THE ETHYNYL HYDROGEN BOND

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PREFACE

I wish to record my deep appreciation of the assistance and guidance given to me by Dr. J.C.D.Brand throughout the work herein described. I wish also to thank Dr G.Eglinton for the assistance he has given me. It is a pleasure to thank Mrs F.Lawrie and Miss M.Mackay for their very capable technical assistance. The X-ray diffraction work was carried out with Dr G.Ferguson without whose help the problem could not have been attempted. Finally, I am indebted to the Department of Scientific and Industrial Research for financial assistance in the form of a Research Studentship.

J.T.

SUMMARY

The nature and properties of the hydrogen bond are discussed with special reference to the ethynyl hydrogen bond. Proof is given of the electron accepting capacity of the C-H group and of the electron donating capacity of the "pi" electron system of aromatic rings. The theory of the calorimetric, spectroscopic and diffraction methods of studying the hydrogen bond are discussed in detail especially as it applies to the investigations discussed in this thesis.

An investigation of the ethynyl hydrogen bond was conducted in which the chief acetylenic electron acceptor used was benzoyl acetylene. Instruments were constructed for a calorimetric study of the ethynyl hydrogen bond, the apparatus being checked for accuracy by determining the heat of solution of potassium chloride in water. Heats of mixing of benzoyl acetylene in a variety of solvents were obtained and from these the enthalpy of hydrogen bond formation between the benzoyl acetylene and the active solvents was obtained.

An infrared investigation of benzoyl acetylene and phenyl acetylene in a wide variety of solvents was carried out, the frequency shifts, half band widths and maximum intensities of the bands being noted. This indicated the wide range of compounds capable of hydrogen bonding and also provided evidence of bonding to the "pi" electron system of aromatic compounds as distinct from bonding to particular electronegative atoms. A quantitative study of benzoyl acetylene in benzene, various methylated benzenes and in n-butyl ether was carried out allowing the determination

of association constants and degrees of association. This was repeated at a variety of temperatures allowing the calculation of hydrogen bond strengths. Results obtained using the infrared technique were found to be subject to considerable error.

A quantitative study of benzoyl acetylene in the same solvents as above was carried out using the nuclear magnetic resonance method. This provided a very accurate method of determining association constants and degrees of association. It was intended to carry out temperature studies using this technique but this was impossible due to non-delivery of equipment. This method was also applied to the study of 1:4 dichlorobut-2-yne and propargyl chloride in benzene - cyclohexane mixtures and indicated the probable existence of hydrogen bonds between the methylene protons of these molecules and the "pi" electrons of benzene.

An X-ray diffraction investigation of the ethynyl hydrogen bond was carried out with Dr. G. Ferguson. For this purpose ortho-bromobenzoylacetylene was prepared and photographed. A two-dimensional Fourier map of the molecule is shown and the first accurate measurement of a known C-H ...... O hydrogen bond is given.

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I. INTRODUCTION

I. 1. GENERAL

The work, described in this thesis, on the ethynyl hydrogen bond was carried out by the author as the result of an interest, expressed by Drs. J.C.D. Brand and G. Eglinton of this university, in the quantitative nature of the ethynyl hydrogen bond where the electron donor was an aromatic molecule. The initial results obtained by Brand and Eglinton using a rock-salt prism infrared spectrometer were communicated to a meeting of the Infrared Discussion Group held in Edinburgh in March 1958. A fuller discussion of the bonding of acetylenes to ethers was given by Brand, Eglinton and Morman[1] in 1960. At that point the author was asked to carry out a study of acetylene-donor - solvent association.

I. 2. THE HYDROGEN BOND - HISTORICAL

The remarkable development of investigations into the nature and properties of the hydrogen bond in the past decade has been due partly to the increasing understanding of the importance of this form of bonding in both biological and non-organic systems and partly to the ready availability of spectroscopic and other physical techniques which have been used to determine the presence and properties of the hydrogen bond. One of the earliest reviews of this subject was carried out by Lassettre[2] and there have also been various symposia on hydrogen bonding, of which the most all-embracing was the 1957 Ljubljana Symposium on Hydrogen Bonding. The papers presented at that symposium have been collected by Hadzi[3]. There have, however, been few text books devoted to a critical and comprehensive review of the hydrogen bond though both Coulson[4] and Pauling[5] have given short accounts of this topic. The most recent and most comprehensive text book on the hydrogen bond has been that of Pimentel and McClellan[6].

The existence of those physical effects which have now been shown to be the result of hydrogen bonding was known well in advance of the first mention of this form of bonding. The wide spread nature of this form of association was observed by numerous workers towards the end of the 19th century. Nernst[7] explained the distribution of benzoic acid between water and benzene on the basis of the dimerization of the acid in benzene. Auwers[8,9] showed that this form of "polymerisation" was not confined to molecules containing hydroxyl groups and was probably the first to observe that this "polymerisation" was hindered in ortho-substituted phenols. It was also noted that the most readily formed "polymers" were those in which the monomer possessed hydrogen containing functional groups. Werner[10] proposed structures for ammonium salts in which a hydrogen atom was placed in a position now usually associated with a hydrogen bond i.e.

$$(H_3N \ldots\ldots H) X$$

Oddo and Puxeddu[11] and Pfeiffer[12] proposed configurations for azo derivatives of eugenol and for 1-hydroxy anthraquinone respectively which contained intramolecular hydrogen bonded configurations. However, the first workers to actually recognise the hydrogen bond as the cause of certain forms of association and to name it as such were Latimer and Rodebush[13]. They used the concept of the hydrogen bond to explain the properties of associated molecules such as hydrogen fluoride and acetic acid but more particularly to interpret the unique properties of water. This concept of the hydrogen bond also helped to correlate and explain many of the facts mentioned by earlier workers. The proposal of Latimer and Rodebush was that under suitable conditions a proton could form a bond between two atoms the hydrogen, however, being more firmly attached to one of the atoms than to the other. This form of bonding involved two functional groups which could be in the same or in different molecules. In the former case the result was described as "intramolecular hydrogen bonding" and in the latter case as "intermolecular hydrogen bonding". One of the two functional groups had to act as a proton donor such as the hydroxyl group in phenols or the hydroxyl group in carboxylic acids, and the other had to act as an electron donor such as oxygen in ethers or nitrogen in amines.

In the first decade after the publication of the above theory the hydrogen bond was studied by investigating the physical effects of hydrogen bonding on molecules, such as vapour pressure, molecular weights and dielectric constants. However, by the mid-thirties these techniques were supplemented by the vastly more powerful tools of infrared and raman spectroscopy which allowed a direct study of the hydrogen bond to be carried out[14,15]. At about the same time the technique of X-ray diffraction was also applied to hydrogen bonding studies. These spectroscopic and diffraction methods were themselves supplemented in the early fifties by neutron diffraction which enabled the exact determination of hydrogen positions and by nuclear magnetic resonance which allowed of very accurate quantitative treatment of hydrogen bond association. At the present there exists a very large quantity of

Table 1

Groups involved in Hydrogen Bonding

Acidic Groups	Basic Groups
O-H ; N-H ; F-H ;	
C-H ; S-H ; P-H.	 ; "pi" electrons

Table 2

Estimated energy contributions to each hydrogen bond in ice(in kcals)

a) Electrostatic	6.0
b) Delocalization	8.0
c) Repulsive Overlap	-8.4
d) Dispersion	3.0
Total Theoretical Energy	8.6
Experimental Energy	6.1

experimental data much of it still only qualitative though increasing attempts have been made to obtain an accurate quantitative picture of this form of association. The importance of hydrogen bonding, especially in biological systems, has become increasingly obvious and much work remains to be done on a wide variety of hydrogen bonded systems.

I. 3. THE HYDROGEN BOND - THEORY

Despite the considerable amount of work, both experimental and theoretical, which has been carried out on hydrogen bonding no sound theory, on which quantitative predictions can reliably be based, has as yet been developed. There have been a considerable number of reviews on the subject of the theory of the hydrogen bond[16-20]. As stated earlier the hydrogen bond consists in essence of two functional groups one of which, the acidic group, contains the active hydrogen and the other, the basic group, acts as the electron donor (See Table I). Though no definition of the hydrogen bond has been universally accepted the one given by Pimentel and McClellan[6] has been used by the author as it provided a reasonable and necessarily vague description of the phenomenon. Their definition was as follows; a hydrogen bond exists between a functional group A-H and an atom or group of atoms B in the same or in a different molecule when

a) There is evidence of association or bond formation.

b) There is evidence that the bond which links A-H and B specifically involves the hydrogen atom already linked to A.

The original view of the hydrogen bond as being the result of electrostatic attraction was derived from the empirical observation that the strongest hydrogen bonds were formed when the two groups, joined through the hydrogen of the bond, were strongly electronegative as in the case of hydrogen fluoride i.e.

$$...H - F .... H - F .... H -$$

The principle exponent of this view was Pauling[21,22]. His theoretical interpretation of the nature of the hydrogen bond was based on the knowledge that a hydrogen atom with only one stable orbital could not form more than one "pure" covalent bond and that, therefore, the hydrogen bond itself must have been the result of ionic forces. This view-point was supported by the dielectric properties[23] and by the spectroscopic properties[24] of various hydrogen bonded materials. The electrostatic theory of the hydrogen bond is still held by a large number of workers though it has become more sophisticated than the earlier point - charge calculations. Modern electrostatic theories of the hydrogen bond have employed the concept of orbital hybridization in deciding the charge distribution in the hydrogen bond and specifically in determining the position of the unpaired electrons of the basic group in the bond[25]. However Coulson[20] has pointed out that the electrostatic model could not account for a number of phenomena associated with hydrogen bond formation. For instance, it could not explain why the A-H stretching vibration increases in intensity by a factor much greater than would be predicted by the electrostatic model. In addition there was no apparent correlation between the strength of the hydrogen bond and the dipole moment of the base. The electrostatic theory of hydrogen bonding was also unable to explain why the A-H bending vibration decreased in intensity on hydrogen bonding.

The present view of the hydrogen bond has been detailed by Coulson[20] and he has indicated that, though the hydrogen bond was predominantly electrostatic, it did involve a certain amount of covalent character. Coulson[20] gave a list of forces which contributed to the formation of the hydrogen bond:-

a) Electrostatic interaction.

b) Delocalization effects.

c) Repulsive forces.

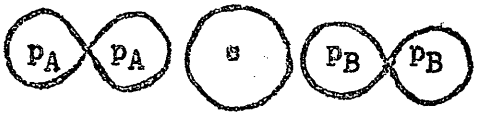
d) Dispersion forces.

In subdividing the phenomenon of hydrogen bonding into the four groups noted above Coulson recognised that the forces mentioned were, to a considerable extent, merely extensions of the electrostatic force. The electrostatic interaction was taken to mean the forces which would have arisen if it were possible to bring the two systems together without any deformation of their charge clouds. Since this was, in practice, impossible distorting forces arose as the two systems polarized one another. The delocalization forces were the result of the permanent distortion of the charge clouds while the dispersion forces were regarded as the result of small scale motions of the electrons in the two halves of the system. The actual overlapping of the charge clouds which, by placing too many electrons in a particular volume of space, violates the Pauli Exclusion principle led to the concept of repulsive forces. Within rather wide limits it was possible to calculate the individual effects of these forces and their contribution to bond energies, vibrational frequencies and dipole moments[26]. (See Table 2).

Figure 1

Molecular Orbitals for Hydrogen Bond Formation

A———H········B

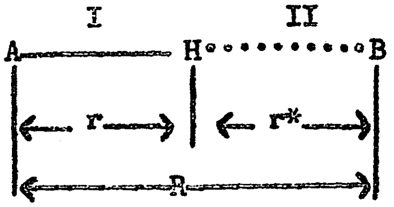


	Symmetrical H. Bond	Unsymmetrical H. Bond	No H. Bond
ψ_3(antibonding)	$(p_A - p_B) - a_3 s$	$(p_A - b_3 p_B) - a_3 s$	$p_A - a_3 s$
ψ_2(nonbonding)	$p_A + p_B$	$b_2 p_A + p_B$	p_B
ψ_1(bonding)	$(p_A - p_B) + a_1 s$	$(p_A - b_1 p_B) + a_1 s$	$p_A + a_1 s$

* * *

Figure 2

A one - dimensional model of the A———H·····B hydrogen bond



* * *

It is of some interest to note the degree of similarity between the theoretical result of Coulson and the value obtained for the hydrogen bond in ice by Bernal and Fowler[27]. It appears unlikely, however, that, in the near future, there will appear a reliable quantitative theory of the hydrogen bond since the standard errors in bond energy calculations are much in excess of the hydrogen bond energies themselves.

Pimentel[28] adopted a molecular orbital description of the hydrogen bond which gave a fairly good qualitative picture of the hydrogen bond in both the symmetric and unsymmetric instances (See Fig. 1).

In each of the orbitals the coefficient b decreases from unity to zero as atom B is moved away from the symmetrical position. On the basis of the above picture it would seem that hydrogen bond formation results from participation of p_B in ψ_1, the bonding orbital. This theory did not involve any violation of the Pauli principle though only the 1s orbital of hydrogen was used since the bonding orbital simply extended to the region on either side of the hydrogen atom giving bonding on either side. The necessity for A and B to be electronegative appeared in the nonbonding orbital ψ_2 where the second pair of electrons must be kept since if A and B were electronegative ψ_2 then represented a favourable repository for these electrons. The above theory therefore represented the electronegativity of A and B as playing a passive role in the hydrogen bond. This theory also permitted an explanation of why a form of hydrogen bond could exist between atoms of low electronegativity as well as between those of high electronegativity. In the former case, of which the electron deficient boranes are a good example, the number of electrons in the system did not require that the ψ_2 orbital be occupied whereas in the latter case the ψ_2 orbital is usually occupied as in the case of HF_2^-.

Another approach to understanding the formation of the hydrogen bond involved an attempt to obtain an empirical potential function which would express the energetics of the vibrational degrees of freedom of the hydrogen bond. In this form of treatment an explicit form was assumed for the potential function associated with the movement of the hydrogen atom within the hydrogen bond. A fairly complete potential function model has been developed by Lippincott and Schroeder[29-31]. The model adopted by these authors was a one-dimensional system based on the potential function

$$V = D_0 \left(1 - \exp\left(- n (r - r_0)^2 / 2r\right)\right) \qquad \ldots\ldots\ldots (1)$$

where D_0 is the A-H bond dissociation energy; r is the A-H internuclear distance; r_0 is the equilibrium A-H internuclear distance in the absence of a hydrogen bond and n is a parameter related to the ionization potentials of the atoms forming the bond. (See Fig. 2).

A number of assumptions were involved in this theory. These were:-

1) The hydrogen atom was located along the line of centres between the two electronegative atoms making up the bond.

2) Bond I was equivalent to a slightly stretched typical covalent bond the amount of stretching being $(r - r_0)$.

3) Bond II was a weak bond equivalent to a highly stretched bond of the type H-B the amount of stretching being $(r^* - r_0^*)$ where $r^* = R - r$.

4) There was a Van der Waals repulsion between the two electronegative atoms A and B which could be described by an exponential function.

5) There was an electrostatic attractive potential between atoms A and B.

6) The potential energy of the stretching of both bonds could be obtained through the application of the potential function given in equation (1).

Of these assumptions, the last was undoubtedly the most fundamental and any discrepancies between the theoretical and the experimental results would be due to the inadequacy of the potential function. In addition the first assumption presumes the A - H ... B bond to be linear, and as will be shown later, a considerable number of hydrogen bonds show a relatively high degree of non-linearity. However, the proponents of the above theory have claimed that it was adequate for both linear and non-linear hydrogen bonds. This approach, according to Lippincott and Schroeder, allowed the prediction of the A-H bonded distance, the A-H stretching vibrational frequency, the A-H ... B hydrogen bond energy and the A ... B force constant from a knowledge of the A ... B bond distance which could be obtained from X-ray diffraction studies. They would appear to have obtained reasonable agreement for their prediction of a correlation between the A ... B distance and the A-H vibrational frequency.

There is as yet no generally accepted theory of hydrogen bond formation, all of the proposals mentioned above having been subjected to some valid criticism. So far it can be said that the electrostatic model of the hydrogen bond has enjoyed the most substantial support though this has been due mainly to the nature of the historical development of the subject and not to any overwhelming superiority of that model. The earliest detailed studies of the hydrogen bond were carried out on molecules such as the HF_2^- ion or the water molecule where the hydrogen bond involved highly electronegative atoms and this has tended to bias observers in favour of the electrostatic approach. In addition the classical theory of the chemical bond allowed hydrogen only one valency and the electrostatic model was, at the time, the only way around that difficulty. The electrostatic model also allowed quantitative calculations of hydrogen bonding and was favoured by the fact that most hydrogen bonds A-H ... B were known to be linear. The disadvantages of this model have already been noted and, in addition, modern electrostatic models have involved extremely complex charge distributions which have detracted from the original simplicity of that approach. The other general approach has been from the stand-point of covalency and was of more recent origin as it was introduced in an attempt to explain the problems left unsolved by the electrostatic model. However the valence bond theory of the covalent bond created the problem of how to fit another valency onto hydrogen. For that reason it may be necessary to approach the theory of hydrogen bond formation from the molecular orbital viewpoint. At the present the nature of the hydrogen bond would appear to lie somewhere between the concepts of an electrostatic bond and a dative covalent bond.

I. 4. THE HYDROGEN BOND - FUNCTIONAL GROUPS

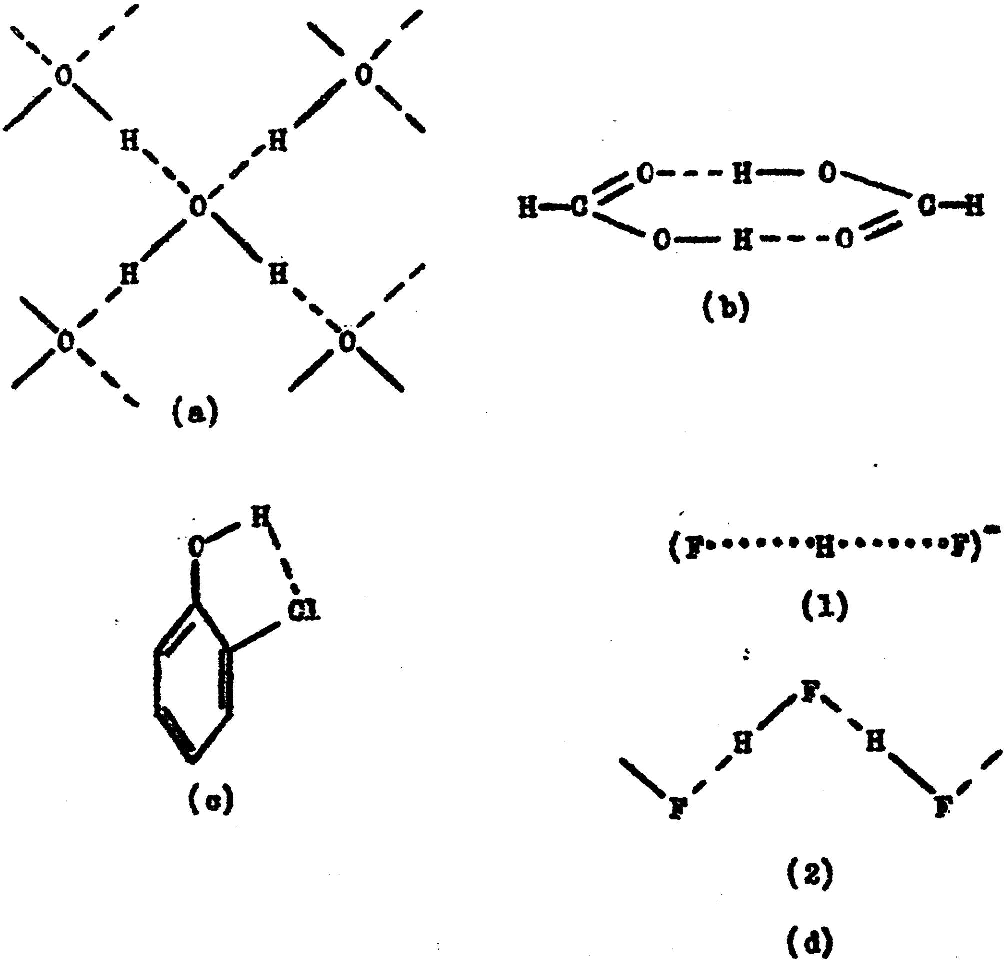
It has been possible to distinguish four basic types of hydrogen bond. These were as follows:-

a) The intermolecular bond which extended over many molecules forming a polymeric structure as in the case of water.

b) The intermolecular bond which extended over two molecules forming

Figure 3

Examples of Hydrogen - Bonded Structures



a dimer as in *formic acid*.

c) The intramolecular bond in which the hydrogen atom linked to other atoms of the same molecule as in cis-ortho-chlorophenol.

d) The particular case of HF_2^- in which the anion of the crystal KHF_2 was shown to exist as a distinct charged unit in the solid. This anion had to be distinguished from the hydrogen bonded liquid, hydrogen fluoride, which forms a polymeric structure.

(See Fig. 3).

In determining which groups could form a hydrogen bond it was necessary to state exactly what was meant by such a bond. Firstly, of course, it specifically involved a hydrogen atom already bonded to some other atom. Although a definition has already been given for the hydrogen bond it is as well to give it here again and to amplify the reasons for that definition. The definition given was based entirely on experimental criteria and was as follows:-

A hydrogen bond was said to exist when

(1) There was evidence of association.

(2) There was evidence that this association specifically involved a hydrogen atom already attached to another atom.

The evidence for the first of these criteria has been obtained from nearly all the chemical methods used for detecting association such as molecular weight determinations. These methods however have only been capable of indicating that a bond does exist not what type of bond it was. A number of techniques are available, however, which provide one with a means of satisfying both criteria and these techniques are those which come under the headings of spectroscopic and diffraction methods. Of

Table 3

Examples of Molecules containing Acidic Groups

A	Example	A	Example
F	Hydrogen Fluoride	Cl	Hydrogen Chloride
O	Carboxylic acids	C	Halogenated alkanes
	Water		Hydrogen cyanide
	Alcohols		Acetylenes
	Phenols		Aldehydes
	Oximes	S	Mercaptans
N	Amides,		
	Pyrrole		
	Amines		
	Ammonia		

Table 4

Examples of Molecules containing Basic Groups

B	Examples	B	Examples
F	F^-, HF	C	Alkenes
O	Carboxylic acids		Alkynes
	Water, Alcohols		Aromatics
	Phenols, Amides	S	Thioamides
	Ketones, Aldehydes		Thiocarbamic acids
	Ethers, Esters		
N	Amines, Pyridines		
	Ammonia, Pyrrole		

these X-ray diffraction, neutron diffraction and electron diffraction indicate the positions of the individual atoms and thus allow an accurate determination of their distance of closest approach. Infrared and raman spectroscopy have enabled the observation of the specific involvement of the hydrogen atom due to changes in the vibrational degrees of freedom of the system and thus changes in the vibrational frequencies of the molecule. High resolution nuclear magnetic resonance has been able to indicate the existence of hydrogen bonding due to its sensitivity to any change in the electronic environment of the hydrogen atoms.

