negative mesomeric effect, should lead to a destabilization of the resonance form and hence to a decrease in the strength of the dimeric hydrogen bond.

Further, some substituents, particularly in the o-position, which are known to have the effect of

inhibiting conjugation because of steric interactions, by destroying the coplanarity of the configuration, would also be expected to reduce the dimer strength.

Finally, since the electronic absorption spectra are determined primarily by mesomeric and steric effects, dimer stabilization or destabilization by various substituent groups, as evidenced by the values of the critical concentrations relative to that of benzoic acid, should be related to the magnitude and direction of these effects.

Thus information regarding the relative strengths of the dimeric hydrogen bonds in the acids investigated, as deduced from the observed spectral changes, will be interpreted on the basis of these assumptions.

B. THE PARASUBSTITUTED BENZOIC ACIDS

The observed spectral changes on altering the solute concentration for benzoic acid, anisic acid, and *p*-fluorobenzoic acid are shown in Figure XI. Similar data for *p*-toluic acid and *p*-hydroxybenzoic acid have been presented in Figures VIII and IX. The critical concentrations have been listed in Table II. The data for these acids from the present investigation and relevant experimental data from other sources are presented in Table III.

Considering first the *p*-methylsubstituted acid, *p*-toluic acid, it is to be expected that the known positive mesomeric effect of the methyl group would strengthen the dimer relative to the unsubstituted acid, by stabilizing resonance forms of type V. The occurrence of the critical concentration at a lower value than for the reference acid indicates that this strengthening of the bond does occur.

This observation may be related to the other data cited in Table III, which confirms the postulated stronger dimeric bond in *p*-toluic acid, since such a relation is indicated by (a) the greater standard heat of dissociation for *p*-toluic acid (b) the slight acid weakening disturbance associated with the *p*-methyl substituent, and (c) the smaller value of the dissociation constant for the substituted acid as compared with benzoic acid. Stabilization of resonance forms of type V, by the methyl group, in the *p*-position, may be visualized as being related to the observed bathochromic wavelength displacement and the increase in the intensity of maximum absorption, which indicate a

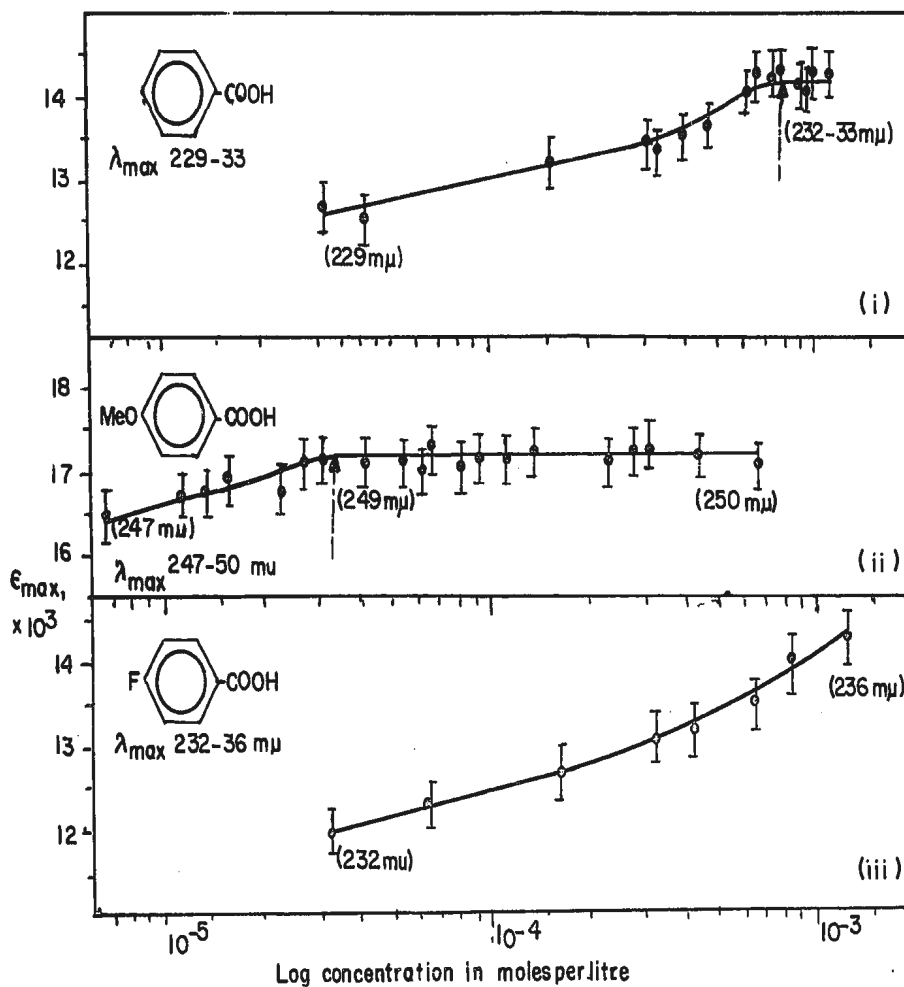


Fig. XI The variation of ϵ_{\max} on changing the concentration for (i) benzoic acid in cyclohexane solution, (ii) anisic acid in cyclohexane solution containing 5% ether, and (iii) p-fluorobenzoic acid in cyclohexane solution.

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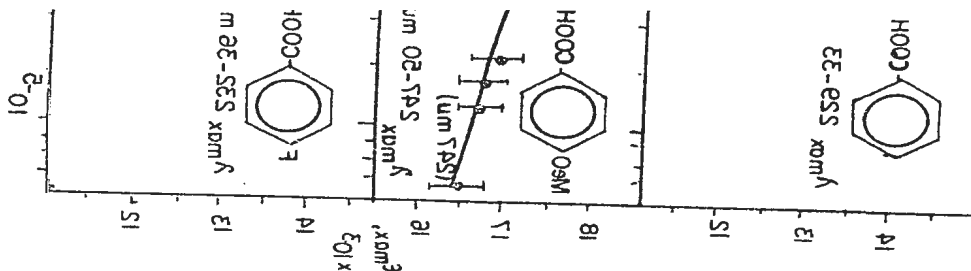


TABLE III

Data for the Parasubstituted Benzoic Acids

Substituent	Critical ^(a) conc. in moles/l. $\times 10^4$	λ_{max} in μ in (a)		ΔH_2° in Kcals. per mole	$K_a \times 10^5$ in water at 25°C.	(molar) K_{21} $\times 10^4$ in C_6H_6 at 30°
		cyclohexane	5% ether- cyclohexane			
p-fluoro	(above range)	232-36 ($\epsilon_D > 14,200$) ^(b)	--	--	7.22 ^(e)	0.78 ^(f)
none	8.0	229-33 ($\epsilon_D = 14,200$)	225-26 ($\epsilon_D = 12,200$)	8.2 ^(c)	6.27 ^(e)	5.3 ^(h) 2.18 ^(g)
p-methyl	4.7	237-42 ($\epsilon_D = 17,000$)	--	8.7 ^(c)	4.24 ^(e)	0.531 ^(g)
p-hydroxy-	0.40	--	247-50 ($\epsilon_D = 14,900$)	--	2.9 ^(e)	--
p-methoxy	0.34	--	247-50 ($\epsilon_D = 17,200$)	8.7 ^(c) 10.0 ^(d)	3.38 ^(e)	2.28 ^(g)

(a) Data from present investigation; (b) ϵ_D is the ϵ value above the critical concentration;
 (c) in benzene at 25° C. (1); (d) in benzene at 40° C. (23); (e) (1,40); (f) by electric
 polarization (51); (g) by ebulliscope measurements (2); (h) by electric polarization (62).

a lowering of the energy of the excited state, which is the expected effect of a group with a positive mesomeric effect.