The hydrogen bond can be written generally as A-H ... B where A-H is considered to be an acidic or electron accepting group and B is a basic or electron donating group. It is broadly true to say that the group A tends to attract electrons away from the hydrogen atom either because of its electronegative character or because of inductive or mesomeric effects within the molecule of which A is a part. Examples of this type of group are given in Table 3 and, in addition, the active atom A for the molecules is given.

As there have been many hundreds of examples discussed in which the acidic group was either fluorine, oxygen or nitrogen and relatively few investigations of systems where the acidic group was chlorine, carbon or sulphur it was considered to be to the point to concentrate attention on the latter systems which are incidentally pertinent to the work described in this thesis. The case for hydrogen chloride acting as a hydrogen bonding acid has been studied by Cook, Lupien and Schneider[32a,b] using freezing point diagrams which have confirmed the existance of a 1:1 complex between the hydrogen chloride and the various bases studied.

Investigations of systems involving C-H hydrogen bonds have been relatively meagre[33,34] though recent work has provided detailed evidence of the existence of this form of hydrogen bond. Of all the compounds which are capable of forming this type of hydrogen bond the one most intensively studied has been chloroform. By comparison with the commoner examples of hydrogen bonding the bonds of the type formed by chloroform are relatively weak and some workers have classified these interactions not as hydrogen bonding but as "polar solvent effects"[35,36] It was obviously of some importance from the point of view of this thesis to clarify any doubts which may exist as to whether C-H groups form hydrogen bonds. The evidence as provided by the infrared frequency shifts of the C-H stretching vibration is rather ambiguous,particularly for chloroform in the presence of oxygenated bases[37],but with nitrogen bases such as pyridine[38] and triethylamine[39] distinct frequency shifts were recorded. Since the two nitrogen bases mentioned above were the strongest bases used in these studies of chloroform it would appear that either chloroform only forms hydrogen bonded complexes with very strong bases or that the small frequency shifts produced by the weak hydrogen bond were masked by other solvent effects. However the sharp increase in intensity of the C-H stretching vibration in these basic solvents as compared with an inert solvent is indicative of the presence of a hydrogen bond. More rigorous evidence for the hydrogen bonding capabilities of chloroform has been obtained from nuclear magnetic resonance investigations[40]. Creswell and Allred[41] have also shown that fluoroform can bond to the oxygen of tetrahydrofuran using nuclear magnetic resonance techniques. There has also been a number of classical approaches such as that by Schulze[42] which has shown the existence of association between chloroform and acetone.

The X-ray diffraction results have shown the existence of hydrogen bonds in hydrogen cyanide resulting in the existence of infinite chains and a short carbon - nitrogen distance in the bond C-H ... N[43]. Evidence for hydrogen bonding by aldehydes through the formyl C-H group has been obtained from infrared studies[44] and from nuclear magnetic resonance investigations[45a,b].

Investigations of systems in which the ethynyl hydrogen acts as a hydrogen bonding agent have multiplied in the last few years. Early evidence of this form of hydrogen bonding was obtained by Stanford and Gordy[46] who found systematic frequency shifts of the ethynyl C-H stretching vibration of phenyl acetylene when it was dissolved in a variety of bases. However most of the research which has been carried out on the ethynyl hydrogen bond has been done using infrared and nuclear magnetic resonance techniques on solutions of the acetylenic compound in a base. Much of the work has been of a semi-qualitative nature in that, while measuring the frequency shifts or the chemical shifts in various solvents, the workers have made little or no attempt to estimate either the degree or the strength of the hydrogen bonding which has occurred[47,48]. Wojtkowiak and Romanet[49] attempted to relate the frequency shifts of octyne-1 in various solvents to the refractive index of the solvent. These authors divided the solvents into three classes a) those in which they considered the association to be due to dipole interactions; b) those solvents which they considered were acting as hydrogen bonding agents and c) those solvents, either aromatic or unsaturated aliphatic, where the acetylene bonded to the "pi" electron cloud. More detailed studies of ethynyl hydrogen bonding have been conducted by Brand, Eglinton and Morman[1] and by West and Kraihanzel[50] which have provided quantitative estimations of the extent of hydrogen bonding. The application of nuclear magnetic resonance by Hatton and Richards[51] to propargyl chloride, phenyl acetylene and benzoyl acetylene and by Nakagowa and Fujiwara[52] to phenyl acetylene in a variety of solvents has indicated that the above technique is specially suited to the study of the ethynyl hydrogen bond. It would appear, therefore, that though hydrogen bonds involving a C-H group tend to be much weaker than those involving an O-H group there is no longer any doubt as to the ability of the C-H group to form a hydrogen bond.

Considerable evidence has also been accumulated to show that S-H groups can also form hydrogen bonds. Gordy and Stanford[53] have shown that mercaptans form hydrogen bonds with strong bases such as pyridine, the S-H stretching vibration in the infrared shifting to lower frequency, broadening, and increasing in intensity,all these features being specific to hydrogen bonding. Infrared investigations of hydrogen bonding involving S-H groups have also been carried out on hydrogen sulphide[54] and benzenethiol[55]. The hydrogen bonding capacity of benzenethiol has also been studied by Copley, Marvel and Ginsberg[56] using heats of mixing data.

So far in this section the groups studied have been those which act as the electron aceptor and also supply the proton in hydrogen bond formation. The groups to be looked at next are the basic or electron donating groups which comprise the other half of the hydrogen bond. The most common examples of these are the groups in which the electron donating centre is a highly electronegative atom such as fluorine, oxygen

Figure 4

Crystal Structure of Methanol

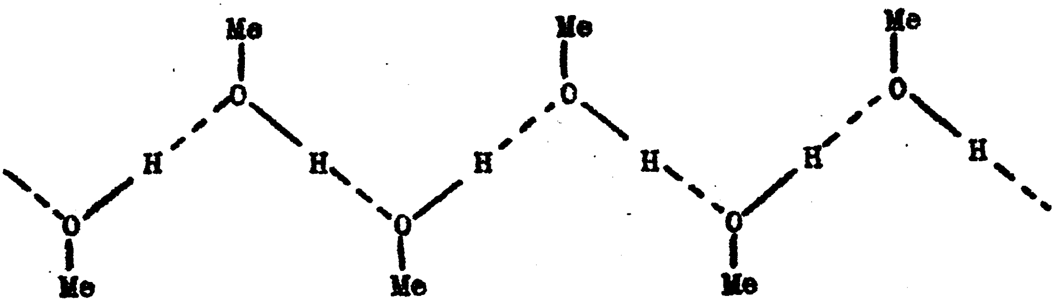
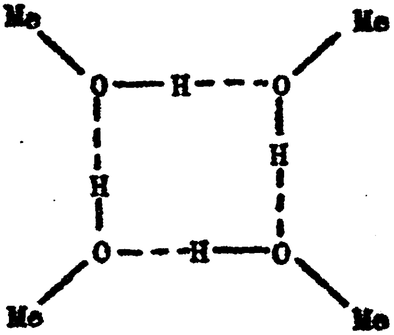


Figure 5

Vapour State Structure of Methanol



or nitrogen. It can be shown, however, that the basic group need not be a particular atom nor need it be a highly electronegative group. The basic group in hydrogen bonding need only be an atom or group of atoms which can act as a good electron donor. With this in mind it is possible to add to the normal list of bases, molecules possessing a "pi" electron system. Table 4 gives a list of compounds which can act as hydrogen bonding bases.

Ammonium fluoride has provided, probably, the commonest example of the fluorine anion acting as base with each nitrogen atom in the structure hydrogen bonded to four tetrahedrally arranged fluorines[5]. Hydrogen fluoride on the other hand has been shown to form a polymeric structure in the liquid state[5]. Though fluorine is the strongest base available for hydrogen bonding the commonest bases are those involving an oxygen atom, the most obvious example of which being ice[27] and water[57] in which polymeric units are formed as a result of the hydrogen bonding. Alcohols have also been shown to form long polymeric chains in the crystal state as in the case of methanol[58]. (See Fig. 4). However in the liquid and vapour states it has been shown that the alcohols tend to form cyclic structures. For instance in the case of methanol Weltner and Pitzer[59] have shown that the molecule exists as a hydrogen bonded tetramer $(CH_3OH)_4$ in the vapour state as indicated in Fig. 5. Ethers as bases in hydrogen bonding have been studied by Joesten and Drago[60] using phenol as the electron acceptor and by Brand, Eglinton and Morman[1] using acetylenes as the acceptors. Barrow[61] and Reeves[62] have conducted extensive studies of carboxylic acids both as electron acceptors and as electron donors. Because of their strong basic properties nitrogenous bases have been used to test the hydrogen bonding capabilities of weak electron acceptors such as chloroform[38,39].

Of more specific interest to the present work is the bonding of electron acceptors to "pi" electron systems as found in alkenes, alkynes and in aromatic ring systems. With regard to hydrogen bonding involving "pi" electron clouds in alkenes and alkynes the data is relatively meagre though Reeves and Schneider[63] have studied complex formation between chloroform and various olefins using nuclear magnetic resonance techniques. Cook, Lupien and Schneider[32a] have also studied the formation of hydrogen bonded complexes between hydrogen chloride and alkenes and alkynes using Freezing point diagrams and have confirmed the existence of 1:1 complexes of the hydrogen chloride and the unsaturated compound.

The evidence relating to the study of aromatic "pi" electron systems as electron donors in hydrogen bonding is fairly substantial. A review by Andrews[64] has covered much of the early work done on this aspect of hydrogen bonding. Pfeiffer[65] was probably the first to attempt an explanation of why aromatic "pi" electron systems can act as centres for association when he postulated the existence of secondary valence forces within aromatic nuclei which he considered were susceptible to saturation by interaction with other molecules. Mulliken[66] has developed a more up-to-date approach to this problem with specific reference to charge transfer complexes which are obviously closely related to hydrogen bonded complexes involving aromatic "pi" electron systems. A number of reports on infrared studies of this type of hydrogen bonding have been published by Josien and her collaborators[67] and Oki and Iwamura[68] have studied intramolecular hydrogen bonding between aromatic "pi" electrons and phenolic groups in the same molecule again using infrared techniques. Baker and Shulgin[69] have also studied intramolecular hydrogen bonds involving "pi" electron systems. The hydrogen bonding of chloroform to aromatic electron donors has been studied by Reeves and Schneider[63] using nuclear magnetic resonance and Cook, Lupien and Schneider[32b] used Freezing point diagrams to study the formation of complexes between hydrogen chloride and aromatic electron donors. The bonding of acetylenes to aromatic electron donors has been studied, using infrared spectroscopy, by Wojtkowiak and Romanet[49] and, using nuclear magnetic resonance spectroscopy, by Hatton and Richards[51]. The references given only indicate a small fraction of the work done on this particularly interesting form of hydrogen bonding. The special interest attached to this form of base lies in the fact that it suggests, in accordance with the molecular orbital description of the hydrogen bond and in opposition to the electrostatic theory, that the base involved in hydrogen bonding need not be a highly electronegative atom but need only be a good electron donor.

I, 5. THE HYDROGEN BOND - STRENGTH OF THE BOND

The formation of any form of chemical bond normally results in some stabilisation of the system involved and this new stability is usually expressed in terms of the energy of the bond formed. It is to be expected that the formation of a hydrogen bond would also result in an increased stability of the system involved and in a lowering of the entropy of the system. This would be expected to make itself evident in the energy attributed to the hydrogen bond and, in addition, the energy of this bond can be expected to vary depending on the system involved. In contrast to the strengths of covalent or electrovalent bonds which are normally in the region of 50 - 100 kcals/mole it has been shown that in general the hydrogen bond strengths lie in the range 1 - 10 kcals/mole. In other words hydrogen bonds have about one-tenth the strength of a normal covalent or electrovalent bond. It is this small bond energy and the small activation energy involved in the formation and fission of a hydrogen bond that makes it so important in biological systems where it is of considerable importance in chemical and physical changes taking place at normal body temperatures.

Much of the data obtained on hydrogen bond strengths has resulted from a study of equilibrium data obtained for the system :-

$$A - H + B \rightleftharpoons A - H \cdots\cdots B$$

at a variety of temperatures and is usually expressed in terms of the enthalpy of association, ΔH, or of the free energy of association, ΔG. As a result of this, those physical techniques which can supply one with the equilibrium or association constants for hydrogen bonding are also capable of being used to determine hydrogen bond strengths. A number of early measurements in this field were made with particular regard to the dimerization of carboxylic acids which was known to be due to hydrogen bonding. Coolidge[70] studied the dimerization of formic acid using heats of dissociation and obtained a value of 7·063 kcals/mole for the hydrogen bond strength while MacDougall[71] used vapour density measurements to determine the hydrogen bond energy in the acetic acid dimer obtaining a value of 8·200 kcals/mole for the hydrogen bond energy. Considerable

Table 5

Hydrogen Bond Strengths(Kcals/mole)

Hydrogen Bond Type	Compound	Dimer in Gas	Dimer in CCl_4	Pure Liquid
O-H······O	CH_3CO_2H	7.0	5.4	5.8
	H_2O	5.0	-	3.4
	CH_3OH	4.5	4.6	4.7
	C_6H_5OH	-	4.3	-
N-H······O	$CH_3CONHCH_3$	-	3.9	-
N-H······N	NH_3	4.4	-	-
	CH_3NH_2	3.4	-	-
F-H······F	HF	6.8	-	-
C-H······N	HCN	3.3	-	4.6

Table 6

The Effect of Mixing Different Types of Hydrogen Bonded Compounds

Types Mixed	Change in Hydrogen Bonding on Mixing	Temperature Change
1) AB + N	H. bonds broken only	Always a Fall
2) B + A	H. bonds formed only	Always a Rise
3) AB + A	H. bonds broken and formed	Mostly a Fall
4) AB + AB	H. bonds broken and formed	Mostly a Fall
5) AB + B	H. bonds broken and formed	Mostly a Fall

---

doubt has been cast, however, on the validity of much of the early work on hydrogen bond strengths due to difficulties with the experimental techniques and also as to what was actually being measured. Though there is still some doubt about certain aspects of the measurement of hydrogen bond strengths acceptable determinations of the enthalpies of hydrogen bonds have become more numerous. The methods used to determine these include calorimetry, infrared spectroscopy, nuclear magnetic resonance and vapour density measurements to mention only the most common ones. Table 5 gives a list of selected values of hydrogen bond strengths measured in kcals/mole. Much of the trouble which lies behind the uncertainty involved in the measurement of hydrogen bond strengths is due to the weakness of this form of bond which has allowed considerable confusion with other forces acting on the molecule. In other words, molecular forces other than hydrogen bonding can and do complicate the elucidation of the strength of the hydrogen bond. Very few systems have been studied by more than one technique and even in those cases where a number of approaches to the problem have been attempted the results are, to say the least, unsatisfactory.

I. 6. THE HYDROGEN BOND - PHYSICAL PROPERTIES

As it was initially the peculiar physical properties of certain compounds which led to the discovery of hydrogen bonding it is obvious that this form of complexing has a unique effect on the molecules taking part. These physical effects are most easily observed where hydrogen bonding has resulted in a molecule associating with itself to form a dimer or a polymer. This shows itself in the apparent molecular weight of the substance and much of the early work on hydrogen bond association was based on methods involving molecular weight determinations. In addition since this form of bonding restricts the freedom of individual molecules it should show itself in changes in boiling points and in melting points of the compounds studied. Again, since the molecules taking part in hydrogen bonding have a specific charge distribution and since the dielectric constant is known to depend directly on the number of molecules per unit volume, the condensed nature of hydrogen bonded substances would tend to increase the dielectric constant of the material.

A study of molecules such as water, hydrogen fluoride and ammonia, which are known to be hydrogen bonded, in relation to similar substances, has shown that the boiling point and the melting point of these hydrogen bonded compounds are considerably higher than would otherwise be expected. In the case of water, from an extrapolation of the boiling points and melting points of hydrogen telluride, hydrogen selenide and hydrogen sulphide, one might expect those for water to be - 80°C and - 100°C respectively. That they are in fact 100°C and 0°C respectively indicates firstly, that the molecule is polymeric. It also indicates that in the solid state, as ice, the molecules are hydrogen bonded together and that, though many of the hydrogen bonds are broken on melting, more than half of them are retained in the liquid state and are only ruptured on the vapourisation of the water. The same interpretation holds for ammonia and for hydrogen fluoride though in the latter there is still evidence of hydrogen bonding in the vapour state.

Latimer and Rodebush[13] in their paper on the hydrogen bond postulated that the polymerisation of molecules such as water and ammonia by this type of bonding explained the high dielectric constant values obtained for these substances. It has in fact been possible to carry out a quantitative theoretical treatment of the dielectric constant of water in terms of hydrogen bond formation[72]. The high dielectric constant of hydrogen cyanide has also been explained in terms of hydrogen bonding between the cyanide molecules giving a linear polymer whose dielectric constant is directly proportional to the number of units in the polymer. Hydrogen bond formation has also been shown to affect the solubility of organic liquids in water and other solvents, the viscosity of liquids and the choice of crystal structure which itself determines the cleavage and hardness of the crystal.

II. PHYSICAL METHODS OF STUDYING THE HYDROGEN BOND

II. 1. GENERAL

In the last chapter a whole variety of physical techniques have been mentioned which have, at some time, been applied to studying the phenomenon of hydrogen bonding. These methods can be classified into those which, though they prove that association is taking place, do not specifically point out the hydrogen as being concerned in their association and into those methods which, as well as indicating the presence of association, point decisively to the active participation of the hydrogen in the complex. The former group have been described as the classical methods and were the first to be applied to the study of hydrogen bonding. Their method of approach to the problem is rather indirect since by their nature they are applied to studying those properties thrust upon the molecule as a result of its hydrogen bonding. The latter group consist of the spectroscopic and diffraction techniques and these tend to concentrate attention on the hydrogen bond itself and in particular on the hydrogen taking part in that bond. The work presented in this thesis has involved the application of methods from both groups of techniques though particularly from the latter group and the purpose of this chapter is to show how these methods have been adapted for hydrogen bonding studies and to give a short theoretical background to the methods themselves.

II. 2. CALORIMETRIC TECHNIQUES

Hydrogen bonds are known to occur in all three phases of matter though they tend to break down as the temperature increases and are therefore found only occasionally in gases. Most classical physicochemical methods of studying association have been shown to be applicable to the study of hydrogen bonding and most of these methods have been applied to the hydrogen bonded substance in the liquid state. Though that state of the material is usually the one of most practical interest it is unfortunately also the one which presents the greatest theoretical disadvantages mainly because of the lack of an adequate theory of liquids. An important factor in quantitative studies of hydrogen bonding is that the extent of such bonding can be drastically altered by a variation in either the solvent or the temperature. If one wishes to eliminate all possibility of solute - solvent interaction (i.e. hydrogen bonding) then it is essential to choose a truly inert solvent. If, however, one wishes to study solute - solvent hydrogen bonding, as in this thesis, the only serious problem remaining is the accurate control of the temperature. For accurate physicochemical work it is essential to use some form of apparatus which will allow the maintenance of a constant temperature in the system. If this apparatus is to be used to study changes in temperature due to the mixing of two substances then the instrument normally used is known as a calorimeter.

Most chemical processes are accompanied by a measurable absorption or evolution of heat. It follows from the First Law of Thermodynamics that the magnitude of the heat change is proportional to the quantity of the substance involved and depends also on the physical state of the reactants and the products. The heat change accompanying a physical or chemical process is measured by some form of calorimeter, the measured rise or fall in the temperature multiplied by the total heat capacity of the calorimeter giving the quantity of heat in calories which has been absorbed or released. The calorimeter is most often used to measure heats of dilution or heats of mixing. There are two principal difficulties in the practical application of calorimetry; these are the problem of determining the total heat capacity of the calorimeter and all its contents and the exchange of heat between the calorimeter and its surroundings. The former can be overcome if the calorimeter and its contents are weighed separately and if the specific heat of each object is known. This is usually extremely difficult, if not impossible, and the problem is overcome by obtaining the "water equivalent" of the system. This is done by supplying a known amount of heat to the system and determining the rise in temperature which it produces. This heat is usually supplied electrically and is measured in Joules where

$$\text{Joules} = \text{Volts} \times \text{Amps} \times \text{Seconds} \qquad \ldots\ldots (2)$$

The above method, to be accurate, must involve a high degree of precision in the measurement of the electrical quantities and therefore usually involves the use of a potentiometric technique. The second problem in the use of a calorimeter is most readily overcome by the use of a Dewar vessel as the calorimeter. Since the temperature changes involved in calorimetry are usually small a sensitive method of determining this temperature change is required and this is usually done with a Beckmann thermometer or with a sensitive thermocouple.

The enthalpy of the system is derived thermodynamically in the following manner. No mechanical work is done during the process carried out at constant volume and it follows, therefore, that the increase in energy ΔE of the system equals the heat q_v absorbed at constant volume

i.e. $\Delta E = q_v$ ...... (3)

If the pressure is also constant as in experiments carried out under atmospheric pressure then :-

$$\Delta E = E_2 - E_1 = q_p - w = q_p - P(V_2 - V_1)$$

Hence $q_p = (E_2 + PV_2) - (E_1 + PV_1)$ ...... (4)

where q_p is the heat absorbed at constant pressure.

On this basis it is possible to define a new function called the enthalpy in the following manner:-

$$H = E + PV$$

Therefore $\Delta H = H_2 - H_1 = q_p$ ...... (5)

The increase in enthalpy equals the heat absorbed at constant pressure.

The enthalpy (H) like the energy (E) is a function of the state of the system alone and is independent of the path by which that state is reached.

Most chemical changes involve heat changes and these are known as exothermic if the heat is evolved and endothermic if the heat is absorbed.

Since most chemical processes take place under constant pressure (atmospheric conditions) the enthalpy change (ΔH) is used to express the heat change in the process. This is best represented by writing down the chemical equation for the process, specifying the states of all the initial and final compounds and then appending the heat change, noting the temperature at which it was measured.

When a solid or a liquid compound, which is known to be hydrogen bonded in that state, is added to a solvent in a calorimeter there are a number of physical processes which can take place. In a naive way if the hydrogen bonded solid or liquid is added to an inert solvent and the final solution is dilute enough to separate all the solute molecules from one another then the heat of mixing of these two compounds should be a measure of the strength of the hydrogen bond in the solute. If however the solvent used is not inert then the problem becomes more complex because the heat of mixing will be the result of the breaking of the hydrogen bonds within the solute and the formation of hydrogen bonds between the solute and the solvent. Table 6 gives a list of a variety of effects which can result on mixing different types of molecules.