The data for the *p*-substituted acids next indicate that both the *p*-hydroxy substituent (cf. Figure IX) and the *p*-methoxy substituent (cf. Figure XI) have the effect of lowering the value of the critical concentration, that is, of strengthening the dimeric bond. This stronger hydrogen bond would be expected from valence bond considerations and from the related experimental data given in Table III. Both substituents are known to decrease the acid strength (although contrary to the spectral data, the values indicate that in this case *p*-hydroxy- forms a stronger dimer than does *p*-methoxybenzoic acid), and to cause appreciable bathochromic wavelength shifts compared with benzoic acid. Further, a greater value of the standard heat of dissociation is reported for anisic acid. There is, however, some disagreement among the values for the dissociation constant. The data from ebullioscopic measurements indicate that in benzene solution anisic acid dissociated more than benzoic acid. On the other hand, electric polarization data suggest the opposite order. This lack of quantitative agreement between the various experimental data, both among themselves and with the data from the present investigation, requires discussion at this stage.

Many of the dissociation constants reported, cf. for example (2,60), refer to water-saturated benzene solutions and since the dimer-monomer equilibrium may be appreciably affected by the presence of water (49), the method used in the present investigation would be expected to yield results

which are not in quantitative agreement and the present results may be a closer approximation to the actual properties of the acids because these studies were carried out in dilute solution with usually only cyclohexane or 5% ether in cyclohexane present.

On the basis of the assumption that the observed spectral changes are influenced primarily by mesomeric and steric effects, and since it is in fact the excited state of the molecules which is being examined here, quantitative agreement between the present and other data would not be expected because it may be foreseen that the mesomeric effect will not contribute in the same way to the ground state and to the excited state. Further the inductive effect may be an important consideration in the ground state but may be expected to be less of a contributing factor in the excited state - determined as it is by interactions which can be illustrated as resonance structures. Thus mesomeric and inductive effects may be assumed to affect the acid dissociation process in a different way than they affect the dimer-monomer equilibrium as determined by electronic absorption spectra, since the latter are assumed to be determined predominantly by mesomeric effects, while the former will be more influenced by inductive effects and other interactions. Thus while qualitative agreement would be expected among data determined by analogous electronic interactions, quantitative agreement would neither be expected nor is it,

in fact, obtained.⁹

Returning to the main theme, the data next show that a p-fluoro substituent gives rise to a weakening of the dimeric hydrogen bond, as evidenced by the absence of any sharp break in the curve of solute concentration vs. maximal absorption, i.e. a critical concentration, within the range. The continual increase in the ϵ_{\max} values throughout the investigated range of concentrations, as shown in Figure XI, suggests that the critical concentration is greater than that of benzoic acid, and hence, that the dimer bond is weaker. This observation is again in agreement with the relevant data cited in Table III, in that these data indicate an increased acid strength. However, contrary to the results of this work, the dissociation constants determined by electric polarization indicate that the substituted acid dissociates less than benzoic. This opposite trend is also suggested by the observed bathochromic wavelength displacement. A possible explanation for this shift in the ultraviolet region (25) is that the p-fluoro substituent raises the energy of the ground state but lowers the energy of the excited state.

In order to investigate this problem further, the infrared carbonyl bands of benzoic acid and p-fluorobenzoic acid were determined at the same concentration in carbon tetrachloride solution¹⁰. The observed spectra are shown in

Figure XII.

9 Better agreement might be expected between the critical concentrations and wavelength shifts - both being determined primarily by resonance interactions. However, the data merely suggest that mesomeric effects influence (a) ultraviolet light absorption, (b) dimer-monomer equilibrium and (c) acid dissociation in the order (a) > (b) > (c)

10 Infrared data were determined in this solvent because of the insolubility of some acids in cyclohexane. Acids soluble in both recorded almost identical spectra in both solvents.

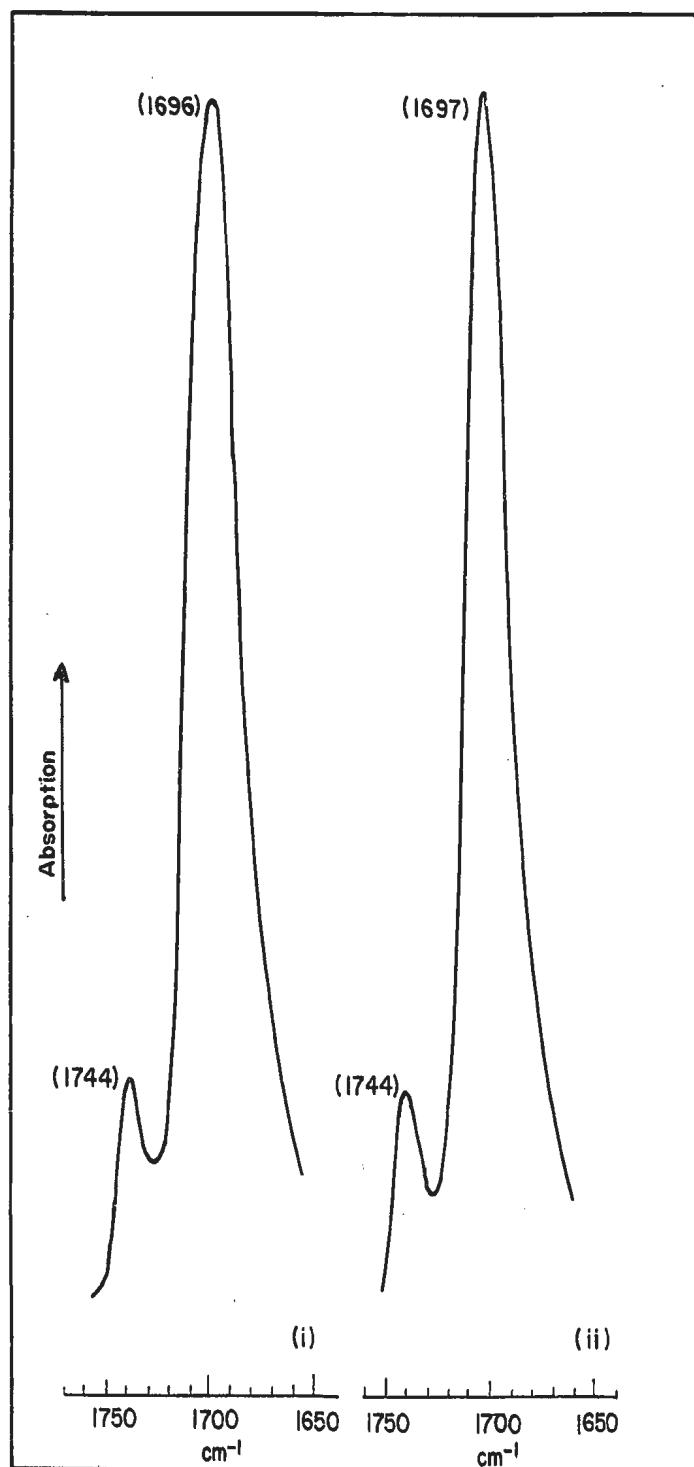


Fig. XII The infrared carbonyl stretching bands in carbon tetrachloride solution at a concentration of ca. 3.5×10^{-2} moles/litre of (i) benzoic acid (ii) p-fluorobenzoic acid. Values of ν_{max} are given in brackets.