In a system where hydrogen bonds are only broken there is bound to be an increase in entropy due to an increase in the disorder of the system, coupled with a drop in the temperature of the whole system due to the necessity of acquiring energy for the break-up of the hydrogen bonds. In a system where hydrogen bonds are only formed the reverse situation will apply with a drop in entropy and an increase in the temperature of the system. Where hydrogen bonds are both formed and broken the two processes compete with one another and it is usually impossible to predict the final result. Madgin and Briscoe[73] determined the heat of mixing of a number of binary mixtures without attempting to explain them and on the basis of that paper it was possible to verify experimentally the predictions as to temperature change expressed for the various systems in Table 6. There has, however, been relatively few attempts made to determine hydrogen bond strengths using heats of mixing. Von Elbe[74] found the hydrogen bond strengths of methanol, n-propanol and tert-butanol to be 5·8 kcals/mole by determining their heats of mixing in hexane or heptane as solvent. The hydrogen bond strength of chloroform in ether was claimed by Earp and Glasstone[75] to be about 6-7 kcals/mole while Vinogradov and Linnel[76] obtained a value of 3·8 kcals/mole for the hydrogen bond strength of pyrrole in pyridine. Recently hydrogen bonded complexes of chloroform in acetone[77] and in dioxan[78] have been studied using calorimetric techniques giving a hydrogen bond strength in the former case of 2·7 kcals/mole. In the latter case it was shown that both a 1:1 and a 1:2 complex of dioxan-chloroform was formed and the equilibrium constants for their formation were given. Joesten and Drago[60] in an attempt to correlate the infrared frequency shift of the phenolic hydroxyl stretching vibration with the enthalpy of the hydrogen bond listed a considerable number of enthalpies for complexes of phenol with nitrogen and oxygen donors.

II. 3. INFRARED SPECTROSCOPIC TECHNIQUES

Though hydrogen bonding was originally studied using the classical physicochemical techniques such as calorimetry these are being rapidly superseded by more rigorous methods. This is the result of the fact that the classical methods were only capable of detecting the existence of association and were not able to show that hydrogen was specifically involved in that association. Because of this limitation it is impossible to deduce directly the existence of hydrogen bonds using classical technique A method of studying hydrogen bonding was therefore required which would indicate both that association was taking place and that hydrogen was directly involved in the association. The application of infrared spectroscopy to the study of hydrogen bonding was found to fulfill these requirements. This technique has, for some time, provided the most sensitive and characteristic test of the existence of hydrogen bonding and is the approach most used by those who study this phenomenon.

The energy required to produce molecular vibrations is of the same order of magnitude as that supplied by infrared radiation and this provides, therefore, a convenient means of studying the vibrational motions of molecules. All molecules have 3N degrees of freedom where N is the number of atoms in the molecule. These degrees of freedom are of three types, translational, vibrational and rotational. In the case of a non-linear molecule there are three translational and three rotational degrees of freedom leaving (3N - 6) vibrational degrees of freedom. Each of these vibrational degrees of freedom corresponds to either a stretching or a bending vibration between atoms in the molecule. Since these vibrations involve different aspects of the molecular geometry they will require differing quantities of energy and will therefore absorb infrared radiation of differing frequencies. These frequencies are considered to be characteristic of particular molecular vibrations and depend on the masses of the vibrating atoms, the molecular geometry and the force constants of the bonds involved. As a result of this correlation between the infrared vibrational frequencies and the bond force constants which are themselves directly related to the chemical bond order, infrared spectroscopy is particularly valuable as a source of information on the subject of chemical bonding and molecular structure. There are, in essence, two main types of molecular vibration these being the stretching vibrations which involve a linear displacement of two neighbouring atoms with respect to one another and deformation or bending vibrations which involve an angular displacement of two or more neighbouring atoms. Obviously if the form of association being studied involves

Figure 6

Infrared Vibrations Sensitive to Hydrogen Bonding

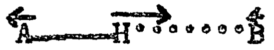
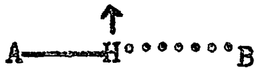
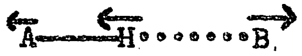
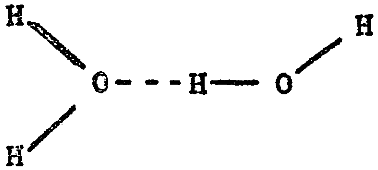
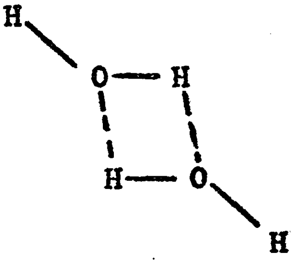
Symbol	Vibrational Modes	Description
1) ν_s		A-H stretching vibration (3500 - 2500 cm.$^{-1}$)
2) ν_b		A-H rocking vibration(in plane) (1700 - 1000 cm.$^{-1}$)
3) ν_t		A-H rocking vibration(out of plane) (900 - 300 cm.$^{-1}$)
4) ν_σ		A····B stretching vibration (250 - 50 cm.$^{-1}$)
5) ν_β		A-H···B bending vibration (less than 50 cm^{-1})

Figure 7

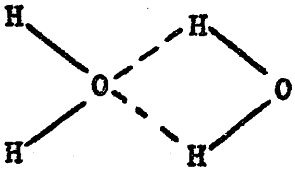
Possible Structures of the Water Dimer



(a) Open Chain



(b) Cyclic



(c) Bifurcated

hydrogen bonding then the molecular vibrations most affected will be those involving the hydrogen atom which is taking part in the bonding. In other words the stretching and bending vibrational frequencies particular to the A-H bond will be the ones most affected by hydrogen bonding of the type A-H ... B. In Fig. 6 are shown those vibrations which are most indicative of hydrogen bonding with the approximate region of the spectrum in which they occur. It should be noted that the vibrations listed here do not include any which might involve the bond joining the electron donating group (B) to the rest of the molecule to which it belongs. Though these bonds are known to be affected by hydrogen bonding comparatively little work has been carried out on them. It should also be noted that English subscripts have been used for those vibrations which existed prior to hydrogen bond formation and Greek subscripts for those vibrations which have resulted from hydrogen bonding.

The effect of hydrogen bonding on the A-H stretching vibration was first observed for the case of intramolecular hydrogen bonding by Ellis[79] in 1929 who noticed that the O-H stretching vibrational frequency in acetylacetone was shifted to lower frequency. Freymann[80] who studied solutions of alcohols found the same kind of effect and in addition noticed that both the intensity of the O-H stretching vibration and its frequency appeared to depend on the concentration and temperature of the solution. As a result of these observations he attributed this behaviour to molecular association. However, the most comprehensive evidence of the sensitivity of the A-H stretching vibration to hydrogen bonding was shown by Hilbert, Wulf, Hendricks and Liddel[81]. For the reasons already stated the application of infrared spectroscopy to the study of hydrogen bonding expanded rapidly and a number of empirical relationships were established regarding the effect of this form of association on the infrared spectra of the molecules taking part. It was shown that the spectral changes observed were generally the same for all types of compounds both organic and inorganic and that there was in addition similar effects to be obtained for solids, liquids and gases. The A-H stretching vibration (ν_s) shows considerable shifts to lower frequency and the half-width of the band ($\nu_{\frac{1}{2}}$) is considerably increased on hydrogen bond formation. It has also been shown that the integrated absorption coefficient of the A-H stretching vibration increases considerably on hydrogen bonding. The temperature, concentration and solvent used have also been shown to affect the frequency and intensity of the stretching vibration. Of the other vibrational modes noted in Fig. 6 the new vibrations formed as a result of hydrogen bonding have been little studied and the information available on them is as yet meagre and comparatively unreliable. The effects of hydrogen bonding on the A-H bending vibration (ν_b) are considerably weaker than for the stretching vibration. However with the bending mode the frequency shifts to higher values while the data for half band widths and intensity changes is somewhat unreliable. The following discussion will concern itself solely with the A-H stretching vibration.

As has previously been noted infrared spectroscopy can be used to study hydrogen bonding in solids, liquids and gases. These divisions of the topic can themselves be further subdivided into the study of pure compounds and the study of mixtures or solutions of one compound in another. Hydrogen bonding studies in gases using infrared spectroscopy are comparatively rare because, firstly, in order to study a substance in the gas phase the vapour pressure of the compound must be greater than a few millimetres at a reasonable temperature. The low pressures one normally obtains are only suitable for the study of strong hydrogen bonds as in dimerized carboxylic acids[82] whereas with the weaker bonds found in alcohols and amides it is extremely difficult to obtain suitable conditions. The other problem in studying hydrogen bonding in the gas phase by infrared spectroscopy results from the overlapping of the rotational envelopes of the bands which makes interpretation rather difficult, especially in those low molecular weight compounds like hydrogen chloride where the rotational envelope covers a large range of frequency. The majority of hydrogen bonded systems have been studied in the liquid state though even here there can arise considerable doubts as to the interpretation of the results due to uncertainty concerning the number and relative importance of the hydrogen bonded species present in the liquid. This is because liquids, which hydrogen bond in their pure state, tend to form a variety of different polymeric units all possessing their own particular vibrational frequency and band intensity. These polymeric bands usually merge together to give one broad featureless band whose vibrational frequency, in so far as it can be measured, is the average of all the individual vibrational frequencies present. This makes the problem of obtaining quantitative information from such spectra exceedingly difficult. The most effective way of overcoming this problem is to study the hydrogen bonded substance in dilute solution. This method allows one to control, to a considerable extent, the actual species present. At higher concentrations, solute-solute interactions interfere and interpretation becomes increasingly more complex. When one is studying solutions it is important to specify three conditions, the concentration, the temperature and the solvent as all three can seriously affect the type and degree of hydrogen bonding occuring in the solution. As a result of the low energy involved in hydrogen bond formation, it is to be expected that a change of a few degrees in the temperature of the solution will seriously affect the position of the equilibrium in the hydrogen bonded system :-

$$A - H + B \rightleftharpoons A - H\cdots\cdots\cdots B$$

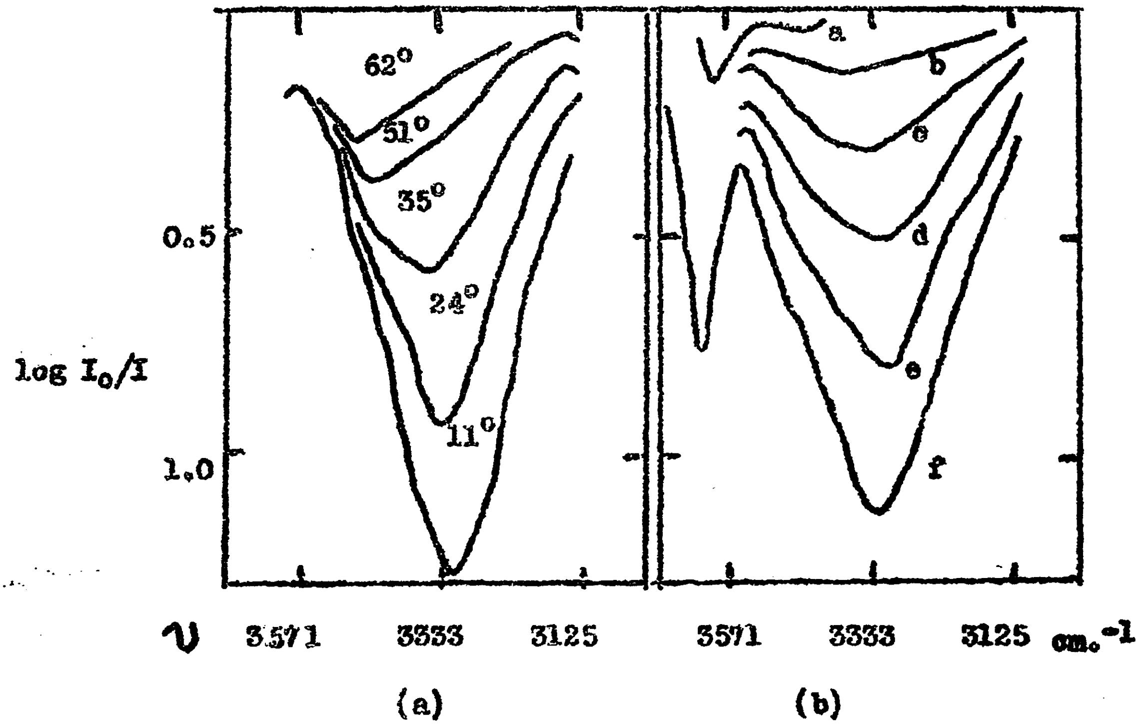
In addition it is important to note that many solvents which were once thought to be inert such as chloroform and benzene are now known to act as proton or electron donors in hydrogen bonding as has been shown by West[83] for solutions of phenols in olefinic and aromatic solvents where there is a two or three per cent downward shift in frequency of the O-H vibrational frequency in the presence of these solvents. Since much solution work involves the study of solute-solvent interactions and is therefore carried out at low concentrations it is essential to remove all traces of water which may have been absorbed as this can considerably alter the results obtained.

Hydrogen bonding in the solid state has also been studied by infrared spectroscopy and here the problem of interpretation arises as a consequence of crystal interactions which produce frequency shifts, intensity changes and band splitting and which hinder the assignment of purely hydrogen effects. A variety of methods have been used for the study of hydrogen bonding in solids but all have been shown to have disadvantages and it is usually necessary to employ all of these techniques in conjunction. Low melting solids can be studied by melting a sample of the solid on a sodium chloride plate and, after placing the other plate on top of this, allowing the compound to solidify. This produces a thin crystalline film which can then be studied. Unfortunately the molecule in this case has a fixed orientation with regard to the infrared radiation causing considerable changes in the intensities of the molecular frequencies. This fixed orientation of the molecule in the solid state is overcome by having in essence a large number of tiny crystals all randomly oriented and this is achieved by the use of a "mull" or of a "potassium chloride pressed disc". The former method consists of mixing thoroughly the solid with a liquid paraffin (Nujol). It has the disadvantage that the C-H stretching vibrations of the paraffin tend to obscure those of the hydrogen bonded solid. The latter method consists of grinding a small amount of the solid compound with dry potassium chloride and pressing the resultant mixture to give a transparent disc. This method suffers from the disadvantage that different grinding or preheating treatment and the use of potassium bromide instead of potassium chloride can have a drastic effect on the spectrum[84].

A more recent approach to the infrared study of hydrogen bonding has the advantage that the stretching frequencies of the A-H bond are relatively narrow[85]. This is the "Matrix Isolation" technique which involves the freezing of a gaseous mixture of the hydrogen bonded substance in a large amount of an inert gas at a temperature low enough to prevent diffusion in the matrix. Van Thiel, Becker and Pimentel[86] have shown, using this technique, that the hydrogen bonded dimer of water does not

Figure 8

Effect of Temperature and Concentration on Hydrogen Bonding



Infrared spectra of benzyl alcohol in CCl_4

(a) At various temperatures (11 - 62°C, 0.24 M)

(b) At various concentrations: a. 0.0486 M; b. 0.0972 M; c. 0.155 M; d. 0.194 M; e. 0.243 M; f. 0.278 M.

have an open chain or bifurcated structure but is almost certainly cyclic and that under these circumstances the hydrogen bond is non-linear.(Fig.7) This technique offers a number of important theoretical and experimental advantages as in the narrowing of the hydrogen bonded A-H vibrational bands but it requires rather complex low - temperature apparatus and very careful temperature control to avoid diffusion in the matrix.

So far this discussion has concentrated on the various techniques used in infrared spectroscopy and on the precautions which must be taken in applying them to the study of hydrogen bonding. The effect of temperature, concentration and solvent on the infrared spectra of hydrogen bonded complexes has already been mentioned and will now be dealt with in more detail.

a) THE EFFECT OF TEMPERATURE

For both pure liquids and solutions the raising of the temperature by 20 - 50°C considerably reduces the intensity of the association band of the stretching vibration. This is particularly obvious in the spectrum of benzyl alcohol in carbon tetrachloride over the temperature range 11°-62°C (Fig.8a)[87]. The sensitivity of the A-H stretching vibration(ν_s) to temperature changes has been explained for pure liquids and for highly concentrated solutions on the following basis :-

1) Hydrogen bonded systems involve monomeric and polymeric species in rapid equilibrium.

2) Each polymer has a characteristic A-H stretching frequency and the higher the polymer the lower is this frequency.

3) Each polymer has a characteristic absorption coefficient A and the higher the polymer the higher this is.

4) A small shift in the equilibrium produces a considerable spectral change.

In these circumstances the temperature effect appears to be due chiefly to a shift in the equilibria involving a number of polymers each with its own frequency and absorption intensity. Although this effect is undoubtedly important another temperature effect of even greater significance in the quantitative study of hydrogen bonding has been proposed by Finch and Lippincott[88]. These workers showed that both the A-H stretching frequency and the absorption intensity of each hydrogen bonded species could change with temperature. This effect is particularly noticeable in dilute solutions and has been used by Cole and MacRitchie[89] to determine hydrogen bond strengths in solutions of trans-dihydrocryptol in dioxan. By determining the equilibrium constants for hydrogen bonding at different temperatures it is possible to obtain the enthalpy of the hydrogen bond. The most significant results are undoubtedly obtained at low concentrations since there is then only two species present, the monomer and either the dimer or a solute-solvent complex.

b) THE EFFECT OF CONCENTRATION

The same notions which were used to explain the effect of temperature on pure liquids or highly concentrated solutions can also be applied to explain the effect of concentration. This type of effect was first noted by Freymann[80] in an investigation of the effect of temperature and concentration on solutions of alcohols in carbon tetrachloride and in benzene. Fig. 8b illustrates the effect of altering the concentration of benzyl alcohol in carbon tetrachloride as solvent[24]. As in most examples of hydrogen bonding the infrared spectrum in Fig. 8b shows the presence of two peaks, one a sharp band at high frequency which represents the unbonded A-H stretching vibration and a rather broad peak at a somewhat lower frequency representing the bonded A-H stretching vibration. A change in the concentration produces considerable changes in the relative intensities of the "free" and "bonded" peaks. At low concentration the spectrum consists mainly of the "free" peak with only a trace of the "bonded"; this corresponding to a solution in which the benzyl alcohol exists mainly as monomer, only a small proportion being hydrogen bonded. At high concentration, however, though both peaks are still present the dominant one from the point of view of intensity is the "bonded" peak indicating that the equilibrium has swung in favour of hydrogen bonded benzyl alcohol as against the monomeric alcohol. Since the carbon tetrachloride is virtually inert the hydrogen bonding indicated in Fig. 8b must be solute-solute bonding. The control of the extent of hydrogen bonding by concentration effects is the most commonly used method of obtaining quantitative data such as association constants. The nature of the complex can be determined by taking spectra for the solute at a number of different concentrations and different path lengths such that the number of molecules in the path is kept constant. If no change in intensity is noted then the complex must involve only one molecule of the solute.

c) THE EFFECT OF THE SOLVENT

From the point of view of hydrogen bonding there are two classes of solvent; those which do not form hydrogen bonds with the solute and are considered to be inert; and those which can interact with the solute. Originally many solvents such as chloroform and benzene were thought to be inert but there is now clear evidence that there are in fact very few solvents which can be so described. This solvent interaction can be shown in the following way. At high concentration it has been shown that the environmental influence of a particular solvent can exert considerable influence on the distribution of monomeric and polymeric species. However even at low solute concentration when no polymer exists it is still evident that different solvents produce different spectra for the same solute. It would appear that every feature of the A-H stretching vibration(ν_s) is sensitive to solvent effects. This effect is more clearly understood if the solvent can be regarded as a potential proton or electron donor to which the solute molecule can bond, thus producing a solute-solvent hydrogen bonded complex. Although this solvent interaction can complicate the interpretation of the spectrum if one is studying polymeric species at high concentrations of solute it becomes of considerable importance in quantitative studies at low solute concentration. This is because a dilute solution of, say, a proton donating solute in an electron donating solvent produces a well defined species which is relatively easy to interpret and provides the most accurate and informative data on hydrogen bonding equilibria in solutions. Much of the hydrogen bonded studies of solutions have been carried out using binary mixtures of solvents as in the investigation of hydrogen bonding in carboxylic acids using a carbon tetrachloride - triethylamine solvent[90]. However the authors of the above work noticed that the spectra obtained under these conditions were those of hydrogen bonded complexes between the triethylamine and the carboxylic acid. This type of solute-solvent interaction undoubtedly invalidates much of the earlier work done with supposedly inert solvents. It is now accepted that very few solvents can be considered to be truly inert and much effort has recently gone into attempts to find a satisfactory theory of solute-solvent effects[91]. However the principal solute-solvent effect of interest here is where the solvent acts as an electron donor in hydrogen bonding. This aspect of solution studies of hydrogen bonding is becoming increasingly important, the most comprehensive studies having been carried out by Huong, Lascombe and Josien[92]. These workers attempted to explain the "solvent shifts" on the basis of a theory developed by Kirkwood[93] and Bauer and Magat[23] which will be dealt with later.

So far this discussion has dealt with the various physical factors which can alter the appearance of an A-H stretching vibration in the infrared spectrum. The particular changes in the vibrational band itself will now be discussed and an attempt will be made to show that they provide a means of determining the extent and the strength of hydrogen bonding. The two most prominent effects of hydrogen bonding on the A-H stretching vibration(ν_s) are the shifting of the vibrational band to lower frequency and an increase in the intensity of the band. Another effect which has been related to hydrogen bonding has been the increase in the half-band width($\nu_{\frac{1}{2}}$) which is of course a measure of the broadening of the band. The drop in frequency of the vibrational band($\Delta\nu_s$) on hydrogen bonding has been the effect most studied and numerous attempts have been made to use this effect as a quantitative estimate of the hydrogen bonding.

The change in ν_s which can be obtained by altering the temperature, concentration or solvent has been shown to have at least a rough correlation with a number of the physical properties of hydrogen bonded systems. The attempt to relate $\Delta\nu_s$ to the physical properties of such systems becomes extremely difficult when the system consists of a series of polymers in equilibrium since all these polymers will have their own distinct physical properties. For this reason attempts to use $\Delta\nu_s$ for quantitative purposes has been restricted almost entirely to very dilute solutions where one is usually dealing with a single hydrogen bonded species such as a solute-solvent complex.

Before going on to discuss the relationship between $\Delta\nu_s$ and the physical properties of hydrogen bonded systems it is advisable to note that, in general,all vibrational stretching modes move to lower frequencies in going from the vapour state to the liquid state and this phenomenon has been studied by Kirkwood[93] and Bauer and Magat[23]. On the basis of rather fragmentary evidence the above authors founded their theory on the notion of a simple diatomic vibrator situated within a hollow cavity in a solvent medium of macroscopic dielectric constant ε. They considered that the frequency shift resulted from an instantaneously induced polarization of the surrounding medium by the vibrating dipole and derived the expression:-

$$\Delta\nu/\nu = C(\varepsilon - 1)/(2\varepsilon + 1) \qquad \ldots\ldots\ldots (6)$$

where C is a constant which depends on the dimensions of the solute molecule and on the detailed nature of the dipole model. Josien and Fuson[94] have shown that except for a few non-polar solvents such as cyclohexane this theory was quite inadequate. A more recent investigation by Bellamy,Hallam and Williams[95] involved a direct comparison of the relative frequency shifts of two different solutes in the same series of solvents,the solvents used covering a whole range of polarities. Using this method one finds that there is a smooth transition in passing from highly polar solvents such as triethylamine through to non-polar solvents such as carbon tetrachloride and this served to indicate that the type of interaction observed was fundamentally the same in all cases,differing only in the magnitude of the interaction energies involved.