The figure shows that the infrared carbonyl absorption of benzoic acid consists almost entirely of the dimer species. The assignment of the intense band at 1696 cm^{-1} to dimer absorption is made on the basis of the assumption that the vibrational restriction imposed by involvement of the carbonyl group in an intermolecular hydrogen bond will result in absorption at lower frequencies as compared with the absorption of the carbonyl group in the non-hydrogen-bonded monomer. A very similar band is obtained for *p*-fluorobenzoic acid. The apparent presence of small amounts of monomer at this concentration, 3.5×10^{-2} moles/litre, is not surprising since for benzoic acid the theoretical curve of Figure VI would indicate ca. 5% of the total acid concentration in the monomer form at this concentration at room temperature, and at 30° C . (the temperature at which the infrared data were obtained) a slightly greater percentage of monomer would be expected.

Because of the errors involved in estimating the intensities of the two bands, any calculations from the observed spectra to determine the relative proportions of monomer and dimer in the two acids, must, in this case, (where the intensities of the carbonyl bands of the two compounds are similar) be assumed to be inconclusive with regard to the question as to which of the two acids - benzoic or *p*-fluorobenzoic - forms the stronger dimeric hydrogen bond.

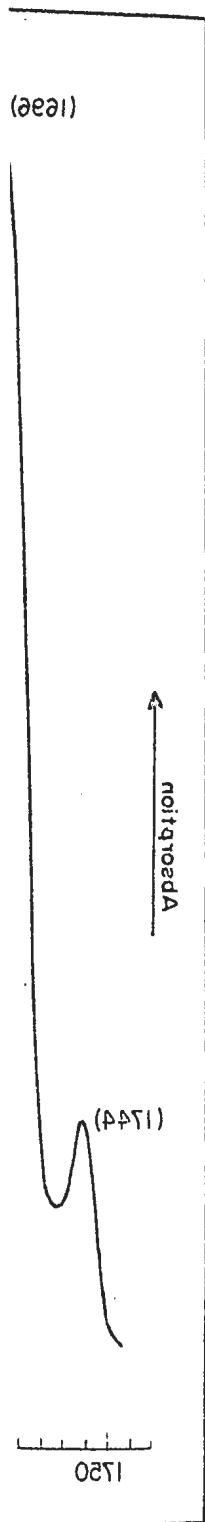


Fig. XII
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C. THE METASUBSTITUTED BENZOIC ACIDS

The critical concentrations of the m-substituted benzoic acids studied in this investigation have been given in Table II, and the actual concentration dependences observed for m-toluic acid, m-hydroxybenzoic acid, m-methoxybenzoic acid, m-fluorobenzoic acid, and for the reference acid are given in Figure XIII. The infrared carbonyl bands for these acids (with the exception of m-hydroxybenzoic acid which was insufficiently soluble) are presented in Figure XIV. Although as above, the relative intensities of the bands are again inconclusive, the band shifts, to be discussed presently, are significant. The data from this investigation and other relevant experimental data are summarized in Table IV.

Applying the general hypothesis that the lower the value of the critical concentration, the stronger is the dimeric hydrogen bond, the data show that the substitution of the m-methyl group gives rise to a strengthening of the dimer. This result is consistent with the data given in Table IV. A stronger dimeric bond for m-toluic acid relative to benzoic acid, is indicated by the greater value of the standard heat of dissociation, the decreased acid strength, the decreased value of the dissociation constant, the bathochromic wavelength displacement in the ultraviolet, and the shift to lower frequencies of both the dimer and monomer bands in the infrared.

On the other hand, m-fluorobenzoic acid whose critical concentration is apparently above the investigated range, may therefore be assumed to have a weaker

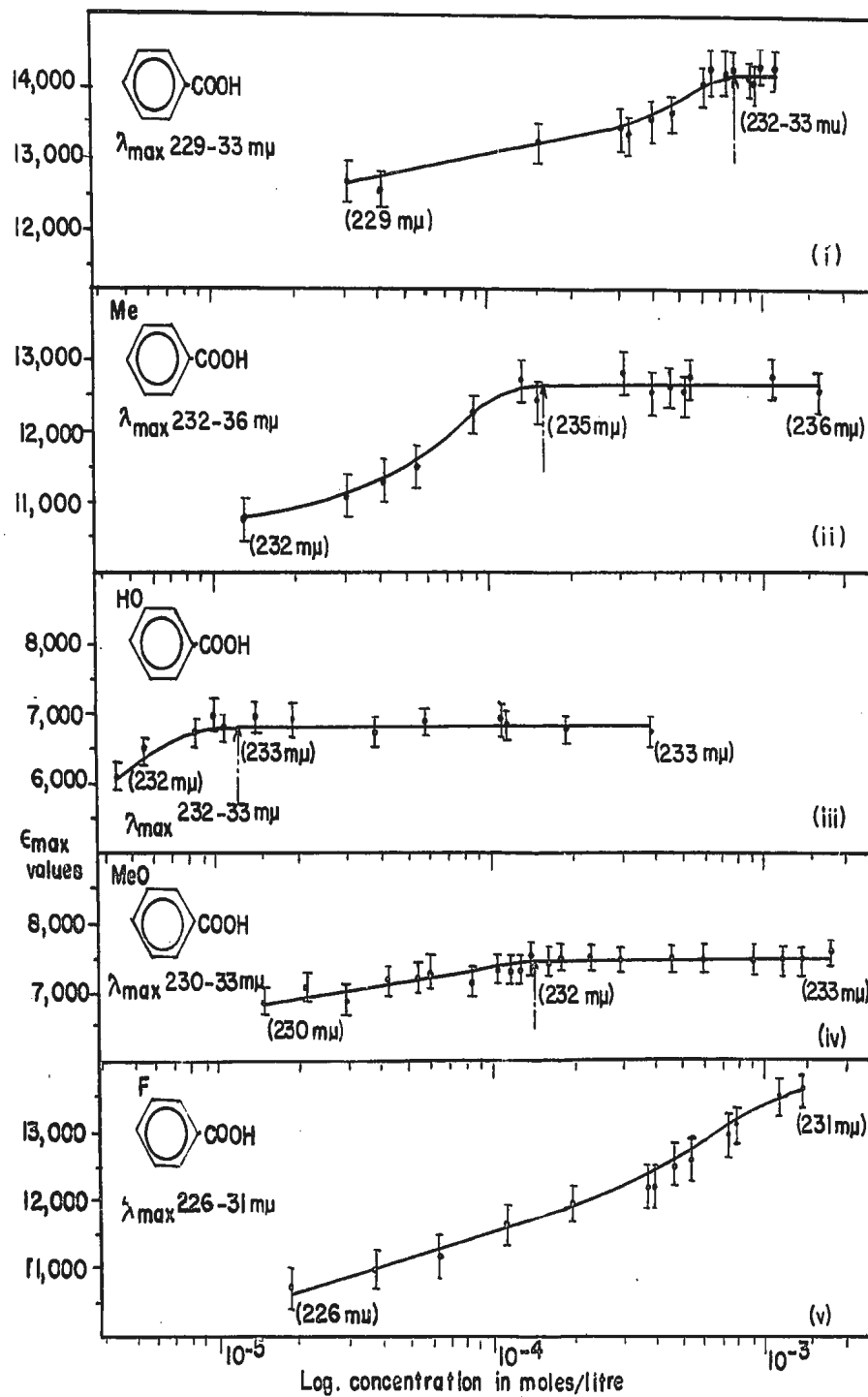


Fig. XIII The variation of ϵ_{\max} on changing the solute concentration of (i) benzoic acid in cyclohexane solution, (ii) *m*-toluic acid in cyclohexane solution, (iii) *m*-hydroxybenzoic acid in cyclohexane containing 5% ether, (iv) *m*-methoxybenzoic acid in cyclohexane solution containing 5% ether, and (v) *m*-fluorobenzoic acid in cyclohexane solution.

m-fluorobenz. ν_{\max} 1696
 m-toluic ν_{\max} 1694
 m-methoxybenz. ν_{\max} 1695
 m-fluorobenz. ν_{\max} 1701

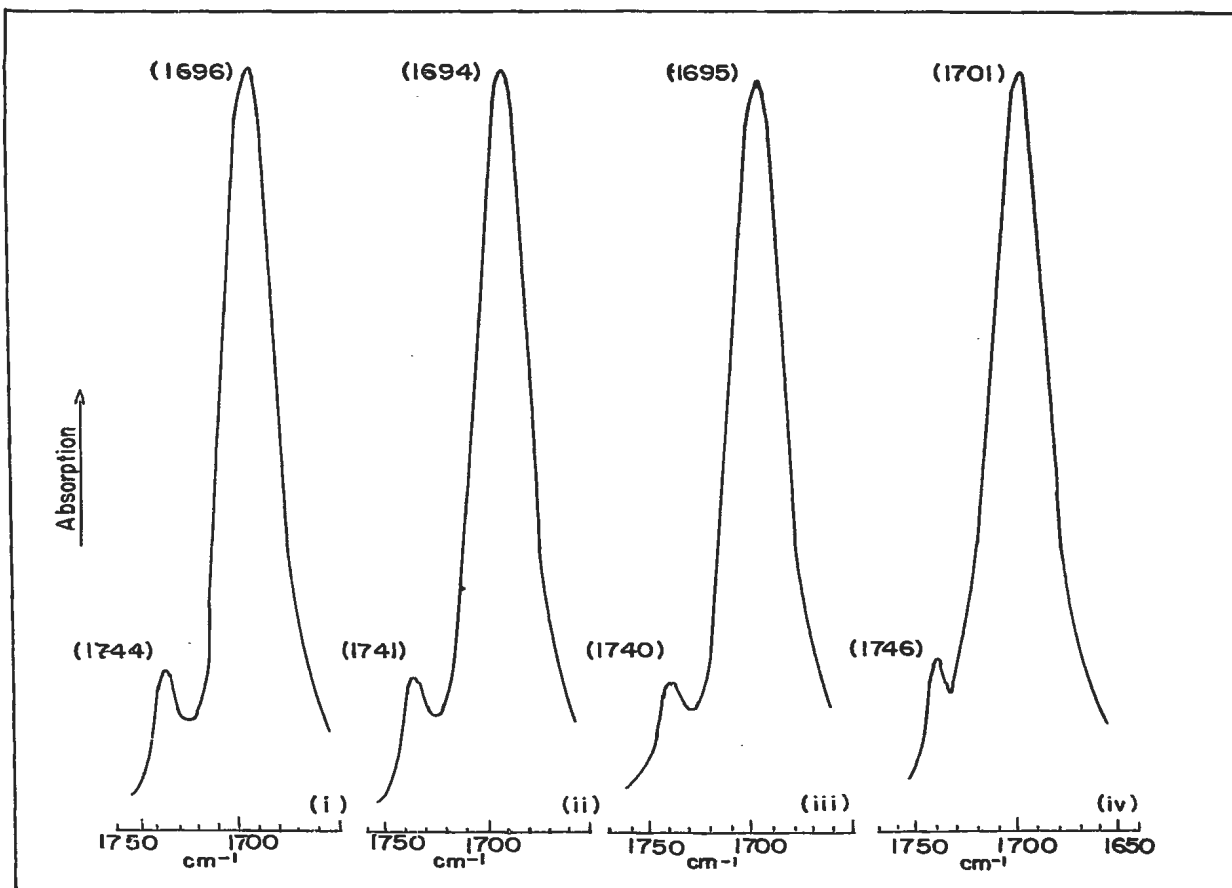


Fig. XIV. The infrared carbonyl stretching bands in CCl_4 solution at a concentration of ca. $3.5 \times 10^{-2} \text{ M}$ of (i) Benzoic, (ii) m-toluic, (iii) m-methoxybenzoic, and (iv) m-fluorobenzoic acid. Values of ν_{\max} are given in brackets.