Relationships have been obtained,by a variety of workers, between the frequency shifts $\Delta\nu_s$ of the A-H stretching vibration and the energy of the hydrogen bond(ΔH), the half band width($\nu_{\frac{1}{2}}$), the intensity change(ΔB), the base strength of the solvent or the acid strength of the solute and the A......B distance. Badger and Bauer[96],for instance,claimed to have discovered a direct relation between the frequency shift($\Delta\nu_s$) and the enthalpy or strength of the hydrogen bond(ΔH). More precisely they stated that there appeared to be a direct relationship between $\Delta\nu/\nu_s$ and the energy of the hydrogen bond. There has,however,been considerable doubt as to the validity of this relation and Pimentel and McClellan[6] were unable to obtain a linear relation for the case of phenol in a variety of bases. Recently Joesten and Drago[60] have obtained such a linear relationship for phenol in certain nitrogen and oxygen bases. It would appear from their work that this relation only holds for very restricted systems. In other words a linear relationship is only observed for a number of systems in which the proton and electron donors are very similar.

Lord and Merrifield[97] obtained a linear correlation between the frequency shift($\Delta\nu_s$) and the A····B distance and implied that this relationship was general in that it could be applied to all A·····B hydrogen bonds. However Nakamoto,Margoshes and Rundle[98] have shown that there is a distinct relationship between the frequency shift($\Delta\nu_s$) and the length of the A····B bond(R) for each type of hydrogen bond. They have also shown that intramolecular hydrogen bonds do not show the same kind of $\Delta\nu_s$-R relationship as do the intermolecular hydrogen bonds. It would appear that as the A····B distance increases then the frequency shift approaches zero asymptotically and this fits in with the "covalent" description of the hydrogen bond as postulated by Lippincott and Schroeder[29]. Attempts at deriving relations between the frequency shift and acid or base strengths have only been successful where the systems studied have been very similar.

The increase in the band width($\nu_{\frac{1}{2}}$) was observed to be a feature of hydrogen bonding in a number of the preliminary investigations of this form of bonding by infrared spectroscopy but it is only recently that it has been systematically studied. Huggins and Pimentel[99] have found a very good linear relationship between the frequency shift($\Delta\nu_s$) and the half band width($\nu_{\frac{1}{2}}$). Though this correlation holds for intermolecular systems it does not appear to do so for intramolecular hydrogen systems and may therefore be used as a method of distinguishing between the two types of hydrogen bond. There is also a relation between the frequency shift($\Delta\nu_s$) and the change in the integrated absorption intensity of the band(ΔB). The results obtained by those workers attempting to obtain such a correlation have tended to vary quite considerably, partly because of the extreme sensitivity of the intensity to temperature changes and partly due to the integration of the intensity being carried out over different limits. The data obtained by Huggins and Pimentel[99] indicated that there is a direct simple relationship between $\Delta\nu_s$ and ΔB and also showed a considerable difference in the behaviour of intramolecularly bonded compounds as compared with the intermolecularly bonded ones.

Despite the fact that the shift of the vibrational frequency on hydrogen bonding has received the most intensive study it is by no means the most sensitive indication of hydrogen bonding available to the infrared spectroscopist. It has already been noted that the integrated absorption intensity of the A-H stretching mode can increase by as much as an order of magnitude on hydrogen bond formation. This change in the intensity(ΔB), which, as we have already seen, bears a linear relationship to the frequency shift($\Delta\nu_s$), appears to be just as much a characteristic feature of hydrogen bonding as is the frequency shift itself. The intensity change of the absorption band on hydrogen bonding was neglected in much of the earlier work because the increased breadth of the band on hydrogen bonding tended to mask the change in intensity of the band. Any small change in the hydrogen bonding equilibrium caused by either temperature, concentration or solvent effects is immediately paralleled by a change in the integrated absorption intensity of the band. This remarkable behaviour of the intensity of the A-H stretching vibration appears to be regulated by the charge distribution in the hydrogen bond and its movement during vibration. Huggins and Pimentel[39,99] have studied the ratio of the absorption intensity after hydrogen bond formation to that of the monomer in an inert solvent and have shown that except for those cases in which the interaction is very weak the intensity ratio is at least five, which makes the intensity effect by far the most sensitive of the infrared effects. The integrated absorption intensities of the A-H stretching vibration have been used by Brand, Eglinton and Morman[1] to determine the association constant for the benzoyl acetylene - ether complex and by Cole and MacRitchie[89] to determine the strength of the hydrogen bond formed between trans-dihydrocryptol and dioxan.

Many of the early workers in this field neglected the intensity change of the A-H stretching frequency because of the simultaneous broadening of the band. This broadening of the infrared absorption band is denoted by an increase in the half band width($\nu_{\frac{1}{2}}$) and, along with the frequency shift ($\Delta\nu_s$) and the increase in absorption intensity(ΔB), has come to be regarded as definitive evidence for the presence of a hydrogen bond. The broadening of the A-H stretching vibration is observed in liquids, solids, gases and solutions on hydrogen bonding. The wide degree of correlation between the frequency shift and the band broadening is indicative of the fact that most if not all hydrogen bonded systems show this type of behaviour. This band broadening also appears to be unique to hydrogen bonded systems and is important, therefore, in determining not only the presence of a hydrogen bond but also the detailed nature of the bonding. A number of reasons have been put forward in an attempt to explain this unusual broadening effect and three of these will be discussed here. The first explanation of this effect was proposed by Badger and Bauer[100] and this was that the broadening was due to interaction between the A-H stretching vibration and the low frequency deformation vibrations of the hydrogen bond. Some support has been lent to this view by work on the carboxylic acids which showed constant intervals in the fine structure of the broad band. However, though this theory is still widely held, there is considerable uncertainty with regard to the value of the intervals observed and in many cases the selection of these values appears to be quite arbitrary. Fénéant[101] has postulated that the broadening is due to the superposition of a number of sharper bands belonging to a variety of hydrogen bonded species. Though it is possible to explain some of the broadening in pure liquids and highly concentrared solutions by this effect it has been noted in dilute solutions, where only one hydrogen bonded species is known to exist, that the bonded A-H stretching vibration is still very broad. Sheppard[102] considers that there are two factors contributing to the broadening of the A-H stretching vibration. The first contribution arises from a strong anharmonic interaction between the A-H stretching vibration(ν_s) and the A····B stretching vibration(ν_σ) with the latter vibration varying over a considerable range, due to thermal effects on the hydrogen bond, thus creating a wide range of frequencies. The second contribution is considered to come from Fermi resonance of the A-H stretching vibration with various overtones and combination bands of similar frequency. Sheppard considered that the combination of these two factors gave a workable method of understanding the broadening of vibration bands on hydrogen bonding and also listed a number of mechanisms which have been put forward to explain the smooth contours of many of these bonded A-H stretching vibrations. There is as yet, however, no completely consistent explanation of the broadening of the

A-H stretching vibration on hydrogen bonding.

The only vibrations discussed till now have been those involving the proton taking part in the bond but it is obvious that there will also be changes in those vibrations of the base mostly involved in the bonding though the effects will be somewhat smaller. There is fairly substantial support for the belief that spectral changes in the base occur on hydrogen bonding though of course most of the work has involved a study of the A-H vibrational modes. Most of this information comes from results obtained with carboxylic acids,ketones and esters. In all these cases it has been shown that the carbonyl vibrational stretching frequency shifts to a lower frequency and increases in intensity on hydrogen bonding. These effects are however much weaker and less conclusive than those observed for the A-H stretching vibrations.

In conclusion,therefore,the infrared stretching vibration of the A-H group has been studied in considerable detail and can be strongly indicative of the presence of a hydrogen bond. Shifts to lower frequencies,increases in the intensity and half band width are together a definitive criterion of hydrogen bonding and are all known to be sensitive to changes in the temperature,concentration or solvent. All three criteria have been used to obtain qualitative and quantitative evidence of the hydrogen bonding equilibria though there is as yet considerable difficulty in understanding their true physical significance. The most specific and sensitive of these criteria is the change in the integrated absorption intensity of the A-H stretching vibration on hydrogen bonding and it provides the best quantitative estimates of the equilibrium constants of hydrogen bonded systems. The measurement of these association constants at a variety of temperatures provides one with a method of obtaining thermodynamic paramete for the hydrogen bond.

II. 4. NUCLEAR MAGNETIC RESONANCE TECHNIQUES

As has already been noted, though there are a number of techniques which can be used to indicate the presence of association there are very few which will also show the specific involvement of hydrogen in that association and therefore verify that one is indeed studying hydrogen bonding. Infrared spectroscopy which is one such technique has already been dealt with in the preceding section and has been used as a specific test of hydrogen bonding for almost thirty years. Nuclear magnetic resonance can also be used as a specific test for hydrogen bonding and, although its application to this field is much more recent[103] than that of infrared spectroscopy, it has proved to be as useful a tool as the latter for the investigation of hydrogen bonding.

For a detailed account of the theory behind nuclear magnetic resonance the standard text of Pople, Schneider and Bernstein[104] is available and that book also provides a discussion of the application of nuclear magnetic resonance to hydrogen bonding. In infrared spectroscopy the basic phenomenon is the vibration of the atoms in the molecule with respect to one another. In nuclear magnetic resonance however the basic phenomenon is the reorientation of the axis of nuclear spin. Since all nuclei are charged, the combination of this charge and the spin allows the assignment to each nucleus of a definite angular momentum and magnetic moment. The total angular momentum of a nucleus is quantised into a number of components, this number being related to the nuclear spin quantum number(I). It should be noted however that this quantisation only takes place in the presence of an external magnetic field so that the resonance of the nucleus depends on the magnetic moment of the nucleus and on the strength of the external magnetic field. This resonance effect, when obtained for individual or isolated nuclei, is of little interest to the chemist. Its interest and usefulness lies in the fact that, in the molecule, the electronic environment of the nucleus modifies the magnetic field "seen" by the nucleus and this electronic environment reflects the chemical bonding of the molecule. The influence of the electrons on the position of resonance of the nucleus is a phenomenon known as the Chemical Shift and is proportional to the applied field(H_o). The chemical shift is usually obtained from measurements carried out on high resolution equipment with magnetic fields of 10,000 or 14,000 gauss and radiofrequencies of 40 or 60 megacycles for the case where the nucleus being studied is hydrogen. Since the magnetic field applied to the sample must be very homogeneous the size of the sample used is limited and investigations are usually carried out on pure liquids or on solutions. The sensitivity of the equipment at present available usually places a lower limit on the concentration of about 0·1 molar.

Chemical shifts are calculated on the basis of the following equation:-

$$\delta = (H_s - H_R)10^6/H_R \qquad \ldots\ldots\ldots\ldots(7)$$

where δ is the chemical shift;

H_s is the field required for resonance of the sample;

H_R is the field required for resonance of a reference compound.

In actual practice results are often expressed in terms of cycles per second to which the chemical shift(δ) in the above equation can be converted by dividing the right-hand side of equation (7) by the radiofrequency expressed in megacycles per second. The reference standard used is of considerable importance and a variety of compounds have been used in the past as a standard. The standard reference compound now used for organic compounds in which one is studying the hydrogen nuclei is tetramethylsilane and the scale used in conjunction with this reference is the τ scale defined as follows:-

$$\tau = 10 - \Delta\nu_{Me_4Si} \times 10^6 / \text{Oscillator frequency in c/s} \quad .....(8)$$

where $\Delta\nu_{Me_4Si}$ is the difference between the proton signal of the compound being studied and that of tetramethylsilane measured in cycles per second.

The parameter τ is given in parts per million(p.p.m.) and is such that absorption at a higher field corresponds to a more positive τ value. However other reference standards have been used and, in the study of hydrogen bonding, will continue to be used purely for convenience. In many cases cyclohexane has been used as a reference standard and, being an inert solvent, is particularly suitable for hydrogen bonding studies. Other standards used have been benzene, water and chloroform but because of their proton or electron donating capacity they are unsuited for hydrogen bonding problems. These remarks refer particularly to internal references; that is reference compounds which are actually dissolved in the sample. When external references are used the reference compound is contained in a sealed capillary tube within the sample tube. Though this eliminates any possible interaction between the reference and the sample the fact that the bulk susceptibilities of the sample and the reference are not the same means that the fields seen by them are different and a correction for the bulk susceptibility must be introduced.

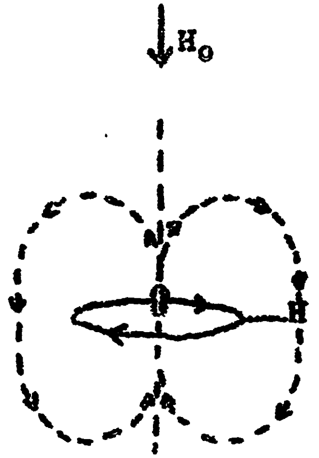
As with infrared spectroscopy the choice of solvent is extremely important. In nuclear magnetic resonance spectroscopy it is particularly important to choose a solvent which has the minimum number of hydrogen atoms as the presence of such atoms tends to obscure part of the spectral range. If this is impossible it is then important to choose a solvent whose proton signals will not interfere with the solute proton resonance signals. In hydrogen bonding studies unless one is conducting a study of solute - solvent hydrogen bonding it is important to pick an inert solvent which will not interfere with the association being studied. Carbon tetrachloride and cyclohexane are the most suitable solvents though even these two have disadvantages as in the streng proton resonance signal of cyclohexane and in the apparent participation of carbon tetrachloride in some form of association.

Evidence of hydrogen bonding using nuclear magnetic resonance is supplied by the change in the chemical shift of the proton involved in the hydrogen bond. As has already been indicated the chemical shift is related to the extent to which the proton is shielded by the electrons in its vicinity. The greater the degree of shielding then the greater must be the external magnetic field if the proton is to achieve resonance and, as a result, the proton resonance signal moves to higher field. Where the shielding supplied by the electrons is small the external magnetic field needed to make the proton resonate is smaller and the proton resonance signal moves to low field. Proton resonance signals are normally displaced to lower fields on the formation of a hydrogen bond[105]. However investigations of the hydrogen bonding of chloroform to aromatic solvents in which the "pi" electrons acted as electron donors showed a shift of the proton resonance signal of the chloroform to high field.[63] This displacement of the proton resonance signal to high or low field on hydrogen bonding has been investigated by Pople[106] who claims that, in the system A-H····B, the B system will disturb the electronic structure of the A-H bond and consequently modify the currents induced in that bond by the primary magnetic field,and thus produce a change in the screening of the proton. If the hydrogen bond is thought of as being partly covalent then electrons will be donated from the lone pair of the B system into the A-H bond. This would lead to an increase in the electron density around the hydrogen and therefore to an increase in the screening,which is opposite to the experimental observations. If however the hydrogen bond is considered to be electrostatic in nature then the strong electric field thus created would inhibit the diamagnetic current of the proton and thus decrease the shielding. This does not mean that the electron density at the proton is less since the nuclear magnetic resonance method does not measure that quantity directly and it is therefore possible that there may be an increase in the electron density at the proton and also a decrease in shielding on hydrogen bond formation. Ramsey[107] has attempted to provide a theoretical treatment of this effect and has described the diamagnetic shielding in terms of an expansion involving the inverse power of ρ where ρ is itself the inverse of the distance of the electron from its nucleus. The expression is of the form :-

$$\delta = f_1(1/\rho) - f_2(1/\rho^3) + \text{---------} \qquad \text{.......}(9)$$

If this equation was dominated by the first term then the magnetic shielding would be determined by the electron distribution in much the same way as is the energy and this would imply that one could obtain a good correlation between the chemical shifts and a number of physical properties such as the electronegativity. This is found not to be the case for protons. From the negative sign of the second term it can be seen that a higher electron density (weighted by the $1/\rho^3$ term) would produce a shift towards lower field. Despite the apparent similarity of the treatments of Pople and

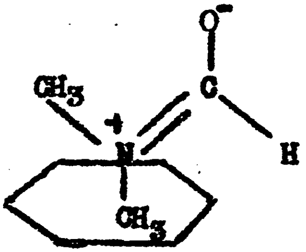
Figure 9



Ring Currents in the Aromatic Ring

Figure 10

Complex of N,N Dimethylformamide in Benzene



Ramsey the direction of the displacement of the proton resonance signal cannot be said to provide definite evidence in favour of the electrostatic nature of the hydrogen bond. Since the shielding of the external magnetic field depends not so much on the density of the electrons as on their distribution round the nucleus a satisfactory theory of the proton chemical shift will probably depend on a more exacting description of the electron distribution in the hydrogen bond.

So far the type of displacement of the proton resonance signal which has been discussed is a displacement to low field resulting from the bonding of the hydrogen to a particular atom. There is however another form of hydrogen bonding in which the hydrogen bonds to "pi" electron systems such as that in benzene and in these cases the shift is to high field. Of course, if the aromatic molecule possesses an electron donating substituent such as a hydroxyl group, the A-H group will tend to bond to that substituent and will therefore approach the aromatic ring from the side. If however there is no such substituent attached to the ring the active hydrogen bonds to the "pi" electrons of the aromatic ring and therefore forms a bond perpendicular to the plane of the ring. What is of interest is that, where the bonding is to a substituent attached to the ring, the proton resonance signal moves to low field while if the bonding is to the "pi" electrons then the proton resonance signal is displaced to high field. These different effects can be explained in terms of the large anisotropy in the magnetic susceptibility of aromatic molecules which is commonly referred to as the " ring current " effect[108]. In order to illustrate how the ring current effect influences nuclear magnetic resonance measurements one can consider a very simple model as shown in Fig. 9.

In this model the aromatic ring is regarded as a simple circular conducting loop. A magnetic field H_0 applied normal to this loop induces a circular current which generates a secondary magnetic field opposed in direction to that of the applied field. This secondary field can be approximated very crudely by a dipole placed at the centre of the ring. This dipole has magnetic lines of force as illustrated by the broken lines in the diagram. Suppose one is measuring the proton resonance position of the hydrogen atoms in benzene, one of which is shown here. The component of the secondary field is then in the same direction as the applied field; in other words it enhances the applied field H_0. Therefore to bring this proton into resonance will require an external field H which is less than H_0 and the resonance is shifted to lower applied field. On the other hand protons which find themselves in positions immediately above or below the plane of the aromatic ring will have their resonances shifted to higher applied field. This is because here the component of the secondary field is opposed to that of the applied field and hence, to bring such protons into resonance, one has to apply a field H greater than H_0. Only one orientation of the aromatic ring with respect to the external field has been considered. If the external field is applied parallel to the plane of the ring there will be no induced ring current and no resonance shifts. So even after averaging over all directions the net effect observed will still be as indicated.

This simplified theory allows one to explain why protons which hydrogen bond to groups attached to the benzene ring have their resonance signal shifted to low field whereas those which bond themselves to the "pi" electron cloud of benzene, say, have their resonance signal displaced to high field. With regard to the latter phenomenon, the ring current theory has been applied by a number of workers to the problem of determining

Table 7

Thermodynamic Parameters for Chloroform - Solvent Complexes

Thermodynamic Parameters	Chloroform - Acetone	Chloroform - Triethylamine
$K(28^{\circ}C)(m.f.)^{-1}$	1.8	3.0
$K(-25^{\circ}C)(m.f.)^{-1}$	4.0	12.0
ΔH kcals/mole	-2.5	-4.0

Table 8

Thermodynamic Parameters for Fluoroform - Tetrahydrofuran

Thermodynamic Parameters	Fluoroform - Tetrahydrofuran	Fluoroform-d_1 - Tetrahydrofuran
$K(25^{\circ}C)(m.f.)^{-1}$	4.77 ± 0.02	4.95 ± 0.02
ΔH kcals/mole	-(2.593 ± 0.024)	-(2.727 ± 0.022)

Table 9

Thermodynamic Parameters for Methyl Iodide, Iodoform - Toluene

Thermodynamic Parameters	Methyl Iodide - Toluene	Iodoform - Toluene
ΔH kcals/mole	1.3 ± 0.5	1.6 ± 0.2
ΔS e.u.	4.9 ± 0.4	6.4 ± 0.2

the distance of the proton from the plane of the ring. The most rigorous treatment has been that of Johnson and Bovey[135] who considered the "pi" electron system as consisting of two doughnut shaped rings above and below the plane of the molecule and obtained an equation as follows:-

$$\delta = (ne^2/6\pi mc^2a) \cdot (1/((1+\rho)^2+z^2)^{\frac{1}{2}}) \cdot (K+(1-\rho^2-z^2)E/((1-\rho)^2+z^2) \quad .(10)$$

where δ is the chemical shift in p.p.m.; n is the number of free "pi" electrons; m and e are the mass and charge of an electron; a is the radius of the benzene ring and K and E are complete elliptic integrals. ρ is a measure of the distance of the proton from the centre of the benzene ring in that plane and z measures the distance from the benzene ring in a perpendicular direction. On the basis of the above equation one can obtain the distance of the proton from the benzene ring and it is found, rather surprisingly, that the values obtained are remarkably similar to those obtained by Reeves and Schneider[63] using a much simpler approach.

Nuclear magnetic resonance spectroscopy, in so far as it has been utilised in the study of hydrogen bonding, has been concerned, mainly, with the weaker forms of hydrogen bonding. For instance much of the evidence given previously for the assertion that chloroform could act as a proton donor or that aromatic solvents could act as electron donors in hydrogen bonding has come from this source. Huggins, Pimentel and Shoolery[40] not only showed that chloroform could act as a proton donor in hydrogen bonding but also obtained values for the association constants of chloroform - -acetone and chloroform - triethylamine complexes at different temperatures and were able, therefore, to give an estimate of the hydrogen bond strength in these complexes. (See Table 7)

The hydrogen bonding of chloroform to a variety of aromatic molecules and to a number of olefines was studied by Reeves and Schneider[63] who found a shift in the proton resonance signal to high field in those aromatic solvents such as benzene and toluene where the bonding was to the "pi" electrons and a shift to low field in the case of nitrobenzene where the proton bonded to the nitro group and in the case of the olefines where the bonding was again to the "pi" electrons of the double bond. These workers measured the shift in the proton resonance signal relative to cyclohexane as an internal reference and as an inert solvent. Korinek and Schneider[105] have shown that the following solvents reduced the shielding of the proton in chloroform in the order shown:-

$Et_3N > Me_2CO > Et_2O > PrCN > PrF$

This could be regarded as a measure of the electron donating capacity of these solvents in hydrogen bonding. Recently Creswell and Allred[109] have studied the system chloroform - benzene - cyclohexane and have obtained the following parameters:-

$K_{25^oC} = 1.06 \pm 0.30(\text{m.f.})^{-1}$; $\Delta H^o = -1.97 \pm 0.35$ kcals/mole;

$\Delta S^o_{25^oC} = -6.5 \pm 0.5$ cals. mole^{-1} deg.$^{-1}$.