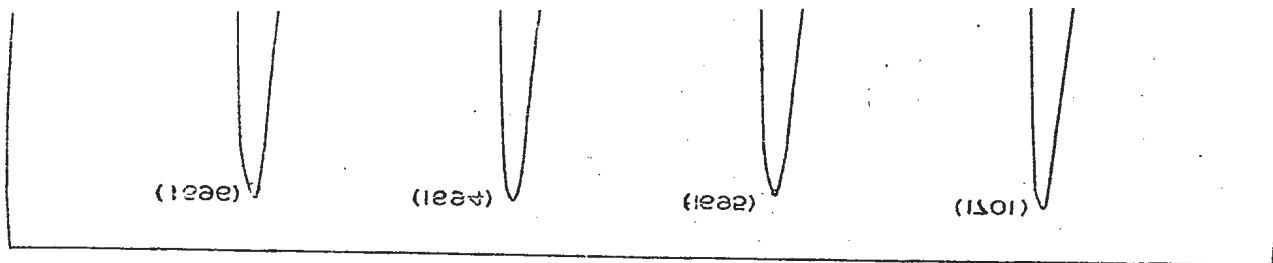


TABLE IV

Data for the Metasubstituted Benzoic Acids

Substituent	Critical ^(a) conc. in moles/l. $\times 10^4$	λ_{\max} in μ in (a)		ν_{\max} in cm^{-1} ^(c)		ΔH_2° in Kcals. per mole	$K_a \times 10^5$ in H_2O at 25°C .	(molar) K_{21} $\times 10^4$ in C_6H_6 at 30°
		cyclohexane	5% ether- cyclohexane	Dimer	Monomer			
<u>m</u> -fluoro-	(above range)	226-31 ($\epsilon_D > 13,000$) ^(b)	--	1701	1746	--	13.6 ^(f)	0.56 ^(g)
none	8.0	229-33 ($\epsilon_D = 14,200$)	225-26 ($\epsilon_D = 12,200$)	1696	1744	8.2 ^(e)	6.27 ^(f)	2.18 ^(h)
<u>m</u> -methyl -	1.6	232-36 ($\epsilon_D = 12,600$)	--	1694	1741	9.4 ^(e)	5.35 ^(f)	2.00 ^(g)
<u>m</u> -methoxy-	1.4	--	230-32 ($\epsilon_D = 7,450$)	1695	1740	--	8.17 ^(f)	--
<u>m</u> -hydroxy-	0.12	--	232-33 ($\epsilon_D = 6,825$)	(d)	(d)	--	8.3 ^(f)	--

(a) Ultraviolet data from present investigation; (b) ϵ_D is the ϵ value above the critical concentration; (c) Infrared data from present investigation - ν_{\max} of carbonyl bands in CCl_4 at 30°C . at a concentration of ca. 3.5×10^{-2} moles/litre; (d) insufficiently soluble; (e) in benzene at 25°C . (1); (f) (1,40); (g) by electric polarization (51); (h) by ebulliscope measurements (2).

dimeric bond. Again, the acid dissociation constants, the slight hypsochromic wavelength shift in the ultraviolet, and the frequency displacement in the infrared, support the proposed weaker dimeric hydrogen bond for m-fluorobenzoic acid. However, the electric polarization data for the dissociation constants are not in agreement with the results of the present investigation, (see p. 40 et seq.).

The m-hydroxy and m-methoxy substituted acids are also of interest since here, perhaps surprisingly, the data indicate that both substituents cause an increase in the strength of the dimer. This observation, interpreted in the light of the general assumptions, suggests that interactions, as represented by resonance forms of type V, p. 35, are favoured in the excited state by the substitution of these groups in the m-position. However, the ordinary inductive effect of these m-substituents (due to the greater electronegativity of the oxygen atom) would be expected to cause a withdrawal of electrons from the carbonyl group and thus weaken the dimeric bond. The proportion of ionized acid would similarly be increased and this accounts for the increased acidity as noted in Table IV. Further, although it has been proposed previously that inductive effects will be a minor influence in the excited state, the probability that the mesomeric effect will operate from the m-position is certainly small, and consequently inductive effects would be expected to predominate, notwithstanding the fact that their contribution will be small. Thus it appears likely that the "anomalous" increase in dimer formation in the case of

these two acids relative to benzoic acid, may be due to stabilization of resonance forms of type V, in the excited state, by substitution of a hydroxy or methoxy group in the m-position by an electromeric interaction, which is more important as an influence on the dimer-monomer equilibrium, as determined by electronic absorption spectra, than the normal -I effect, and which will be referred to as an I_e effect.

The observed bathochromic wavelength displacement in the ultraviolet region for the two substituents, and the shift to lower frequencies in the infrared for m-methoxybenzoic acid, supports the view that these substituents stabilize resonance structures¹¹.

The I_e effects, proposed as a cause of strengthening of the dimer by the m-hydroxy and m-methoxy substituents, may be deduced either from the value of the critical concentrations or from the wavelength displacements with reference to the unsubstituted acid. The order, deduced in this manner from the data summarized in Table IV, from both the critical concentrations and the wavelength shifts, is for the + I_e effects - OH > OMe > CH₃ > H > F. Similarly the wavelength displacements reported for other m-substituents (28,30), indicate an order of F > Cl > Br > I > H for the - I_e effects.

¹¹ Further experimental evidence for this effect is provided by the reported bathochromic wavelength displacement due to a m-hydroxy substituent in compounds like benzoic acid (30).

D. THE ORTHOSUBSTITUTED BENZOIC ACIDS

The critical concentrations of the o-substituted benzoic acids investigated are listed in Table II, and the experimental curves of the concentration vs. the maximal absorption in the ultraviolet region for benzoic acid, o-toluic acid, o-methoxybenzoic acid, and o-fluorobenzoic acid are given in Figure XV. This data for salicylic acid has been given previously in Figure X. The infrared carbonyl bands for benzoic acid, o-toluic acid, salicylic acid, and o-fluorobenzoic acid are presented in Figure XVI and the data for these acids have been summarized along with other relevant data in Table V. o-methoxybenzoic acid will be dealt with separately in Section V.

The data show that o-toluic acid affords a weaker dimeric hydrogen bond than that of benzoic acid. This is in agreement with the reported increase of the acid strength and the increased dissociation constant by o-toluic acid. However, the standard heat of dissociation for the substituted acid is reported to be slightly higher than for benzoic.

This effect of dimer destabilization is ascribed to steric interactions (40) which are indicated also by the considerably decreased maximal absorption coefficient values of o-toluic acid where monomer absorption is predominant (i.e., at ca. 10^{-4} moles/litre) as compared with the value obtained for benzoic acid solutions of similar concentration (cf. Figure XV). These steric interactions which may be visualized by the destabilization of resonance form of

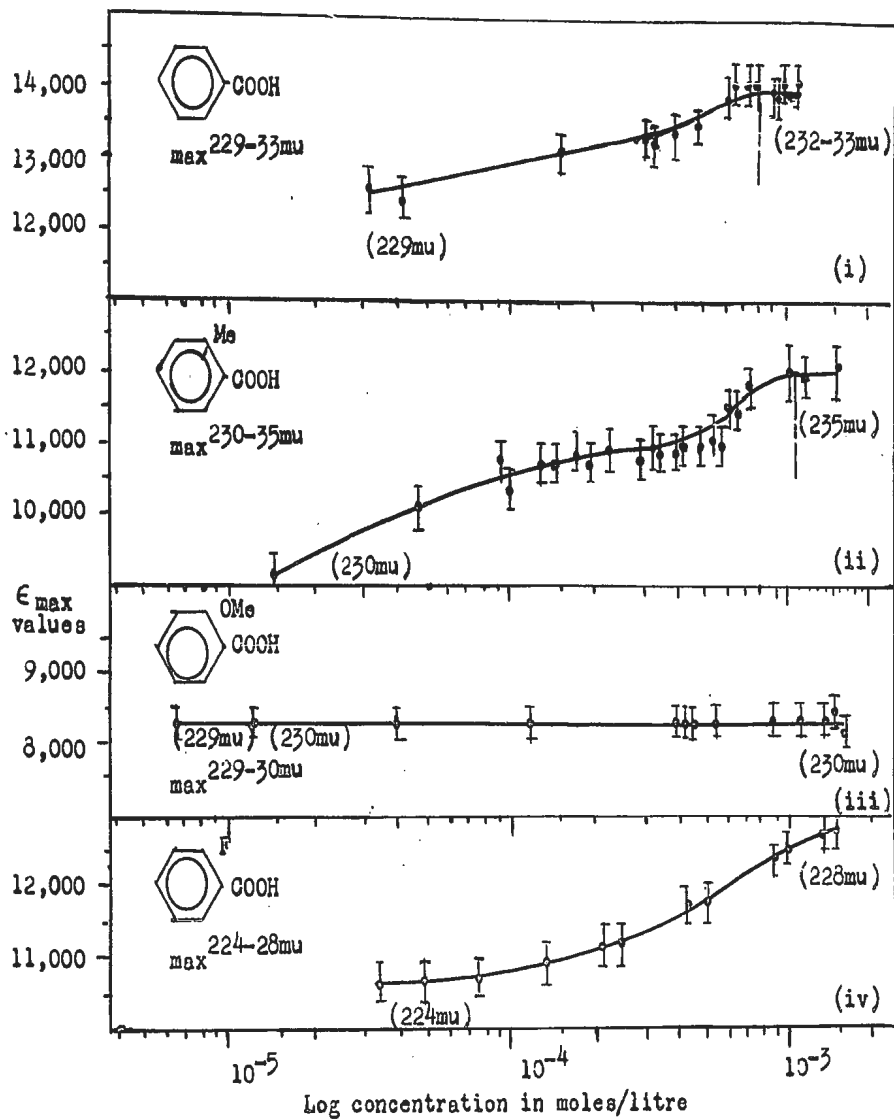


Fig. XV. The variation of ϵ_{\max} on changing the solute concentration in cyclohexane solution for (i) benzoic acid, (ii) o-toluic acid, (iii) o-methoxybenzoic acid, and (iv) o-fluorobenzoic acid.

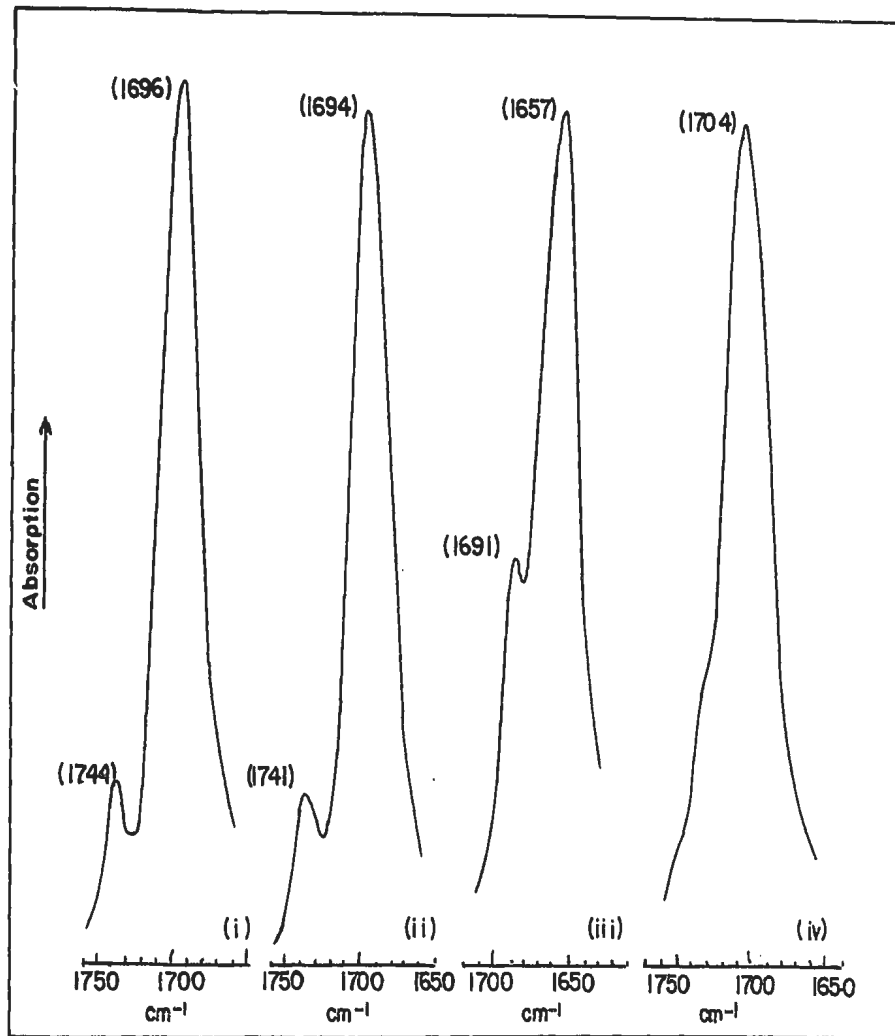
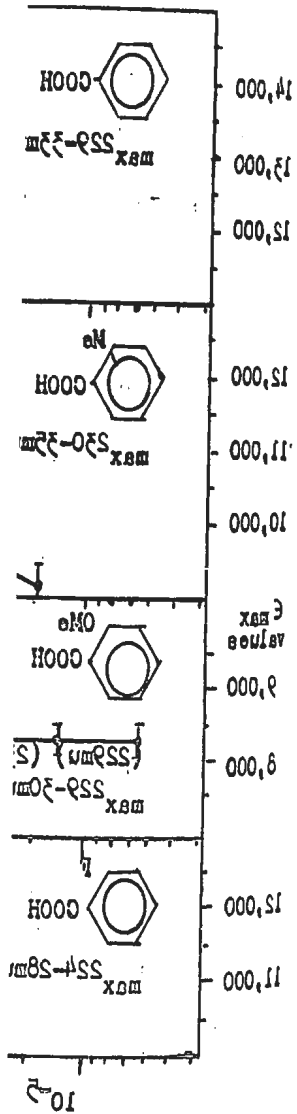


Fig. XVI The infrared carbonyl stretching bands in carbon tetrachloride solution at a concentration of ca. 3.5×10^{-2} moles/litre of (i) benzoic acid, (ii) *o*-toluic acid, (iii) salicylic acid, and (iv) *o*-fluorobenzoic acid. Values of ν_{\max} are given in brackets.

Fig. XV. The infrared spectra of benzoic acid, *o*-toluic acid, salicylic acid, and *o*-fluorobenzoic acid.