In a later paper the same authors[41] investigated the association between fluoroform and tetrahydrofuran and the association between fluoroform-d_1 and tetrahydrofuran obtaining the parameters noted in Table 8.

Both investigations employed the following theoretical treatment. The association constant K was expressed in terms of an equation:-

$$K = C(S + A + B - C)/(A-C)(B-C) \qquad \text{........(11)}$$

where C is the number of moles of complex formed; S is the number of moles of inert solvent; A is the initial number of moles of the halide and B is the initial number of moles of benzene or tetrahydrofuran. The shift in the proton resonance signal was equated with the amount of complex formed as follows:-

$$\delta_{observed} = (C/A)\delta_{complex} + ((A-C)/A)\delta_{free} \quad ......(12)$$

or $$\delta_{observed} = C/A(\Delta) + \delta_{free} \quad ....(13)$$

where Δ is the hydrogen bond shift ($\delta_{complex} - \delta_{free}$).

For assumed values of the association constant K the fraction C/A was evaluated from equation (11). The plot of $\delta_{observed}$ as a function of C/A was a straight line only for the correct value of K. After K was determined to within 0·10 (m.f.)$^{-1}$ the Δ and δ_{free} were obtained from the slope and intercept respectively. Though nuclear magnetic resonance has been used chiefly for the study of hydrogen bonding in solutions it has also been applied to pure liquids though this involves more complex problems of analysis due to the variety of hydrogen bonded forms often found in these pure liquids. Feeney and Sutcliffe[110] postulated a monomer-tetramer equilibrium for diethylamine on the basis of proton resonance studies at room temperature and at the melting point of the diethylamine and obtained a value of 1·7 kcals/mole of tetramer for the heat of formation of the tetramer itself. Hydrogen bonding in carboxylic acids has been investigated by Reeves[62] and Oki and Iwamura[111] have applied nuclear magnetic resonance to the study of intramolecular hydrogen bonding between hydroxyl groups and "pi" electron systems in tertiary unsaturated alcohols.

These hydrogen bonded systems in which an ethynyl hydrogen acts as the bonding proton in hydrogen bonding have also been investigated by nuclear magnetic resonance. Nakagawa and Fujiwara[52] noted that the proton resonance signal of the ethynyl hydrogen in phenyl acetylene was shifted to low field in the presence of solvents such as triethylamine, ether or acetone and concluded that this shift was due to hydrogen bonding between the acetylenic proton and the oxygen or nitrogen atoms of the solvent. They also noted that where benzene was the solvent the shift was to high field and postulated that, in that case, bonding was to the "pi" electrons of the benzene. Phenyl acetylene was shown to be self associated in the pure liquid from the fact that in the inert solvents, cyclohexane and carbon tetrachloride, the ethynyl proton resonance signal shifted to high field as compared with the pure liquid. This self bonding is between the ethynyl proton of one molecule and the "pi" electrons of the triple bond of another such molecule. A study of propargyl chloride, phenyl acetylene and benzoyl acetylene in a variety of solvents has been conducted by Hatton and Richards[51] using cyclohexane as both inert solvent and as internal reference. The results obtained were similar to those given by Nakagowa and Fujiwara[52] in that in aromatic solvents where the bonding was to the "pi" electrons there was an upfield shift of the ethynyl proton resonance signal whereas those aromatic solvents in which the basic group was an electron donating substituent produced a shift to low field. When thiophene was used as a solvent the shift was again to high field indicating that the bonding was to the "pi" electron system of the ring and not to the sulphur atom in the ring.

Another important point noted by Hatton and Richards[51] was that in propargyl chloride the shift to high or low field by the ethynyl proton was not only imitated but was exceeded by similar shifts in the methylene proton resonance signal. This led the authors to doubt the validity of their results as a true indication of hydrogen bonding particularly between the ethynyl proton and the aromatic "pi" electron systems. In such cases they postulated that the shifts were more likely to be due to the greater anisotropy of the solute as compared to cyclohexane in the solution. Work carried out by Abrahams[112] on methyl iodide and iodoform in various aliphatic and aromatic solvents would however suggest that the methylene protons could themselves take part in hydrogen bonding. This author considered that methyl iodide and iodoform formed solute-solvent complexes with the aromatic molecule in which the dipole axis of the solute lay along the hexagonal axis of symmetry of the aromatic ring with the solute protons towards the ring. The following table (Table 9) lists the results obtained for methyl iodide and iodoform in toluene. Abrahams also investigated the solvent anisotropy effect by comparing the shifts at low concentration of a non-polar solute in an anisotropic solvent with that of the same solute in an isotropic solvent of identical bulk susceptibility. Taking cyclohexane in benzene and cyclohexane as solvents an anisotropy shift for benzene of +0·42 p.p.m. was obtained. Abrahams also noted that solvent anisotropy effects were largely eliminated by the use of an internal reference of similar molecular dimensions to the solvent. Hatton and Richards[113] have applied nuclear magnetic resonance methods to an investigation of the shape of the complex formed between N,N dimethylformamide and aromatic solvents such as benzene. These authors found that there was a distinct difference between the high field shifts of the two methyl groups in aromatic solvents and explained this result on the basis of a preferred orientation of the N,N dimethylformamide with respect to the aromatic solvent, the two molecules being parallel to one another as indicated in Fig. 10. The bonding was attributed to the nitrogen with its fractional positive charge thus placing the α methyl group near the centre of the ring and the β methyl group some distance from the centre as shown. As a result a strong induced diamagnetic moment at the centre of the ring would then produce a bigger shift upfield for the α methyl than for the β methyl group as was observed.

In the study of hydrogen bonding by nuclear magnetic resonance techniques little information of value will be obtained if the concentration of electron donor relative to electron acceptor is kept fixed. It is essential, as was recognized initially by Huggins, Pimentel and Shoolery[40], that a range of concentrations must be studied. Though some work has been carried out on the measurement of association constants at different temperatures much remains to be done and this method of investigation of hydrogen bonding will not be fully effective until this has been done. This technique probably rivals infrared spectroscopy as a means of studying hydrogen bonding and will probably provide much new information on the redistribution of the electrons on hydrogen bond formation. At the present however it has a number of disadvantages as compared with infrared spectroscopy:-

1) Different hydrogen bonded complexes cannot be individually examined.
2) Higher concentrations are necessary.
3) Gas and solid samples are not easily studied.

The last two of these disadvantages are however gradually disappearing with the advent of more advanced instrumentation. It is undoubtedly true, however, that the combination of nuclear magnetic resonance and infrared spectroscopy afford considerable scope for the development of the study of hydrogen bonding.

II. 5. DIFFRACTION TECHNIQUES

So far attention has been confined to the hydrogen bond in pure liquids and in solutions and little attention has been paid to this phenomenon as it exists in the solid state though all three methods so far discussed can be applied to such an investigation. The hydrogen bond is of considerable importance when present in crystalline solids since it is possible to predict that a molecule containing both acidic and basic groups will tend to crystallise in a lattice whose structure involves and is determined by hydrogen bonds[114]. There have been a number of reviews concerned with the hydrogen bond in the crystalline state of which the one by Donohue[114] dealing with results obtained using X-ray diffraction techniques and the one by Hamilton[115] dealing with neutron diffraction results are probably the most comprehensive. The importance of the hydrogen bond, particularly in organic solids, lies in the fact that organic crystals are usually held together by weak Van der Waals interactions and the formation of a hydrogen bond can stabilise the crystal structure to the extent of a few kilocalories. This extra stability of the crystal makes itself felt in a number of physical properties of which the most obvious is the melting point of the solid. This is perhaps most noticeable in the difference between the melting point of water(273°K) and that of hydrogen sulphide(190°K) which can largely be attributed to the extra stability conferred on the lattice as a result of the strong hydrogen bonds in ice.

A number of important techniques exist for the investigation of atomic positions in a crystal lattice and all of these are important in the study of hydrogen bonding because of their ability to fix the position of the hydrogen atom relative to the other atoms in the molecule. This gives one an indication as to whether hydrogen bonding is occuring and, if it is,

Table 10

Scattering Amplitudes for X-rays and Neutrons

	X-rays				Neutrons	
$\sin\theta/\lambda$	0	0.2	0.4			
f_O	8.26	5.60	3.10	0 $(\mathring{A})^{-1}$	0.58	10^{-12} cm.
f_C	5.89	3.20	1.99		0.66	
f_H	1.00	0.50	0.14		−0.38	
f_D	1.00	0.50	0.14		0.65	

Table 11

Hydrogen Bond Lengths and Angles from Neutron Diffraction

$A-H\cdots\cdots B$	r_{A-H} $(\mathring{A})$	$r_{A\cdots\cdots B}$ $(\mathring{A})$	$\theta_{A-H\cdots\cdots B}$
$F-H\cdots\cdots F$	1.13	2.26	180°
$O-H\cdots\cdots O$	0.94–1.085	2.44–2.90	151°–180°
$N-H\cdots\cdots O$	0.99–1.02	2.91–3.034	151°–167°
$O-H\cdots\cdots N$	1.02	2.77	140°
$N-H\cdots\cdots N$	1.00	3.35	164°
$O-H\cdots\cdots F$	0.98	2.715	168°
$O-H\cdots\cdots Cl$	0.95	3.18	164°
$N-H\cdots\cdots Cl$	1.02	3.20	156°
$N-H\cdots\cdots F$	1.03	2.84	158°

information as to the strength and the length of such a bond. The methods most commonly used are X-ray diffraction and neutron diffraction the latter being the most important and definitive method available for actually locating the hydrogen position. Though neutron diffraction is the most efficient method it has the disadvantage that it requires a powerful neutron source which is not generally available and as a result the X-ray diffraction technique is the one most commonly used though it usually cannot be used to determine accurately the hydrogen positions. The difference in the ability of the two techniques to detect hydrogen atoms lies in the fact that in X-ray diffraction the scattering amplitude of an atom depends on the number of electrons surrounding it and therefore the bigger the atom the greater is its scattering factor whereas in neutron diffraction,the neutrons,although scattered by the nucleus do not depend,in any regular manner,on the size of the nucleus itself.(See Table 10)

The following table (Table 11) abstracted from the review by Hamilton[115] provides a list of r_{A-H}, $R_{A\cdots B}$ and $\theta_{A-H\cdots B}$ for different types of hydrogen bond which have been studied by neutron diffraction. It is particularly noticeable from the above table (Table 11) that by no means all the hydrogen bonds studied were linear and that in fact many of them depart some way from linearity. There also appears to be a rough correlation between the strengths of the hydrogen bonds and the $r_{A\cdots B}$ distance. In addition the shorter the $r_{A\cdots\cdot B}$ distance the more symmetrical is the hydrogen bond. From this we see that though it is obviously of some importance to determine the exact position of the hydrogen atom in the bond and though few X-ray measurements have been able to achieve this,it is still possible to measure the $r_{A\cdots\cdot B}$ distance using X-ray diffraction methods and thus obtain a measure of the strength of the hydrogen bond. It is perhaps significant that hydrogen bonds of a particular type are found to possess very similar $r_{A....B}$ distances so that this distance appears to be characteristic of the type of bond formed.

The method of structural determination known as X-ray diffraction was begun by the discovery of von Laue in 1912 that X-rays were diffracted by crystals. The subject has long been on a sound theoretical basis and the advent of computing facilities has enabled the tackling of structures which could not have been studied previously because of the labour involved and has also allowed more intensive refinement of the information available on smaller molecules. The major problem which still exists is,of course,the "phase problem" and methods for overcoming it have been proposed by numerous workers,the most well known being the Patterson method. The most important method which allows one to determine the phases is that in which there is an atom in the structure which has an atomic number high compared to other atoms in that structure. The heavy atom coordinates can be found fairly readily by Patterson methods since the heavy atom will tend to dominate the phases of the diffracted spectra. Structure factor calculations based on the heavy atom contribution alone provides a set of phase angles which can be applied to the observed structure amplitudes in the summation of a Fourier series. In the resulting electron density distribution some or all of the lighter atoms may be distinguished. These atoms are then included in the next structure factor calculation which provides an improved set of phase angles; successive rounds of Fourier summations and structure factor calculations serving to reveal the positions of all the atoms in the structure.

Figure 11

Diffraction of X-rays by Crystal Lattice

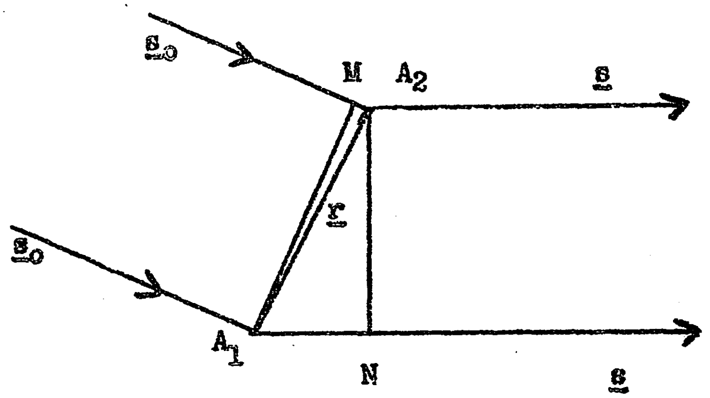
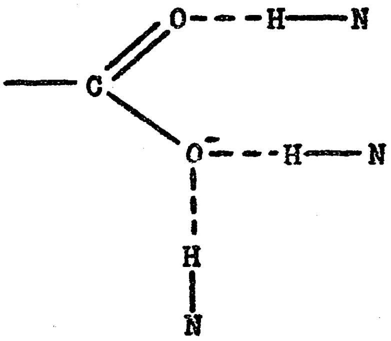


Figure 12

Hydrogen Bonding in Amino Acids



The first information one obtains from X-ray diffraction data are the unit cell dimensions and possibly the space group of the system. If the positions of the atoms in the crystal unit are known it is possible to calculate structure factors to compare with those obtained from the experimental data. The structure factor expressions can be derived from considerations of a primitive lattice defined by the lattice vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$. Each lattice point is assumed to be the site of an electron as for example A_1 and A_2 in Fig. 11. The two lattice points are related by the vector:-

$$\underline{r} = u\underline{a} + v\underline{b} + w\underline{c} \qquad \text{..........(14)}$$

If a parallel beam of X-rays of wavelength λ falls on the lattice in a direction specified by a vector $\underline{s}_0$ of magnitude $1/\lambda$ and after diffraction travels in the direction defined by the vector $\underline{s}$ of magnitude $1/\lambda$ the path difference between the two scattered waves is:-

$$A_1N - A_2M = (\underline{r}\cdot\underline{s} - \underline{r}\cdot\underline{s}_0) = \underline{r}\cdot\underline{S} \qquad \text{........(15)}$$

$$\text{where } \underline{S} = \underline{s} - \underline{s}_0$$

For the waves scattered by A_1 and A_2 to be in phase the path difference must be a whole number; in other words $\underline{r}\cdot\underline{S}$ must be integral. Therefore from equation (14) $(u\underline{a} + v\underline{b} + w\underline{c})\underline{S}$ is integral and, since u, v and w are integral, each term must be integral. i.e.

$$\underline{a}\underline{S} = h\,, \quad \underline{b}\underline{S} = k\,, \quad \underline{c}\underline{S} = l \qquad \text{..........(16)}$$

where h, k and l are integers.

These are known as the Laue equations; the integers h, k and l are the Miller indices of the diffracting plane.

The structure factor equation is:-

$$F = \sum_{n=1}^{N} f_n \exp 2\pi i(hx_n + ky_n + lz_n) \qquad \text{.........(17)}$$

where N is the number of atoms in the unit cell; (x_n, y_n, z_n) are the coordinates of the n^{th} atom and f_n is the atomic scattering factor of the n^{th} atom.

The quantity F is called the structure factor and its modulus $|F|$ is the ratio of the amplitude of radiation scattered in the order h,k,l by the contents of one unit cell to that scattered by one electron under the same conditions and is known as the structure amplitude. Since the phase of the scattered wave is not an observable quantity what is observed, the intensity of the scattered wave, is proportional to $|F|^2$.

Then if $F = A + iB$

$$F \cdot F^* = F^2 = A^2 + B^2$$

where F^* is the complex conjugate of F

$$\text{and} \quad A = \sum_n f_n \cos 2\pi(hx_n + ky_n + lz_n)$$
$$B = \sum_n f_n \sin 2\pi(hx_n + ky_n + lz_n) \qquad \text{..........(18)}$$

These are the equations used in practice for calculating structure factors. Since a crystal is periodic its electron density could be represented by a Fourier series which is a sum of sines and cosines. The appropriate equation is as follows:-

$$\rho(xyz) = (1/V) \sum \sum_{-\infty}^{\infty} \sum |F(hkl)| \cos(2\pi(hx+ky+lz) - \alpha_{hkl}) \qquad \text{......(19)}$$

where ρ is the density of scattering matter at a point with fractional coordinates (xyz) in the unit cell; V is the volume of the unit cell and α_{hkl} is the phase angle associated with the amplitude F(hkl). If the crystal contains a centre of symmetry α is limited to the values 0° or 180° and equation (19) reduces:-

$$\rho(xyz) = (1/V) \sum \sum_{-\infty}^{\infty} \sum \pm F(hkl) \cos 2\pi(hx+ky+lz) \qquad \text{.......(20)}$$

Again if only the projection of the electron density of a centrosymmetric structure on a plane is being considered equation (20) further simplifies to:-

$$\rho(xy) = (1/A)\sum_{-\infty}^{\infty}\sum \pm F(hk) \cos 2\pi(hx+ky) \qquad \ldots\ldots\ldots(21)$$

As has already been noted the drawback with the Fourier series is that in equation (19) the phase angles associated with the structure amplitude are not known. Patterson devised a synthesis as a method of obtaining information about crystal structures using only the phaseless $|F|^2$'s. The Patterson function of an electron density distribution

$$\rho(xyz) = (1/V)\sum\sum_{-\infty}^{\infty}\sum F(hkl) \exp -2\pi i(hx+ky+lz)$$

is defined as

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\cdot\rho(x+u,y+v,z+w)\, dx\, dy\, dz \qquad \ldots\ldots\ldots(22)$$

and can be expressed as the Fourier series

$$P(uvw) = (1/V)\sum\sum_{-\infty}^{\infty}\sum |F(hkl)|^2 \exp -2\pi i(hu+kv+lw) \qquad \ldots\ldots\ldots(23)$$

which can be computed without ambiguity since the $|F(hkl)|^2$'s are directly related to the observed intensities. There are various methods of refinement such as the Difference Fourier synthesis and the least squares refinement which will not be dealt with here.

The first X-ray diffraction study of a hydrogen bonded system as such was carried out by Bernal and Fowler[27] in which they assumed a particular form of open lattice structure to account for the physical properties of ice. Since then there has been a considerable amount of work carried out on hydrogen bonded compounds and this can be subdivided into various classes depending on the type of hydrogen bond i.e. on the nature of the atoms or groups A and B in the hydrogen bond A-H····B.

a) Oxygen ······ Oxygen

It has been suggested by Carpenter and Donohue[116] that it is possible to classify this type of bond into three groups depending on the position of the oxygen atom.

1) Those involving a carboxyl group and its acidic hydrogen where the length varies from about 2·50 Å in oxalic acid to about 2·65 Å in the carboxylic acid dimers.

2) Those involving hydroxyl groups as in the alcohols and phenols where the length of the bond varies from about 2·7 Å to 2·8 Å.

3) Those involving water molecules as in ice and certain hydrates where the length varies from 2·76 Å to about 2·9 Å.

This type of classification is however rather arbitrary and is still somewhat uncertain.

b) <u>Nitrogen ······· Oxygen</u>

These are the type of hydrogen bonds one finds most commonly in amino acids and proteins and they therefore play a fundamental part in protein structure. These amino acids usually exhibit three strong intermolecular nitrogen ····oxygen bonds resulting in a very compact group. The type of resonance structure shown in Fig. 12 is stabilised by hydrogen bond formation as shown in DL - alanine[117].

c) <u>Carbon ······ Oxygen</u>

The information available on this type of bond is almost negligible there being only one measured value as such for the C ······ O distance in a complex of diethyl ether and bromo - dichloromethane studied by Hassel[118,119] in two dimensions. The value given in that instance for the C - H ····· O hydrogen bond distance was 3·1 Å. Recently Sutor[120] has reviewed the carbon - oxygen distances in a number of organic structures and has postulated that these "closest distances" may well

Table 12

Possible C-H······O Hydrogen Bond Distances

Compound	r(C·······O)(Å)	Group involved
Caffeine	3.18	CH······O (keto)
Theophylline	3.22	CH······O (keto)
Glycyl-L-tyrosine hydrochloride	3.07	CH_2······O (water)
Ethylene carbonate	3.11	CH_2······O (keto)
1:3:7:9-Tetramethyluric acid	3.00	CH_3······O (keto)
Acetylcholine bromide	3.00	CH_3······O (acetyl)
Caffeine	3.24	CH_3······O (keto)

Table 13

Infrared Spectrum of Benzoyl Acetylene (In Nujol)

ν cm.$^{-1}$	Assignment	ν cm.$^{-1}$	Assignment
3195	$\nu(\equiv C-H)$	1595	Aromatic Substitution
2067	$\nu(C\equiv C)$	1583	
1640	$\nu(C=O)$	740	Aromatic Monosubstitution
		720	

be due to hydrogen bonding. (See Table 12) It is of some interest that the value given by Sutor[120] is comparable with that given by Hassel[118] and there is some reason to believe that the groups indicated in Table 12 may be joined by C - H ····· O hydrogen bonds. A further paper by Sutor[121] containing detailed evidence to justify her postulate has recently been published.

There is as yet no X-ray diffraction work on the measurement of hydrogen bonds in systems where the electron donor is an aromatic "pi" electron system; the only information about hydrogen bonded distances in such complexes coming from the ring current approach in nuclear magnetic resonance spectroscopy.

III. EXPERIMENTAL

III. 1. GENERAL

In carrying out a detailed quantitative study of that comparatively weak form of association known as hydrogen bonding it was important to ensure that all impurities which might compete or interfere with the association were removed. All compounds used in these investigations had to be pure and free from moisture. All the solvents used were spectroscopically pure or were "AnalaR" or were dried and then distilled before use. Where solids were used these have been recrystallised and sublimed to analytical purity. As hydrogen bonding is extremely sensitive to changes in temperature, concentration and solvent all three variables have been indicated.

In this work the hydrogen bonding properties of the acidic $C\equiv C-H$ group have been investigated. In particular the ability of ethynyl hydrogens to form a hydrogen bond with a basic group has been studied. The acetylenic compounds used in this investigation were phenyl acetylene and benzoyl acetylene. The former was obtained commercially (B. D. H. Ltd.) and distilled under reduced pressure (82°C/80mm. Hg). The benzoyl acetylene was prepared by the method of Bowden, Heilbron, Jones and Weedon[122] from phenylethynyl carbinol (supplied by L. Light & Co. Ltd.) as follows:-

To a stirred solution of phenylethynyl carbinol (3g.) in acetone (5c.c.) a solution of chromium trioxide (1·75g.) in water (5c.c.) and concentrated sulphuric acid (1·5c.c.) was slowly added. This operation was carried out under ice cooling and in an atmosphere of dry nitrogen over a period of one hour. After the contents of the flask had been stirred for a further thirty minutes the mixture was diluted with water and the product was extracted with ether. Evaporation of the ethereal solution gave a yellow solid which was recrystallised from aqueous methanol to give benzoyl acetylene (1·79g). This pale yellow solid had a melting point of 48°-49°C (Literature value 50°-51°C). The solid was then sublimed under reduced pressure (35°C at 0·2 mm. Hg) giving a white solid with a melting point of 48°-48·5°C. The infrared spectrum of a "mull" of this compound with Nujol was run on a Perkin - Elmer 13 infrared spectrometer over the region 650-3600 cm^{-1}. The following infrared bands characterise the compound (See Table 13). The ultraviolet spectrum of benzoyl acetylene in n-hexane (spectroscopic) was recorded on a Perkin-Elmer 137 Ultraviolet recording spectrophotometer over the spectral range 190-390 mμ using 1, 2, 5, 10, 40 mm. cells. The following bands were obtained :-

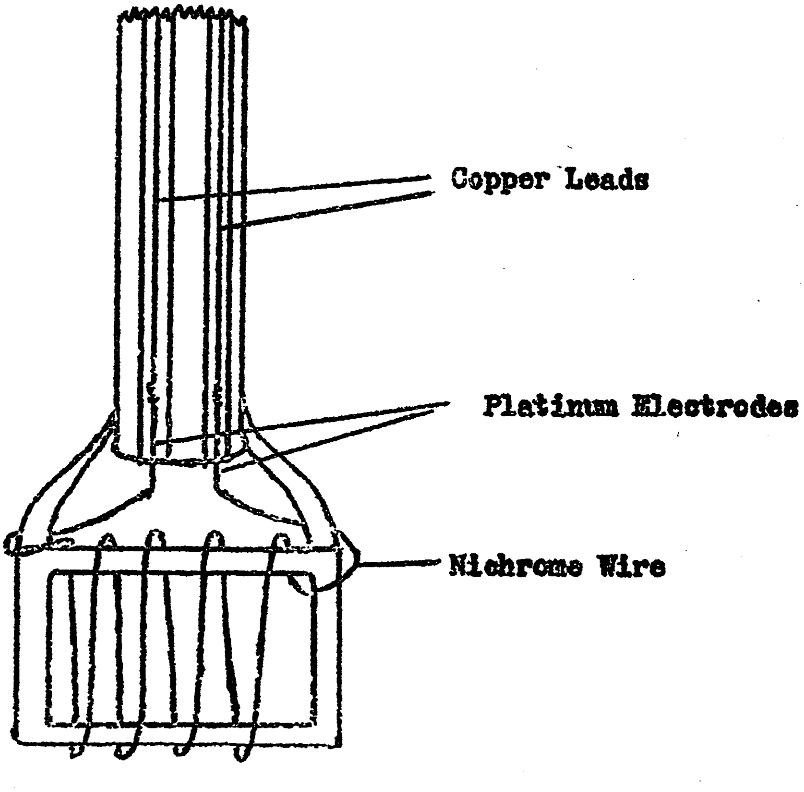
201 mμ (ε 18,525), 213 mμ (ε 14,300), 260 mμ (ε 18,850)
287 mμ (ε 2,307), 299 mμ (ε 1,040).

III. 2. CALORIMETRY

In this series of experiments the proton donor was benzoyl acetylene prepared and purified as detailed above. The solvents used were cyclohexane (spectroscopic), benzene and toluene (AnalaR) and p-xylene, mesitylene and n-butyl ether, the latter three being dried and distilled before use. As a means of testing the accuracy of the equipment used, potassium chloride was dissolved in distilled water and its heat of solution was measured. The potassium chloride used was an "AnalaR" reagent.

Figure 13

The Heater



The apparatus used in these experiments consisted of the following items:-

a) The Calorimeter and the thermometer

The calorimeter used was a 500 c.c. silvered Dewar flask having a tightly fitting rubber bung. Holes were bored in this bung to accommodate the various pieces of apparatus used in the experiments. The temperature changes in the calorimeter were measured using a Beckmann thermometer.

b) The Heater (Fig. 13)

This consisted of a pyrex glass tube 10 mm. in diameter, flattened at one end with a small glass former 25 mm. by 37·5 mm. sealed on to it at that end. Round this glass former was coiled approximately one yard of Nichrome wire (Resistance approximately 7 ohms per foot) each end of this wire having been attached to separate pieces of platinum wire by spot welding. The two pieces of platinum were passed through the closed ends of the pyrex tube into two separate thin glass tubes using a glass to metal seal and were spot welded to copper wires which led to the heating circuit. Due to a variety of mechanical failures it was necessary to rebuild this piece of apparatus more than once and the resistance of the heater was found to alter for each model. However the resistance of the heater was determined very accurately for each case as will be noted later.

c) The glass phial and the stirrer

The phial consisted of a piece of glass tubing blown out to a thin walled bulb at one end. The stirrer was of the vibro-rotatory type.

d) The Heating Circuit (Fig. 14)

This was similar to that of Pitzer[123] and was as shown in Fig. 14.

The current in the circuit was supplied by three two - volt accumulators

Figure 14

The Heating Circuit

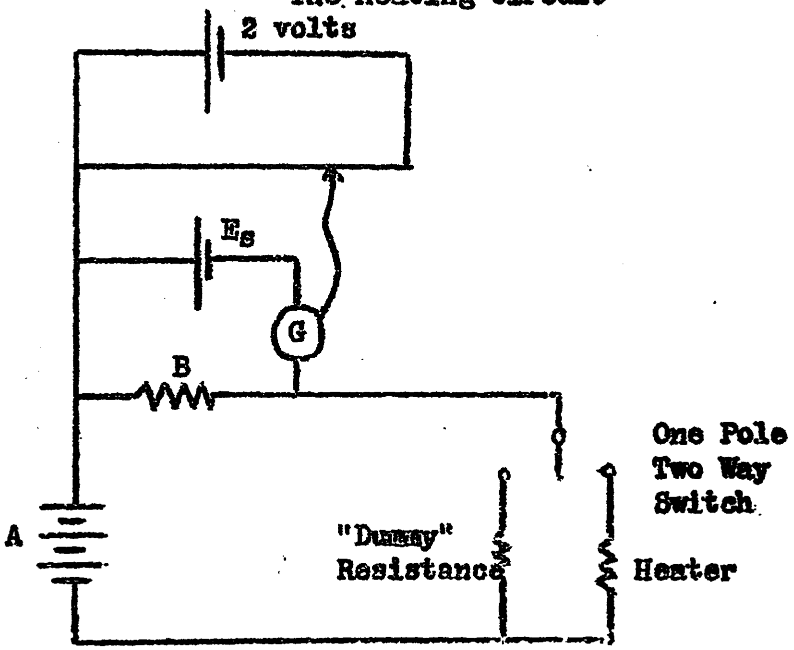
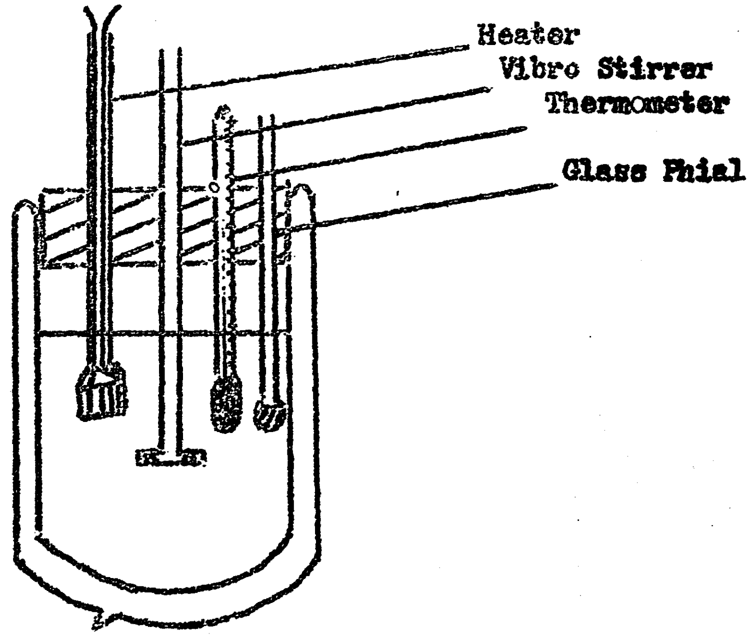


Figure 15

Calorimeter with Fittings



linked in series (A). Also present in the circuit was a standard one ohm resistance (B) maintained in an oil bath at constant temperature. Linked in parallel with this standard resistance was a Direct Current Potentiometer which was used in conjunction with a galvanometer (G) to measure the current passing through the circuit. A small switch box was constructed so that, by means of a one pole - two way switch, the heater or the substitute resistance could be put into the circuit. The "dummy" resistance was an ordinary 22 ohm resistance (approximately the same resistance as that of the heater). In use the current was allowed to flow for over one hour before each run, with the dummy resistance in the circuit, to allow the six volt accumulator supply to settle. The resistance of the heater was determined by using a circuit in which the standard one ohm resistance, the dummy resistance and the heater were in series and noting the reading on the potentiometer across the one ohm resistance and then across the heater. The ratio of the potentiometer reading across the heater to that obtained across the standard resistance gave a measure of the resistance of the heater.

The Direct Current Potentiometer has a two dial system for measuring voltages. One range of the instrument extended from 0-1·4 volts in steps of 0·1 volts while the other range extended from 0-0·1 volts in steps of 0·001 volts. It was possible to measure the voltage to the fourth decimal place. The instrument was powered by a two volt accumulator and standardised with a 1·018 volts Weston Standard Cell (E_s)

To check the accuracy of this equipment it was decided to determine the heat of solution of potassium chloride in water and to check the value obtained against the known results. In this experiment 400 c.c.

of distilled water, which had been allowed to equilibrate overnight in the constant temperature room, were placed in the Dewar and one gram of "AnalaR" potassium chloride was placed in the glass phial. The apparatus was set up as shown in Fig. 15 with the vibro-mixer and the electrical circuit on, the current passing through the "dummy" resistance. The system was left thus for over one hour to allow the temperature in the calorimeter to equilibrate and the electrical apparatus to settle down. Temperature readings were then taken every thirty seconds for the next thirty minutes during which time the actual experiment was conducted. After the first ten minutes the glass phial was broken, allowing the potassium chloride to mix with the water. Approximately eighteen minutes after the run was begun the potentiometer was standardised using the Weston cell and at twenty minutes the heater was switched into the circuit for either one or two minutes during which time the voltage drop across the one ohm resistance (equivalent to the current passing through the circuit) was measured on the potentiometer. The heater was switched off after a fixed interval, this period of time being measured with a stop watch accurate to 0.5 seconds. Temperature readings were stopped after thirty minutes and were then plotted against time giving a graph of the type shown in Fig. 16. Since the resistance of the heater was known and the current passing through it was also known, it was possible to determine the number of joules produced in a given time and therefore the number of calories equivalent to the rise in temperature. Knowing this it was possible to equate the fall in temperature on mixing the potassium chloride with the water to a specific number of calories. Following the method of Caro and Staveley[124], the data for the heat of solution of potassium chloride in water have been calculated and corrected to a dilution of one mole of potassium chloride in 160 moles of water. The results obtained are given in Table 14 the error being approximately ± 0·08 kilocalories per mole. The fact that the average of the two results obtained gave a value almost exactly the same as Staveley's was almost certainly fortuitous.

Table 14

Heat of Solution of Potassium Chloride in Water

a) Current (I) through heater 0·2919 amps

Resistance (R) of heater 21·5223 ohms

Time heater in circuit (t) 123 seconds

No. of cals. produced ($I^2Rt/4{\cdot}18$) 55·02 cals.

A rise in temperature of 0·128°C is equivalent to 55·02 cals.

A fall in temperature of 0·134°C is equivalent to - 55·60 cals.

But number of moles of KCl equals 0·01341 moles

No. of cals. produced per mole equals - 4294 cals./mole.

Moles H_2O/Moles KCl equals 1656·7

Correcting to a ratio of 160 requires subtraction of 30 cals.

No. of cals. produced per mole equals - 4264 cals./mole

b) Current (I) through heater 0·2527 amps.

Resistance (R) of heater 21·5223 ohms.

Time heater in circuit (t) 120 seconds

No. of cals. produced ($I^2Rt/4{\cdot}18$) 39·27 cals.

A rise in temperature of 0·100°C is equivalent to 39·27 cals.

A fall in temperature of 0·141°C is equivalent to - 55·37 cals.

But number of moles of KCl equals 0·01341 moles

No. of cals produced per mole equals - 4128 cals/mole

Moles H_2O/Moles KCl equals 1656·7

Table 14 (Cont'd).

b) Correcting to a ratio of 160 requires subtraction of 30 cals.

No. of cals. produced per mole equals - 4098 cals/mole.

For the investigation of the heats of mixing of benzoyl acetylene with a variety of solvents a fixed weight of the benzoyl acetylene, corresponding to either 0·01, 0·0075 or 0·005 moles of that substance was placed in the phial. 400 c.c. of the solvent were placed in the calorimeter and the experiment was conducted as detailed above. It was then possible to equate the fall in temperature on the addition of benzoyl acetylene to the solvent with a specific number of calories absorbed from the system and, by correcting this for the number of moles of benzoyl acetylene present, it was possible to obtain the heat of mixing per mole of benzoyl acetylene in that particular solvent. (See Table 15)
The heat of mixing of the benzoyl acetylene in cyclohexane was taken to be due to the breakdown of the hydrogen bonds present in the solid state and, when this correction was applied to systems where benzoyl acetylene was added to an electron donating solvent, a measure of the enthalpy of the hydrogen bond between benzoyl acetylene and the solvent was obtained. (See Table 16)

Table 15

Heats of Mixing of Benzoyl Acetylene in various solvents

Solvent		Moles of Benzoyl Acetylene	Rise in Temp. °C	Fall in Temp. °C	Heat of Mixing kcals/mole
a) Cyclohexane	1)	0·0100	0·453	0·447	- 7·40
	2)	0·0075	0·245	0·343	- 7·42
	3)	0·0050	0·246	0·229	- 7·40

Table 15 (Cont'd)

Solvent		Moles of Benzoyl Acetylene	Rise in Temp.°C	Fall in Temp.°C	Heat of Mixing kcals/mole
b) Benzene	1)	0·0100	0·456	0·279	– 4·55
	2)	0·0075	0·216	0·201	– 4·44
	3)	0·0050	0·113	0·129	– 4·48
c) Toluene	1)	0·0075	0·228	0·210	– 4·74
	2)	0·0075	0·233	0·211	– 4·66
	3)	0·0050	0·127	0·145	– 4·93
d) P-Xylene	1)	0·0100	0·228	0·292	– 4·82
	2)	0·0050	0·133	0·149	– 4·91
e) Mesitylene	1)	0·0050	0·137	0·152	– 4·81
	2)	0·0050	0·136	0·146	– 4·63
f) n-butyl ether	1)	0·0050	0·116	0·122	– 4·53

Table 16

Enthalpies of Benzoyl Acetylene in various solvents

Solvent	Heats of Mixing kcals/mole	Enthalpy kcals/mole
1) Cyclohexane	– 7·41	– 7·41
2) Benzene	– 4·49	2·92
3) Toluene	– 4·78	2·63
4) P-Xylene	– 4·87	2·54
5) Mesitylene	– 4·72	2·69
6) N-Butyl Ether	– 4·53	2·88

III. 3. INFRARED SPECTROSCOPY

All infrared measurements were carried out on the Unicam SP100 double beam recording infrared spectrometer which is capable of recording over the region 375 to 8000 cm.$^{-1}$. However, it acts as a prism grating instrument only over the region 650 to 3650 cm. $^{-1}$, this region being covered by two cams giving a linear wavenumber scan over the ranges 650 to 2150 cm.$^{-1}$ (A cam) and 2150 to 3650 cm.$^{-1}$ (B cam). For the present work the instrument was only used on B cam and then normally only over the region 3100 to 3400 cm.$^{-1}$. In all cases where temperature effects were not being studied the samples were run at the temperature of the cell well in the instrument which was thermostatted within the temperature range 28°-29°C. The spectra were calibrated for frequency using ammonia vapour over the spectral range covered. For all the quantitative spectral runs logarithmic chart paper was used. Liquid cells were used with sodium chloride windows and path lengths of 0·52mms., 0·11mms. and 0·05mms.

For the variable temperature infrared studies the equipment was as follows:-

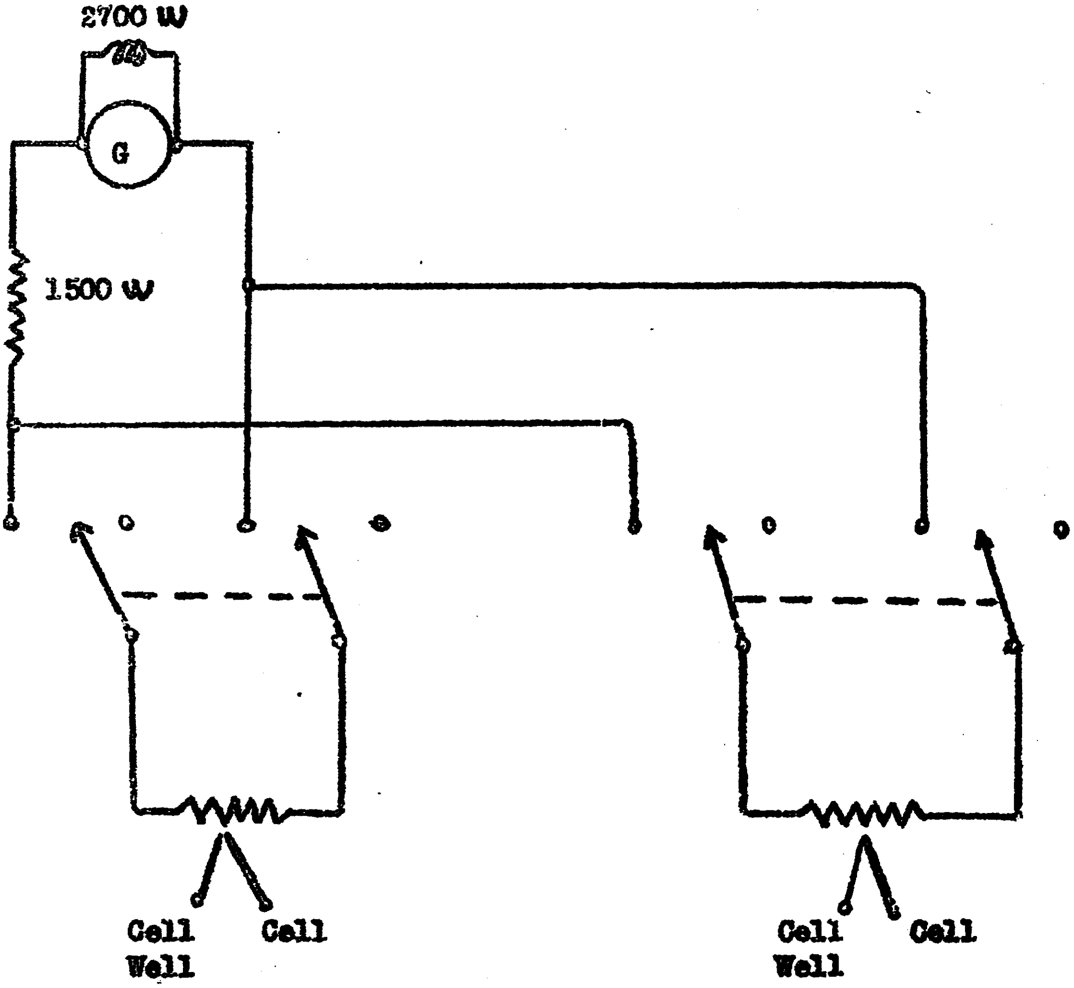
a) Two infrared heated cells with heating jackets of path length 0·3mms. supplied by Research and Industrial Instruments Co. Ltd. Each cell was fitted with steel plugs and it was found that the steel plugs were unable to prevent leakage from the cell on heating. This defect was overcome by fitting the plugs with Teflon washers.

b) Two variacs which were used as a means of controlling the cell temperature. These were calibrated over a range of temperatures.

c) Two thermometers which were used to measure the cell well

Figure 17

Circuit for Temperature Measurements in Infrared Studies



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temperature during the run. It was noted that the temperature of the cell well rose slightly while the cells were being heated.

d) A galvanometer which was calibrated to measure temperature differences between the cell well and the cell of from 0°C to 60°C with an accuracy of ±0·5°C. A resistance of 2700 ohms was placed in parallel with the galvanometer to decrease its sensitivity and this was linked to thermocouples attached to the cells as indicated in Fig. 17. A 1500 ohm resistance was placed in series with the galvanometer which was connected through two, two pole - two way switches to a pair of thermocouples. This allowed one to switch either of the cells into circuit with the galvanometer at any time while keeping the other cell out of circuit.

The benzoyl acetylene and the phenyl acetylene used in these investigations were obtained as indicated earlier. All the solvents used were either of spectroscopic or "AnalaR" quality or were dried and distilled before use. All solutions were made up in graduated flasks and the mixed solvents were made up accurately by weight, all weights being determined to 0·0001 grams.

A preliminary investigation of benzoyl acetylene and phenyl acetylene in a variety of solvents was carried out and the frequencies, intensities and half band widths of the ethynyl hydrogen stretching vibrations were noted. Of the solvents used all were available commercially except for tert-butyl ether which was prepared by the method of Erickson and Ashton[125] from freshly prepared silver carbonate and tert-butyl chloride. The samples were all run with a similar cell containing the pure solvent in the reference beam and the vibrational mode studied in all cases was the ethynyl hydrogen stretching vibration.