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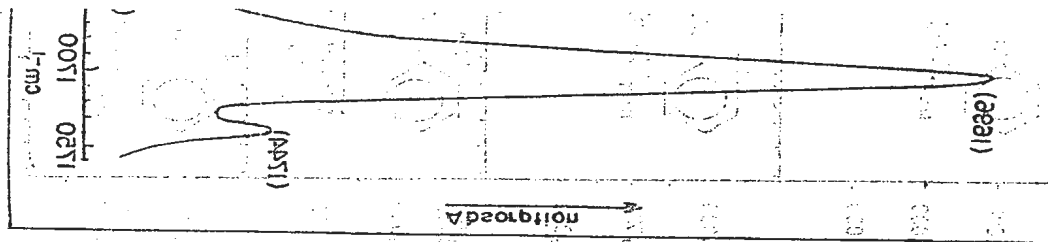


TABLE V

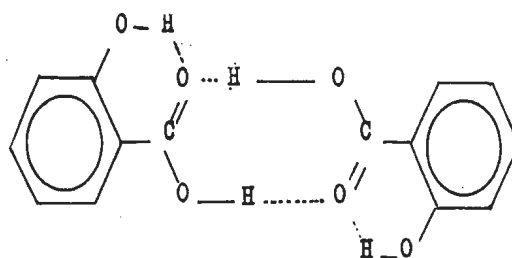
Data for the Orthosubstituted Benzoic Acids.

Substituent	Critical (a) conc. in m/l x 10 ⁴	λ_{\max} in μ (a) in cyclohexane	ν_{\max} in cm^{-1} (c)		ΔH_2^0 in Kcals. per mole	$K_{\text{ain}} \times 10^5$ water at 25°C.	(molar) K_{21} $\times 10^4$ in C_6H_6
			Dimer	Monomer			
<u>o</u> -fluoro-	(above range)	224-28 ($\epsilon_D > 12,800$) (b)	1704	--	--	54.1 (e)	5.2 (f)
<u>o</u> -hydroxy-	14.0	238-42 ($\epsilon_D = 11,000$)	1657	1691	--	105 (e)	95 (g)
<u>o</u> -methyl-	11.0	230-35 ($\epsilon_D = 12,000$)	1694	1741	8.4 (d)	12.3 (e)	2.44 (f)
none	8.0	229-33 ($\epsilon_D = 14,200$)	1696	1744	8.2 (d)	6.27 (e)	5.3 (g) 2.18 (h)

(a) Ultraviolet data from present investigation; (b) ϵ_D is the ϵ value above the critical concentration; (c) Infrared data from present investigation - ν_{\max} of carbonyl bands in carbon tetrachloride at 30°C. at a concentration of ca. 3.5×10^{-2} moles/litre; (d) in benzene at 25°C (1); (e) (1,40); (f) by electric polarization at 30°C (51); (g) by distribution method at 40°C (23); (h) by ebullisopic measurements at 30°C (2)

type V by a partial destruction of the coplanarity of the carboxyl group with the benzene nucleus, account also, on the basis of the general assumptions and arguments, for the higher value of the critical concentration of o-toluic acid¹². The decreased frequencies in the infrared also support the proposed weaker dimeric hydrogen bond in this acid.

The weaker dimeric hydrogen bond exhibited by salicylic acid, as evidenced by the higher value of the critical concentration compared with benzoic acid, is ascribed to a weakening of the dimeric bond by competitive intra-molecular hydrogen bond formation of type VI, a structure which has previously been deduced from X-ray data (15).



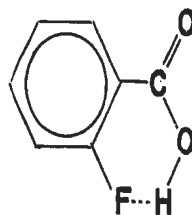
Structure VI

This hypothesis is sustained by the data cited in Table V, i.e., the bathochromic wavelength shift, the considerably higher acid dissociation constant for the substituted acid, and the displacement to lower frequencies of the infrared carbonyl bands in the case of salicylic acid, and the

12 This is not to suggest, however, that such steric factors prohibit the formation of dimers completely since even in the case of 2,4,6-tributylbenzoic acid, at a concentration of 2.3×10^{12} moles/litre, infrared data show an approximate proportion of 1:10 of monomer to dimer (16).

markedly reduced intensity ratio of dimer to monomer, as shown in Figure XVI.

For o-fluorobenzoic acid, the infrared carbonyl band shows the almost complete absence of monomer, and this suggests that the monomer is destabilized by the o-fluoro substituent, and therefore indicates that structures of type VII will not make significant contri-



Structure VII

butions to the observed spectra. At the same time, the ultraviolet data indicate, by apparent occurrence of the critical concentration above the investigated range, that the dimeric hydrogen bond is also weakened by the o-fluoro substituent. This in turn may be explained by assuming that the o-fluoro substituent raises the energy level of both the dimer and monomer, but that the monomer is destabilized more effectively. Qualitative support is again obtained for the weaker dimeric bond from the reported increase in acidity and dissociation noted in Table V, and from the hypsochromic wavelength displacement for the substituted acid which indicates repulsive interaction between the fluoro- and carboxyl- substituents.

V. THE UNIQUE BEHAVIOUR OF
o-METHOXYBENZOIC ACID

A plot of the maximal absorption against solute concentration for o-methoxybenzoic acid has been presented in Figure XV. On changing the solvent to 5% ether in cyclohexane, no appreciable change could be observed - the straight line relation was maintained, the mean ϵ_{\max} values remained invariable at ca. 8,400, and the wavelength of maximal absorption altered only slightly (229 μ in cyclohexane as against 229-230 μ in 5% ether in cyclohexane).

It is proposed that the spectral effect obtained is due to absorption by one species and that this species is a monomeric one. This hypothesis is supported by the following experimental data:

(a) Absence of concentration dependence: The fact that the intensities and wavelengths of the B-band maxima remain constant within experimental error throughout the concentration range examined suggests in the light of the general arguments proposed previously that only one species is making appreciable contributions to the observed absorption.

(b) Solvent effects: The lack of any alteration of the spectra on changing the solvent suggests that there is no appreciable monomer-dimer equilibrium within this concentration range. This explanation is proposed since systems involving a dimer-monomer equilibrium associated with an intermolecular hydrogen bond, undergo changes in both the wavelength and intensity of their electronic

spectra on alteration of the solvent; see for example (3,4,11,12,48,55,69). As a particular example to illustrate the different behaviour, the absorption characteristics of the B-band of acetophenone and benzoic acid are given in Table VI. The observed similarity for acetophen-

TABLE VI
B-Band Absorption of Acetophenone and Benzoic Acid

Solvent	Acetophenone			Benzoic Acid		
	λ_{\max} in μ	ϵ_{\max}	ref.	λ_{\max} in μ	ϵ_{\max}	ref.
Cyclohexane	237-38	12,500	(29)	229-33	12,200-14,200	*
Ether	239	12,600	(21)	225-26	12,200	*
Heptane	238	12,600	(42)	-	-	-
Dioxane	239	12,700	(32)	227-28	7,000-11,000	(32)
Ethanol	240	12,500	(29)	227	10,800-11,600	(29)
Water	244.5	12,100	(32)	223-27	8,700-9,400	(32)

* Present investigation

one in different solvents is striking, especially since the spectra were determined by different workers. The only significant change is a bathochromic displacement in aqueous medium. In the case of benzoic acid, this similarity is definitely absent, and thus, by analogy with these data, the fact that the intensity and wavelength of the B-band of *o*-methoxybenzoic acid undergo no change on solvent alteration, i.e., exhibit a behaviour similar to that of acetophenone, suggests that the observed spectral effect is due to absorption by one species, as is presumably the case with acetophenone¹³.