It was found to be impossible to study benzoyl acetylene in solution with pyridine or its methyl derivatives owing to the formation of highly coloured complexes. However it was possible to study phenyl acetylene in these solvents. Benzoyl acetylene presented a much cleaner ethynyl hydrogen stretching vibration than did phenyl acetylene due to the presence of a Fermi resonance between the ethynyl hydrogen stretching vibration and a combination band in the phenyl acetylene. For this reason it was preferable to use the benzoyl acetylene in quantitative studies. In Table 17 is given a list of results obtained for benzoyl acetylene and phenyl acetylene in a variety of solvents. In some cases, as with the ethers as solvents, the "free" and "bonded" peaks could be observed and measured separately while with a number of the solvents only one broad peak was observed. The significance of these results will be discussed in the following chapter.

<u>Table 17</u>

a) <u>Benzoyl Acetylene</u>

Solvent	ν free cm.$^{-1}$	ν bonded cm.$^{-1}$	ε free	ε bonded	$\nu_{\frac{1}{2}}$ cm.$^{-1}$
N-hexane	3306	-	250	-	9 (f)
Cyclohexane	3303	-	250	-	7·5 (f)
Ethyl Ether	3304	3219	30	70	70 (b)
Isopropyl Ether	3305	3215	52	75	68 (b)
tert-Butyl Ether	3306	3221	55	44	70 (b)
Anisole	3267		93·9		48 (f+ b)
2:5 Dimethyl Furan	3272		94·3		49 (f+ b)
Thiophene	3273·5		100		41 (f+ b)

Table 17 (Cont'd)

a) Benzoyl Acetylene

Solvent	ν free cm.$^{-1}$	ν bonded cm.$^{-1}$	ε free	ε bonded	$\nu_{\frac{1}{2}}$ cm.$^{-1}$
Benzene	3277		95·4		41 (f+b)

b) Phenyl Acetylene

Solvent	ν free cm.$^{-1}$	ν bonded cm.$^{-1}$	ε free	ε bonded	$\nu_{\frac{1}{2}}$ cm.$^{-1}$
n-Hexane	3323	-	125	-	22 (f)
Cyclohexane	3320	-	98·4	-	31 (f)
Ethyl Ether	3320	3250	55	75	-
Isopropyl Ether	3321·5	3247	66	53	44 (b)
tert-Butyl Ether	3321·5	3254·5	68	30	44 (b)
Pyridine	3294	3204	55	52	111 (b)
α-Picoline	3294	3196·5	56	50	111 (b)
2:6 Lutidine	3294	3196·5	44·5	44·5	110 (b)
Tetrahydrofuran	3299	3236·5	43	84	59 (b)
Furan	3293		144		36 (f+b)
2-Methyl Furan	3292		115		41 (f+b)
2:5 Dimethyl Furan	3289		75		62·5 (f+b)
Thiophene	3291		107·6		43 (f+b)
Benzene	3292		108		42·5 (f+b)
Toluene	3292		88		49 (f+b)
P-Xylene	3293		82		55 (f+b)
Mesitylene	3292		68·5		62·5 (f+b)
1:6 Dimethyl Napthalene	3291		93		50·5 (f+b)

Determination of Association Constants

For the quantitative investigations benzoyl acetylene was used as the electron acceptor with the solvents benzene, toluene, p-xylene, mesitylene and n-butyl ether as the electron donors while phenyl acetylene was taken as the electron acceptor with the solvent n-butyl ether. All aromatic solutions were run at a concentration of 0·05 moles benzoyl acetylene per litre of solvent in liquid cells of path length 0·052 cms. at a temperature of 28°-29°C. For each aromatic solvent system a series of runs were carried out, the actual solvent ranging from the pure aromatic solvent through various mole fractions of that solvent in cyclohexane to pure cyclohexane itself. Where n-butyl ether was the solvent, due to the much greater separation of the "free" and the "bonded" peaks, their maximum intensity was rather low and, for the purpose of throwing the broad "bonded" peak into greater relief, the concentration of benzoyl acetylene was taken to be 0·1667 moles per litre of solvent over the solvent range 0·40 to 1·0 mole fraction n-butyl ether in cyclohexane. Due to the relative insolubility of benzoyl acetylene in cyclohexane the concentration of the former had to be lowered to 0·0833 moles per litre of solvent over the solvent range 0 to 0·3 mole fraction n-butyl ether in cyclohexane. In the phenyl acetylene - n-butyl ether system the concentration of the former was taken as 0·1351 moles of phenyl acetylene per litre of solvent. The n-butyl ether systems were run in cells of path length 0·03 cms. at a temperature of 28°-29°C. The spectra were run over the range 3150-3400 cm.$^{-1}$ for the benzoyl acetylene - aromatic solvent systems but, because of the greater spread of peaks in the ether solvent, the range covered in the benzoyl acetylene - n-butyl ether and the phenyl acetylene - n-butyl ether systems was

3100 - 3400 cm.$^{-1}$. The spectra shown in Figs. 18 (a, b, c) are a selection of those found for benzoyl acetylene in benzene, toluene, p-xylene, mesitylene, n-butyl ether and in chlorobenzene.

In calculating the association constants for the hydrogen bonding between the acetylenes and the solvent it was necessary to know the integrated absorption intensity (A) and this was obtained by measuring the area under the peaks between certain frequency limits and correcting this value for the concentration and path lengths at which it was obtained. The limits of the integration for the aromatic solvent systems were taken as 3190 - 3370 cm.$^{-1}$ and, for the n-butyl ether as solvent, the limits were 3110 - 3370 cm.$^{-1}$. The area measured was that enclosed by the peak and the straight line joining the upper and lower frequency limits of the curve. Ordinates were drawn every 2·5 cm.$^{-1}$ within this area and the optical densities at these ordinates measured. The values obtained were summed using Simpsons Rule giving an integrated area in terms of the optical density and the wavenumber (A_1 cm.$^{-1}$). The integrated absorption intensity was then given as

$$A = 2{\cdot}303\ A_1/cl \quad \text{litres moles}^{-1}\ \text{cm.}^{-2} \quad \ldots\ldots (24)$$

where $A_1 = \int \log_{10} I^0/I \cdot d\nu$

and c is the concentration of the solution in moles per litre and l is the path length in centimetres.

If one assumes that, in a system containing an ethynyl compound (A) and an electron donating solvent (B), there are three species A, AB and B in mutual equilibrium and that their solutions in an inert solvent S form an ideal mixture then A + B + S is always dilute with respect to A and $(x_B + x_S)$ is approximately equal to unity (x_B and x_S represent the mole fractions of B and S respectively). Under these conditions the equilibrium constant, in terms of mole fractions, for the system,

$$A + B \rightleftharpoons AB$$

can be written:-

$$K_n = m_{AB}/m_A x_B \qquad \text{..........} (25)$$

in which m_{AB} and m_A are the actual molarities of AB and A respectively and x_B is the stoichiometric mole fraction of B. From considerations of Beers Law[126,127] one can obtain a relation connecting the true integrated absorption intensity of a mixture containing both A and AB (A) with the active solvent mole fraction x_B (Equation 26).

$$x_B/(A - A_A) = x_B/(A_{AB} - A_A) + 1/K_n(A_{AB} - A_A) \qquad \text{........}(26)$$

In the above equation A_A and A_{AB} represent the absorption intensity of the species A and AB the former being measurable in solution in the pure inert solvent S. If $x_B/(A - A_A)$ was then plotted against x_B one should obtain a straight line from whose slope and intercept one can obtain K_n and A_{AB}. The actual experimental points when graphed in the above fashion showed some degree of scatter and the method of least squares was applied to obtain the error in the results. The graphs are as shown in Fig. 19 and the results are given in Tables 18(a-f) and 19.

Table 18

a) Benzoyl Acetylene in Benzene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}10^4$	$x_B/(A - A_A)$
0	6·88	0·609	-
0·1	7·27	0·644	3·30
0·2	7·84	0·694	2·50
0·3	8·27	0·733	2·53
0·4	8·48	0·751	2·91

Table 18 (Cont'd)

a) Benzoyl Acetylene in Benzene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}10^4$	$x_B/(A - A_A)$
0·5	9·05	0·802	2·66
0·6	9·27	0·821	2·90
0·7	9·46	0·838	3·12
0·8	9·68	0·857	3·29
0·9	9·81	0·869	3·52
1·0	10·19	0·903	3·45

b) Benzoyl Acetylene in Toluene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}10^4$	$x_B/(A - A_A)$
0	6·84	0·614	-
0·1	7·83	0·694	1·26
0·2	7·94	0·704	2·23
0·3	8·41	0·745	2·29
0·4	8·67	0·768	2·60
0·5	9·17	0·812	2·52
0·6	9·31	0·825	2·85
0·8	10·11	0·896	2·84
1·0	9·96	0·882	3·73

c) Benzoyl Acetylene in P-Xylene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}10^4$	$x_B/(A - A_A)$
0	6·90	0·614	-

Table 18 (Cont'd)

c) Benzoyl Acetylene in P-Xylene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}10^4$	$x_B/(A - A_A)$
0·1	7·96	0·707	1·07
0·2	8·54	0·759	1·38
0·3	8·68	0·769	1·94
0·4	9·37	0·830	1·85
0·5	9·31	0·824	2·38
0·6	9·65	0·855	2·49
0·7	9·63	0·853	2·92
0·8	10·22	0·903	2·77
0·9	10·02	0·887	3·29
1·0	10·49	0·929	3·18

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d) Benzoyl Acetylene in Mesitylene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}10^4$	$x_B/(A - A_A)$
0	7·12	0·614	-
0·1	7·93	0·702	1·14
0·2	8·32	0·737	1·63
0·3	8·93	0·788	1·72
0·4	8·91	0·789	2·28
0·5	9·15	0·813	2·51
0·6	9·33	0·824	2·86
0·7	10·04	0·889	2·54
0·8	9·46	0·838	3·57

Table 18 (Cont'd)

d) Benzoyl Acetylene in Mesitylene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$$10^4$	$x_B/(A - A_A)$
0·9	9·44	0·836	4·06
1·0	10·25	0·908	3·40

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e) Benzoyl Acetylene in n-Butyl ether - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$$10^4$	$x_B/(A - A_A)$
0	7·09	0·614	-
0·1	8·11	0·747	0·75
0·2	9·03	0·832	0·92
0·3	10·13	0·933	0·94
0·4	21·62	0·996	1·05
0·5	22·41	1·032	1·19
0·6	23·03	1·061	1·34
0·7	23·69	1·091	1·47
0·8	25·02	1·152	1·49
0·9	24·91	1·147	1·69
1·0	25·64	1·181	1·76

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f) Phenyl Acetylene in n-Butyl ether - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$$10^4$	$x_B/(A - A_A)$
0	14·78	0·840	-
0·4	17·19	0·977	2·92
0·5	18·02	1·024	2·72

Table 18 (Cont'd)

f) Phenyl Acetylene in n-Butyl ether - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$10^4	$x_B/(A - A_A)$
0·6	17·97	1·021	3·31
0·7	18·63	1·058	3·20
0·8	18·79	1·067	3·51
0·9	19·18	1·078	3·77
1·0	19·81	1·111	3·69

Table 19

a) Benzoyl Acetylene

Solvent	Slope l.$^{-1}$ moles cm.^{2} 10^4	Intercept l.$^{-1}$moles cm.^{2}m.f.10^4	K_n (m.f.)$^{-1}$	A_{AB} l.moles^{-1} cm.$^{-2}$10^4	Degree of Association
Benzene	0·80 ± 0·34	2·58 ± 0·16	0·31 ± 0·13	1·86 ± 0·52	0·24 ± 0·10
Toluene	2·10 ± 0·37	1·51 ± 0·15	1·39 ± 0·28	1·09 ± 0·08	0·58 ± 0·14
P-Xylene	2·40 ± 0·21	1·00 ± 0·10	2·43 ± 0·31	1·03 ± 0·04	0·71 ± 0·11
Mesitylene	2·89 ± 0·35	0·98 ± 0·35	2·96 ± 0·81	0·96 ± 0·04	0·75 ± 0·26
n-Butyl ether	1·13 ± 0·04	0·64 ± 0·02	1·77 ± 0·09	1·50 ± 0·03	0·64 ± 0·04

b) Phenyl Acetylene

n-Butyl ether	1·64 ± 0·33	2·15 ± 0·22	0·76 ± 0·17	1·45 ± 0·12	0·43 ± 0·11

Determination of the Enthalpy of the Hydrogen Bond

In this series of runs the apparatus was as illustrated previously, the cells used having a path length of 0·03 cms. The concentration of benzoyl acetylene in the aromatic solvents was 0·0833 moles per litre of solvent. In n-butyl ether as solvent the concentration of benzoyl acetylene was 0·1667 moles per litre of solvent. The temperature range covered was from approximately 27°C to around 70°C, spectra being run at the two extremes of the temperature range and at an intermediate value in the region of 50°C. For each solute - solvent system a series of runs at different temperatures was carried out for two different mole fractions of the active solvent in cyclohexane. In addition benzoyl acetylene was run in pure cyclohexane at all three temperatures and no apparent change in the integrated absorption intensity was observed. A_A was therefore considered to be temperature independant over the temperature range covered. The integrated absorption intensity of the band, if association between the benzoyl acetylene and the active solvent was complete, (A_{AB}) was also assumed to remain constant over the temperature range covered. It is possible to rewrite equation (26) as follows:-

$$K_n = (A - A_A)/(A_{AB} - A_A)\, x_B \qquad \text{.............}(27)$$

Using the above equation, if one knows the integrated intensity in the inert solvent(A_A), the mole fraction(x_B) of the active solvent and the integrated intensity of the band if the association between the benzoyl acetylene and the active solvent was complete(A_{AB}), then all that is required to determine the association constant at a particular temperature is the integrated intensity of the band at the particular mole fraction of active solvent being studied(A). The integrated absorption intensity (A) was determined as before. One can thus obtain values for the association constant(K_n) at various temperatures. Then, if the $\log_{10}K_n$ was plotted against the reciprocal of the absolute temperature(I/T), from the Clausius - Clapeyron equation:-

$$\log_{10}K_n = -\Delta H/2\cdot3\ RT + e/2\cdot3 \qquad \ldots\ldots\ldots\ldots(28)$$

the slope of the straight line obtained is equal to the term $-\Delta H/2\cdot3R$ where R is the gas constant. From this slope it is therefore possible to obtain the enthalpy(Δ H) of the association which is a measure of the strength of the hydrogen bond. The application of the least squares technique to the experimental points enabled an estimation of the error in the enthalpy to be made. Fig. 20 shows the effect of temperature on the ethynyl hydrogen stretching vibration in the selected solvents. The results obtained are listed in Table 20 (a - e) and Table 21.

Table 20

a) Benzoyl Acetylene in Benzene - Cyclohexane

$A_A = 0\cdot614$ l.moles^{-1}cm.$^{-2}10^{-4}$; $A_{AB} = 1\cdot86$ l.moles^{-1}cm.$^{-2}10^{-4}$.

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}10^{4}$	$(A - A_A)/(A_{AB} - A_A)$	K_n	$\log_{10}K_n$	$(1/T)10^3$
0·5	8·83	0·814	0·197	0·381	-0·419	3·333
0·5	8·06	0·742	0·115	0·229	-0·639	3·086
0·5	7·66	0·705	0·079	0·159	-0·799	2·915
1·0	9·87	0·910	0·311	0·311	-0·508	3·311
1·0	9·25	0·852	0·236	0·236	-0·627	3·096
1·0	8·44	0·778	0·151	0·151	-0·821	2·907

b) Benzoyl Acetylene in Toluene - Cyclohexane

$A_A = 0\cdot614$ l.moles^{-1}cm.$^{-2}10^{-4}$; $A_{AB} = 1\cdot09$ l.moles^{-1}cm.$^{-2}10^{-4}$.

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}10^{4}$	$(A - A_A)/(A_{AB} - A_A)$	K_n	$\log_{10}K_n$	$(1/T)10^3$
0·8	9·47	0·872	1·189	1·486	0·172	3·322
0·8	8·78	0·809	0·693	0·866	-0·063	3·086

Table 20 (Cont'd)

b) Benzoyl Acetylene in Toluene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$$10^4$	$(A - A_A)/(A_{AB} - A_A)$	K_n	$\log_{10}K_n$	$(1/T)10^3$
0·8	8·06	0·743	0·570	0·463	−0·335	2·915
1·0	9·73	0·896	1·454	1·454	0·163	3·311
1·0	9·18	0·846	0·950	0·950	−0·022	3·096
1·0	8·41	0·775	0·511	0·511	−0·220	2·907

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c) Benzoyl Acetylene in P-Xylene - Cyclohexane

A_A = 0·614 l.moles^{-1}cm.$^{-2}$$10^{4}$; A_{AB} = 1·03 l.moles^{-1}cm.$^{-2}$$10^{-4}$.

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$$10^4$	$(A - A_A)/(A_{AB} - A_A)$	K_n	$\log_{10}K_n$	$(1/T)10^3$
0·5	8·75	0·806	0·865	1·73	0·238	3·289
0·5	8·26	0·761	0·548	1·10	0·040	3·106
0·5	7·73	0·712	0·311	0·62	−0·206	2·924
0·7	9·37	0·863	1·514	2·16	0·335	3·311
0·7	8·57	0·790	0·739	1·06	0·023	3·096
0·7	8·07	0·743	0·455	0·65	−0·187	2·924

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d) Benzoyl Acetylene in Mesitylene - Cyclohexane

A_A = 0·614 l.moles^{-1}cm.$^{-2}$$10^{-4}$; A_{AB} = 0·959 l.moles^{-1}cm.$^{-2}$$10^{-4}$.

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$$10^4$	$(A - A_A)/(A_{AB} - A_A)$	K_n	$\log_{10}K_n$	$(1/T)10^3$
0·5	9·33	0·859	2·432	4·86	0·687	3·328
0·5	8·28	0·763	0·757	1·51	0·180	3·096
0·5	7·74	0·713	0·399	0·80	−0·098	2·924
0·6	9·36	0·862	2·530	4·22	0·625	3·322

Table 20 (Cont'd)

d) Benzoyl Acetylene in Mesitylene - Cyclohexane

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$10^{4}	$(A - A_A)/(A_{AB} - A_A)$	K_n	$\log_{10}K_n$	$(1/T)10^3$
0·6	8·62	0·794	1·088	1·81	0·258	3·106
0·6	7·77	0·716	0·417	0·69	-0·158	2·915

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e) Benzoyl Acetylene in n-Butyl ether - Cyclohexane

A_A = 0·614 l.moles^{-1}cm.$^{-2}$10^{-4} ; A_{AB} = 1·50 l.moles^{-1}cm.$^{-2}$10^{-4}.

x_B m.f.	A_1 cm.$^{-1}$	A l.moles^{-1}cm.$^{-2}$10^{4}	$(A - A_A)/(A_{AB} - A_A)$	K_n	$\log_{10}K_n$	$(1/T)10^3$
0·5	22·93	1·056	0·997	1·99	0·300	3·328
0·5	19·59	0·902	0·482	0·96	-0·016	3·096
0·5	17·34	0·799	0·263	0·53	-0·279	2·924
0·6	23·06	1·062	1·024	1·71	0·232	3·311
0·6	19·23	0·886	0·443	0·89	-0·053	3·096
0·6	17·69	0·815	0·293	0·49	-0·312	2·915

Table 21

Enthalpies of Benzoyl Acetylene - Solvent Hydrogen Bonds

Solvent	Slope	Enthalpy kcals./mole
Benzene	0·84 ± 0·07	3·9 ± 0·3
Toluene	1·17 ± 0·08	5·4 ± 0·4
P-Xylene	1·29 ± 0·07	5·9 ± 0·3
Mesitylene	1·94 ± 0·08	8·9 ± 0·4
n-Butyl ether	1·39 ± 0·06	6·4 ± 0·3

III. 4. PROTON MAGNETIC RESONANCE SPECTROSCOPY

Much of the work carried out using this technique was complimentary to that done using the infrared method. For the quantitative part of this work the benzoyl acetylene was studied in the same solvents as were used in the infrared investigations. The concentration of the benzoyl acetylene was taken as 0·1 moles per litre of solvent and, as before, the actual solvent ranged from the inert solvent through various mole fractions of the active solvent. As cyclohexane was used both as inert solvent and as an internal reference from which to measure the chemical shift it was impossible to obtain results for the shift in the electron donor solvent itself. The instrument used in these investigations was an Associated Electrical Industries R. S. 2 nuclear magnetic resonator, the samples being studied at room temperature(25°C) using a 60 Megacycle probe. To detect the ethynyl proton resonance signal at the low concentrations used it was necessary to operate at high attenuation and at a fairly high filter setting. Calibration was obtained using an audio-frequency unit in the spectrometer and side bands were taken from the internal reference, cyclohexane, over the range 54 to 114 cycles per second(c.p.s.) from the main signal. For each solution, usually at least ten runs, alternately sweeping upfield or downfield, were taken over the spectral range being studied, the final result being taken as the average of these. The actual chemical shifts on hydrogen bonding were measured relative to the position of the ethynyl proton resonance signal of benzoyl acetylene in pure cyclohexane, this being found at 98·7± 0·3 c.p.s. downfield from the main cyclohexane signal. In all cases where aromatic solvents were used the ethynyl proton resonance signal moved upfield relative to the value in pure cyclohexane, whereas when n-butyl ether was the solvent the signal was found to move downfield. If the chemical shift, in c.p.s. from cyclohexane, of the ethynyl proton resonance signal in pure cyclohexane is denoted by δ_A and the chemical shifts in the mixed solvents by δ_1, then the chemical shift due to hydrogen bonding can be taken as $(\delta = \delta_1 - \delta_A)$. In addition if x_B is taken as the mole fraction of the active solvent and δ_{AB} is taken to be the chemical shift if association is complete, then it is possible to use the following equation to determine the association constant:-

$$x_B/\delta = x_B/\delta_{AB} + 1/K_n\delta_{AB} \qquad \ldots\ldots\ldots\ldots\ldots(29)$$

The position of the ethynyl proton resonance signals was obtained with considerable accuracy by placing side bands of known frequency on either side of the proton signal. When x_B/δ was plotted against x_B a straight line graph was obtained from whose slope and intercept it was possible to obtain values for K_n and δ_{AB}. The method of least squares was employed to obtain the limiting errors in the results. Figs. 21 (a - e) indicate the plots obtained. The numerical results are noted in Table 22(a - e) and in Table 23.