¹³ Infrared studies indicate absence of association in acetophenone (44).

(c) Dissociation Constants: The dissociation constant K_{21} of o-methoxybenzoic acid was determined in benzene at 40°C from distribution data by Davies and Griffiths (23), to be 435×10^{-3} as compared with the value of 3.2×10^{-3} for benzoic acid. These data indicate that within the investigated concentration range (i.e., 10^{-5} to 10^{-3} moles/litre), where it has been observed that a solution of benzoic acid becomes predominantly dimeric at 8×10^{-4} moles/litre, o-methoxybenzoic acid, which dissociates to a much larger extent, will hardly be present as a dimer species. It is thus reasonable to assume that the single species, proposed as the cause of the observed spectra, is a monomeric one.

(d) Infrared data: The infrared carbonyl band of o-methoxybenzoic acid is presented in Figure XVII, and indicates that at the same concentration at which the other acids were examined, 10^{-2} moles/litre, there is a definite relative predominance of the monomer over dimer, compared with the much smaller proportion of monomer in the other acids (cf. Figures XII, XIV, and XVI.). This observation conclusively suggests that solutions of much lower concentration, ca. 10^{-5} to 10^{-3} moles/litre of o-methoxybenzoic acid, would have even greater predominance of monomeric species.

Thus the hypothesis that the observed absence of any concentration dependence in the investigated range, for this acid, is due to absorption by one species - a monomeric form of o-methoxybenzoic acid - receives unqualified support

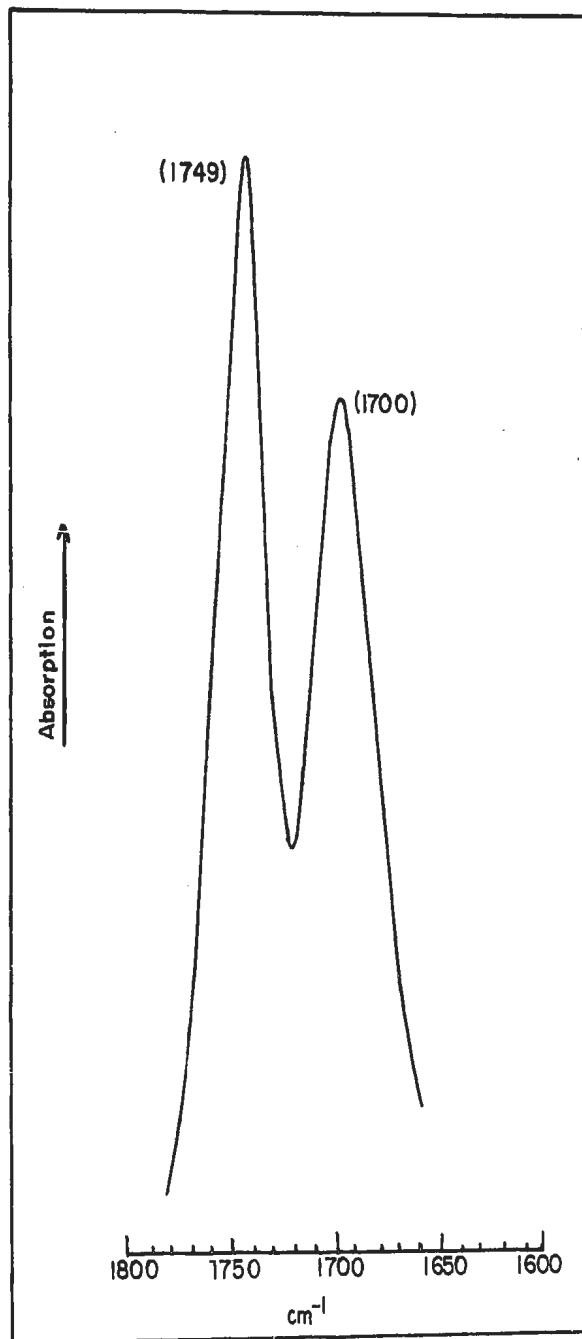
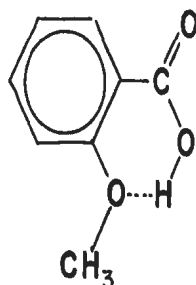


Fig. XVII The infrared carbonyl stretching bands in carbon tetrachloride solution at a concentration of ca. 3.5×10^{-2} moles/litre for o-methoxybenzoic acid. Values of ν_{\max} are given in brackets.

from the experimental evidence cited.

Since it has been thus shown that within the range of concentrations examined there is no appreciable dimer formation, the only alternative is that an intramolecular bond, as shown in Structure VIII is formed preferentially.



Structure VIII

It has been shown that the weaker dimeric bond displayed by salicylic acid is due to competitive intramolecular bond formation, shown as Structure VI, p. 55, The situation in the two acids is slightly different. For salicylic acid, the carboxyl hydrogen is still able to form an intermolecular bond, since it is not directly involved in the intramolecular bond (cf. Structure VI). On the other hand, the carboxyl hydrogen of o-methoxybenzoic acid is directly involved in the intramolecular bond formation as shown in VIII above. A slightly different argument applies, however, to the acid dissociation data. The intramolecular bond in salicylic acid may be assumed to decrease the electron density of the carboxyl oxygen atoms and in this way the acidity of the carboxyl group is increased; while for the o-methoxy-substituted acid, the only intramolecular hydrogen bonded form possible, tends to retain the active hydrogen by means of this hydrogen bond and in this way the acidity may not be increased to nearly the same extent as in salicylic acid.

This explains why these data - $K_a = 105 \times 10^5$ for salicylic acid and $K_a = 8.2 \times 10^5$ for o-methoxybenzoic acid (40) - indicate an opposite order for the relative strengths of the intermolecular hydrogen bonds.

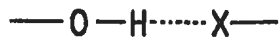
Contrary to the behaviour of o-methoxybenzoic acid, it has been shown that there is no such evidence that the o-fluorosubstituted acid forms a similar strong intramolecular bond (see p. 56) - that is, species of type VII are apparently not an important influence on the observed spectral effects in o-fluorobenzoic acid while for o-methoxybenzoic acid, species of type VIII are the predominant influence on the spectrum of the acid. Thus it is deduced that the intramolecular bond in o-methoxybenzoic acid, of the type O-H...O, is stronger than that occurring in o-fluorobenzoic acid, of the type O-H...F. This conclusion is of importance since it throws light on the nature of the hydrogen bond in these environments.

The exact nature of the hydrogen bond has long been the subject of considerable controversy and discussion, with a wide variety of evidence being presented to support the view that the hydrogen bond is due primarily to an electrostatic interaction, but widespread support has also been voiced for the opposing view that this bond is essentially a covalent one - see for example (14,18,19,57,66).

In the present examples the predominance of electrostatic influences would suggest that the O-H...F bond should be stronger, because of the greater electronegativity of the fluorine atom, than the O-H...O bond, whereas, in fact, it

has been shown above that the latter is stronger.

These observations lead to the conclusion that an intramolecular bond of this type may be considered more predominantly as a covalent linkage of the type



rather than an electrostatic linkage as shown below.



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