Table 22

a) Benzoyl Acetylene in Benzene - Cyclohexane

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
98·7 ± 0·3	0	0	0
91·8 ± 0·5	0·1	6·9 ± 0·6	0·0145 ± 0·0012
86·3 ± 0·3	0·2	12·3 ± 0·4	0·0162 ± 0·0005
81·7 ± 0·4	0·3	17·0 ± 0·5	0·0177 ± 0·0005
73·9 ± 0·4	0·5	24·7 ± 0·5	0·0202 ± 0·0004
74·4 ± 0·2	0·5	24·3 ± 0·4	0·0206 ± 0·0003

Table 22 (Cont'd)

a) Benzoyl Acetylene in Benzene - Cyclohexane

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
69·1 ± 0·3	0·7	29·5 ± 0·4	0·0237 ± 0·0004
64·6 ± 0·3	0·9	34·1 ± 0·4	0·0264 ± 0·0003
65·3 ± 0·4	0·9	33·3 ± 0·5	0·0270 ± 0·0004
64·2 ± 0·4	0·9	34·4 ± 0·5	0·0262 ± 0·0003

b) Benzoyl Acetylene in Toluene - Cyclohexane

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
98·7 ± 0·3	0	0	0
90·9 ± 0·3	0·1	7·7 ± 0·4	0·0130 ± 0·0006
85·0 ± 0·2	0·2	13·6 ± 0·4	0·0147 ± 0·0004
77·5 ± 0·3	0·4	21·1 ± 0·4	0·0189 ± 0·0004
74·0 ± 0·2	0·5	24·6 ± 0·4	0·0203 ± 0·0003
71·6 ± 0·4	0·6	27·1 ± 0·5	0·0222 ± 0·0004
67·8 ± 0·3	0·8	30·8 ± 0·4	0·0260 ± 0·0003

c) Benzoyl Acetylene in P-Xylene - Cyclohexane

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
98·7 ± 0·3	0	0	0
89·5 ± 0·2	0·1	9·1 ± 0·3	0·0110 ± 0·0004
83.0 ± 0.4	0.2	15.7 ± 0.5	0.0128 ± 0.0004
74·3 ± 0·3	0·4	23·8 ± 0·4	0·0168 ± 0·0003
72·0 ± 0·2	0·5	26·7 ± 0·4	0·0188 ± 0·0003

Table 22 (Cont'd)

c) Benzoyl Acetylene in P-Xylene - Cyclohexane

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
69.7 ± 0.2	0.6	28.9 ± 0.3	0.0208 ± 0.0002
67.9 ± 0.2	0.7	30.8 ± 0.3	0.0228 ± 0.0002
66.4 ± 0.3	0.8	32.2 ± 0.4	0.0248 ± 0.0003

d) Benzoyl Acetylene in Mesitylene - Cyclohexane

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
98.7 ± 0.3	0	0	0
88.4 ± 0.2	0.1	10.3 ± 0.3	0.0098 ± 0.0003
82.3 ± 0.2	0.2	16.4 ± 0.3	0.0122 ± 0.0002
74.0 ± 0.2	0.4	24.6 ± 0.3	0.0163 ± 0.0002
71.1 ± 0.2	0.5	27.5 ± 0.3	0.0182 ± 0.0002
68.9 ± 0.4	0.6	29.7 ± 0.5	0.0202 ± 0.0003
67.1 ± 0.7	0.7	31.6 ± 0.7	0.0222 ± 0.0005
65.6 ± 0.3	0.8	33.1 ± 0.4	0.0242 ± 0.0003

e) Benzoyl Acetylene in n-Butyl ether - Cyclohexane

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
98.7 ± 0.3	0	0	0
123.7 ± 0.7	0.3	-(24.6 ± 0.7)	-(0.0122 ± 0.0004)
127.2 ± 0.2	0.4	-(28.6 ± 0.4)	-(0.0144 ± 0.0002)
131.0 ± 0.5	0.5	-(32.4 ± 0.6)	-(0.0154 ± 0.0003)
133.3 ± 0.2	0.6	-(34.6 ± 0.3)	-(0.0173 ± 0.0002)

Table 22 (Cont'd)

e) Benzoyl Acetylene in n-Butyl ether - Cyclohexane

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
136.4 ± 0.5	0.7	-(37.7 ± 0.5)	-(0.0186 ± 0.0003)
137.8 ± 0.3	0.8	-(39.2 ± 0.4)	-(0.0204 ± 0.0002)
140.0 ± 0.2	0.9	-(41.3 ± 0.4)	-(0.0218 ± 0.0002)

No measurements were taken on solutions with mole fractions of n-butyl ether below 0.3, since the $-CH_2-O-$ proton resonance signal of the ether then covered the ethynyl proton resonance signal.

Table 23

a) Solvent	Slope (c.p.s.)$^{-1}$	Intercept (m.f.)(c.p.s.)$^{-1}$
Benzene	0.0149 ± 0.0003	0.0131 ± 0.0002
Toluene	0.0186 ± 0.0004	0.0111 ± 0.0001
P-Xylene	0.0199 ± 0.0001	0.0089 ± 0.0001
Mesitylene	0.0204 ± 0.0002	0.0079 ± 0.0001
n-Butyl ether	-(0.0075 ± 0.0002)	-(0.0160 ± 0.0003)

b) Solvent	K_n (m.f.)$^{-1}$	δ_{AB} c.p.s.	Degree of Association when x_B is 1.0
Benzene	1.14 ± 0.03	67.0 ± 1.5	0.53 ± 0.02
Toluene	1.67 ± 0.04	53.8 ± 1.1	0.63 ± 0.02
P-Xylene	2.27 ± 0.02	50.4 ± 0.3	0.69 ± 0.01
Mesitylene	2.57 ± 0.04	49.0 ± 0.6	0.72 ± 0.02
n-Butyl ether	2.12 ± 0.06	-(62.6 ± 1.2)	0.68 ± 0.02

To investigate the activating power of substituents on neighbouring methylene groups, a number of compounds were studied in carbon tetrachloride and in benzene with tetramethylsilane as the reference standard. The chemical shift of the methylene proton resonance signal on going from carbon tetrachloride to benzene as solvent is indicated in Table 24. The propargyl chloride, methylene chloride and chloroacetonitrile were all commercial products which were dried and distilled before use. The 1:4 dichlorobut-2-yne was supplied by Dr. G. Eglinton.

Table 24

Methylene Proton Resonance Signals - Solvent Effects

Solvent ------- Solute	Carbon Tetrachloride τ, p.p.m.	Benzene τ, p.p.m.	Shift p.p.m.
Propargyl Chloride	5.91	6.58	0.67
1:4 Dichloro-but-2-yne	5.83	6.57	0.74
Methylene Chloride	4.65	5.55	0.90
Chloro-acetonitrile	5.93	7.16	1.23

A more detailed study of 1:4 dichlorobut-2-yne in benzene - cyclohexane solvent mixtures was carried out at a concentration of 0.1 moles of the acetylene per litre of solvent. The peak studied was the methylene proton resonance signal at various mole fractions of benzene. The results obtained were fitted to equation (29) but gave, instead of a straight line graph, a curved line as indicated in Fig. 22(a) showing the probable existence of more than one complex. On the assumption that a 1:1 and a 1:2 complex of the acetylene in benzene was being formed, an equation was set up (equation 30) in which K_1 and K_2 were the association constants for the 1:1 and the 1:2 complexes respectively. In addition δ_{AB} was assumed to be the same for both complexes.

$$\delta/x_B(\delta_{AB}-\delta) = K_1 + K_2\,x_B \qquad \ldots\ldots\ldots\ldots\ldots(30)$$

Using the above equation a straight line graph was obtained(Fig. 22b). Using simultaneous equations involving x_B and δ for values of x_B equal to 0.2,0.6 and 0.8,equation (30) was solved giving the following results:-

δ_{AB} = 43.5 c.p.s. ; K_1 = 1.5 (m.f.)$^{-1}$; K_2 = 2.5 (m.f.)$^{-1}$.

The empirical results obtained are listed in Table 25.

Table 25

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$	$/x_B(\delta_{AB}-\delta)$ (m.f.)$^{-1}$
153.7	0	0	0	0
147.1	0.1	6.6	0.0152	1.789
141.3	0.2	12.6	0.0159	2.028
136.5	0.3	17.2	0.0174	2.185
131.9	0.4	21.8	0.0184	2.508
125.6	0.6	28.1	0.0214	3.028
123.7	0.7	30.0	0.0233	3.180
121.6	0.8	32.1	0.0249	3.526
120.1	0.9	33.6	0.0268	3.750

Both the methylene and the ethynyl proton resonance signals of propargyl chloride are known to shift upfield in benzene solutions. It has in fact been shown by Hatton and Richards[51] that,in going from cyclohexane to benzene as solvent,the methylene proton resonance signal moved upfield by 0.45 compared with a shift of 0.31 for the ethynyl proton signal under similar conditions. A study of the chemical shift of the two sorts of protons at concentrations of 0.2 and 0.5 moles of propargyl chloride per litre of solvent has been carried out. The results obtained are illustrated in Fig. 23(a,b) and in Table 26(a-d). These results give:-

a) For the methylene protons, $K_n = 1.01 \pm 0.02$; $\delta_{AB} = 63.8 \pm 1.3$;

Degree of association ($x_B = 1$) = 0.50 ± 0.01.

b) For the ethynyl proton, $K_n = 0.96 \pm 0.06$; $\delta_{AB} = 37.0 \pm 2.4$;

Degree of association ($x_B = 1$) = 0.49 ± 0.04

Table 26

a) 0.2 moles/litre Propargyl Chloride in Benzene - Cyclohexane (CH_2 protons)

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
150.3 ± 0.2	0	0	0
144.4 ± 0.2	0.1	5.9 ± 0.3	0.0168 ± 0.0008
135.4 ± 0.2	0.3	15.0 ± 0.3	0.0200 ± 0.0004
128.6 ± 0.2	0.5	21.7 ± 0.3	0.0230 ± 0.0003
123.6 ± 0.2	0.7	26.8 ± 0.3	0.0262 ± 0.0003
120.0 ± 0.2	0.9	30.4 ± 0.3	0.0296 ± 0.0003

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b) 0.5 moles/litre Propargyl Chloride in Benzene - Cyclohexane (CH_2 protons)

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
151.3 ± 0.3	0	0	0
145.4 ± 0.3	0.1	5.9 ± 0.4	0.0171 ± 0.0012
136.9 ± 0.3	0.3	14.4 ± 0.4	0.0209 ± 0.0006
130.0 ± 0.2	0.5	21.3 ± 0.3	0.0235 ± 0.0004
124.7 ± 0.2	0.7	26.6 ± 0.3	0.0263 ± 0.0003

Table 26 (Cont'd)

b) 0.5 moles/litre Propargyl Chloride in Benzene - Cyclohexane (CH_2 protons)

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
122.8 ± 0.4	0.8	28.5 ± 0.5	0.0281 ± 0.0004
121.1 ± 0.4	0.9	30.2 ± 0.4	0.0298 ± 0.0004

c) 0.2 moles/litre Propargyl Chloride in Benzene - Cyclohexane (≡CH proton)

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
48.8 ± 0.2	0	0	0
45.5 ± 0.1	0.1	3.3 ± 0.2	0.0300 ± 0.0017
40.4 ± 0.2	0.3	8.5 ± 0.3	0.0355 ± 0.0011
36.2 ± 0.3	0.5	12.6 ± 0.4	0.0397 ± 0.0011
33.3 ± 0.3	0.7	15.5 ± 0.4	0.0452 ± 0.0011
32.1 ± 0.2	0.9	16.7 ± 0.2	0.0540 ± 0.0008

d) 0.5 moles/litre Propargyl Chloride in Benzene - Cyclohexane (≡CH proton)

δ_1 c.p.s.	x_B m.f.	δ c.p.s.	x_B/δ (m.f.)(c.p.s.)$^{-1}$
49.9 ± 0.3	0	0	0
46.9 ± 0.1	0.1	3.0 ± 0.4	0.0332 ± 0.0041
41.7 ± 0.3	0.3	8.1 ± 0.5	0.0370 ± 0.0021
37.7 ± 0.2	0.5	12.2 ± 0.4	0.0411 ± 0.0014
34.5 ± 0.2	0.7	15.3 ± 0.4	0.0457 ± 0.0011
34.0 ± 0.3	0.8	15.9 ± 0.4	0.0504 ± 0.0014
33.1 ± 0.4	0.9	16.8 ± 0.5	0.0536 ± 0.0017

III. 5. X-RAY DIFFRACTION

To study the C-H·····O hydrogen bond in the crystalline state it was necessary to prepare a derivative of benzoyl acetylene which would contain a heavy atom. The derivative prepared was the *o*-bromobenzoyl acetylene. This was especially suited for investigation by X-ray diffraction due to its structural similarity to *o*-bromobenzoic acid which had already been studied in this department[128]. This acetylenic compound had not been prepared previously and the method of preparation was as follows:-

The preparation was carried out in two stages, the first being the preparation of *o*-bromophenylethynyl carbinol following the method of Jones, Skatteböl and Whiting[129]. This carbinol was then oxidised to the *o*-bromobenzoyl acetylene using the method of Bowden, Heilbron, Jones and Weedon[122].

Stage 1.

$$C_2H_5Br + Mg \xrightarrow{T.H.F.} C_2H_5MgBr$$

$$C_2H_5MgBr + HC{\equiv}CH \xrightarrow{T.H.F.} HC{\equiv}CMgBr + C_2H_6$$

$$HC{\equiv}CMgBr + C_6H_4BrCHO \longrightarrow C_6H_4BrCHOHC{\equiv}CH$$

The *o*-bromobenzaldehyde used was a commercial sample. 22.4 g. of this material eventually yeilded 13.4 g.(52%) of the carbinol. The infrared spectrum indicated the same essential features as that of the phenylethynyl carbinol and also showed an ortho substitution pattern. The product was purified by vacuum distillation, the main fraction boiling at 81.5°C at 0.25 mm. Hg.

Stage 2.

$$C_6H_4BrCHOHC{\equiv}CH \xrightarrow[\text{Acetone}]{CrO_3} C_6H_4BrCOC{\equiv}CH$$

The carbinol was oxidised to the ketone, 4.8 g. of the former yeilding 1.14

g. of the latter. The ketone was purified by two sublimations at 43°C and 0.32 mm. Hg giving a light green solid which analysed as follows:- C 51.501% , H 2.681% .(Theoretical C 51.705% , H 2.413%). The melting point of o-bromobenzoyl acetylene was 45.5°-46.5°C.

This product was studied in carbon tetrachloride and in carbon disulphide by infrared techniques verifying that it was the o-bromobenzoyl acetylene. It was also studied in a Nujol mull, in a potassium chloride disc and as a crystalline film using infrared spectroscopy to determine the existence of hydrogen bonding in the solid state. The presence of hydrogen bonds between the ethynyl hydrogen and the carbonyl oxygen was indicated.

a) In Solution

(1) 0.0420 g. acetylene /5 ml. CCl_4 in 0.5 mm. cell

(2) 0.0420 g. acetylene/5 ml. CCl_4 in 0.11 mm. cell.

(3) 0.0320 g. acetylene/5 ml. CS_2 in 0.5 mm. cell.

b) In Solid Phase

(1) KCl disc - approximately 0.0015 g./0.3 g. of KCl. A large degree of scattering occured but hydrogen bonding in the solid state was indicated.

(2) Nujol mull - the compound was not dissolved in the nujol but rather formed a paste. Hydrogen bonding in the solid was again indicated.

(3) Crystalline film - this was obtained from a melt of the product and evidence of hydrogen bonding in the solid was obtained.

The frequencies, half band widths and intensities of the ethynyl hydrogen stretching vibration, the $C\equiv C$ stretching vibration and the $C=O$ stretching vibration are given in Table 27. The changes observed for these vibrations were indicative of hydrogen bonding in the solid state of the $C-H\cdots O$ type.

Table 27

Vibrational Mode	Frequency cm.$^{-1}$	Half Band Width cm.$^{-1}$	Intensity	State
$\nu(\equiv C{-}H)$	3302	10	S	Solution
	3220	30	S	KCl disc
	3220	22	S	Nujol mull
	3225	20	S	Crystalline
$\nu(C\equiv C)$	2100	10	S	Solution
	2097	15	S	KCl disc
	2097	13	S	Nujol mull
	2100	9	S	Crystalline
$\nu(C{=}O)$	1673	10	S	Solution
	1645	15	S	KCl disc
	1645	11	S	Nujol mull
	1662 1649	21	M	Crystalline

With the assistance of Dr. G. Ferguson of Professor Robertson's X-ray analysis group,an X-ray crystal structure investigation of the o-bromobenzoyl acetylene was undertaken. The material was crystallised from a methanol - water mixture,crystallising in the orthorhombic system. The space group of the crystal was found to be P $2_1 2_1 2_1$ and the crystal contained four molecules in a unit cell of dimensions a = 3.94 Å,b = 7.30 Å and c = 27.43 Å. From equi-inclination Weissenberg photographs 559 independent structure amplitudes were evaluated. Initially the structure was solved in its (100) projection by using the Patterson and Fourier techniques discussed earlier. An electron density projection on (100), computed on completion of the two-dimensional work is shown in Fig. 24 indicating the positions of all the atoms other than hydrogen.

This structure is being refined using three-dimensional data and least squares procedures. Refinement is not yet complete, but after six cycles of three-dimensional least squares refinement the residual R has become 8.2%. The C-H·····O distance is 3.260 ± 0.015 Å and this represents one of the first measurements of an authentic C-H·····O hydrogen bond. All other distances in the structure do not differ from the accepted values. As is evident from Fig. 24 the molecule makes use of the C-H·····O hydrogen bond in building up a zig-zag chain of *o*-bromobenzoyl acetylene molecules.

IV DISCUSSION

IV. 1. GENERAL

As has already been indicated, some work has been carried out on hydrogen bonding involving C-H groups as the electron acceptors. These investigations have been almost entirely carried out using infrared and nuclear magnetic resonance spectroscopy. The same techniques have been applied to the study of those systems in which the "pi" electron cloud of unsaturated substances acted as the electron donor. There has, however, been comparatively few investigations of hydrogen bonds involving the ethynyl hydrogen and no detailed study of hydrogen bonding between such an acidic group and aromatic systems. Nakagawa and Fujiwara[52] have looked at phenyl acetylene in a variety of solvents including benzene and Hatton and Richards[51] studied propargyl chloride, phenyl acetylene and benzoyl acetylene in both aromatic and aliphatic solvents. Both of the above groups noted that a form of association existed between the ethynyl hydrogen and the "pi" electron cloud of the aromatic ring but no detailed investigation of this phenomenon was carried out.

The peculiar advantage of using acetylenic compounds is that, owing to the nature of the ethynyl group, the ethynyl hydrogen, as well as being acidic, is relatively unhindered by other groups. This allows the ethynyl hydrogen to approach an electron - donating group with comparative ease. The work described here is a continuation of that begun by Brand, Eglinton and Morman[1]. These workers used infrared spectroscopy to study a number of acetylenic compounds possessing ethynyl hydrogens in n-hexane and in ethyl ether. Benzoyl acetylene was found to associate to the greatest extent with the ethyl ether. The complex formed between the benzoyl acetylene and the ethyl ether was studied using a method already discussed in this thesis. The association constant for the complex benzoyl acetylene - ethyl ether was found to be :-

$$K_n\ (29^{o}C) = 2.0 \pm 0.2\ (\text{m.f.})^{-1}$$

As in the present work all measurements were carried out on the ethynyl hydrogen stretching vibration.

The principal form of hydrogen bonding which will be discussed here is that between the ethynyl hydrogen and the "pi" electron cloud of aromatic molecules. The aromatic solvents, benzene, toluene, p-xylene and mesitylene were chosen with the idea that the methyl substituents would increase the electron density in the aromatic ring. On this basis one would therefore expect that the strength of the hydrogen bond between the acetylenic compound and the aromatic solvent would increase from benzene to mesitylene. For comparison the hydrogen bonding of benzoyl acetylene and phenyl acetylene to the n-donor, n-butyl ether, was also investigated.

IV. 2. CALORIMETRY

In this series of experiments the heat of mixing of benzoyl acetylene with a number of solvents was measured. The apparatus used was checked by determining the heat of solution of potassium chloride in water. A comparison with the literature value suggested that the apparatus was accurate to ± 0.1 kcals/mole. To relate the heats of mixing to the hydrogen bond strengths it was essential to know the heat of mixing of benzoyl acetylene in an inert solvent, cyclohexane. Cyclohexane does not complex with the benzoyl acetylene and, at the dilutions used the infrared spectra indicated that no self association was present. The drop in temperature observed when benzoyl acetylene was mixed with cyclohexane was interpreted on the assumption that the only contribution to the heat change came from the dissociation of hydrogen bonds present in the solid. The heat of mixing was independent of the concentration over the range 0.005 to 0.01 moles of benzoyl acetylene thus indicating that the heat of dilution was negligible. On the further assumption that, in the solid state, there was one hydrogen bond per molecule of benzoyl acetylene - an assumption which was supported by the X-ray structure of the o-bromo derivative - the heat of mixing of benzoyl acetylene in cyclohexane, -7.41 kcals/mole, was identified with the strength of the hydrogen bond in the solid. It was assumed, therefore, that on dissolving benzoyl acetylene in any solvent part of the heat of mixing, equivalent to -7.41 kcals/mole, would be due to the breaking of the hydrogen bonds in the solid state.

On dissolving benzoyl acetylene in cyclohexane two thermodynamic processes take place. Firstly, the hydrogen bonds are broken, this being an endothermic process which is described by the enthalpy of association (ΔH). This enthalpy is a measure of the strength of the hydrogen bonds in the solid benzoyl acetylene. The second process is due to the change in order of the system on breaking the hydrogen bonds and is described by the entropy of association (ΔS). In calorimetry the heat change is due solely to the enthalpy term since the change in order of the system does not involve a change in the energy needed to break the bonds. The entropy term helps to determine the position of equilibrium of the system.

On mixing benzoyl acetylene with the electron donor solvents, a heat of mixing was obtained which was compounded from the following processes. Firstly, the hydrogen bonds in the solid benzoyl acetylene were broken in an endothermic process to which a value of -7.41 kcals/mole has been attached. The second contribution to the heat of mixing arose from the formation of hydrogen bonds between the individual benzoyl acetylene molecules and the solvent molecules. From a knowledge of the heat of mixing and of the portion of it due to the breakdown of the hydrogen bonds in solid benzoyl acetylene it was possible to obtain a value for the enthalpy of the association in the solute - solvent complex. It was known from infrared and nuclear magnetic resonance spectroscopy that the degree of association between the benzoyl acetylene and the active solvent was not unity. To obtain a true measure of the enthalpy of the association it was necessary to correct the calorimetric results for the degree of association. The values for the degree of association in the various complexes were taken from the more accurate nuclear magnetic resonance results and the true enthalpies of association are noted in Table 28.

From the values for the association constants obtained by nuclear magnetic resonance methods it was possible to obtain the free energy of association (ΔG) from the equation :-

$$\Delta G = -RT\ln K_n$$

Knowing both the enthalpy and the free energy of the association the entropy could be calculated and these thermodynamic quantities are given in Table 28.

Table 28

Solvent	$-\Delta H$ kcals/mole	$-\Delta G^{298°}$ cals/mole	$\Delta S^{298°}$ cals/deg.mole
Benzene	5.48	77.5	18.1
Toluene	4.21	303	13.1
P-Xylene	3.68	485	10.7
Mesitylene	3.73	558	10.6
n-Butyl ether	4.23	444	12.7

The first point of interest relates to the strength of the hydrogen bond in the solid benzoyl acetylene. From the C-H····O distance (3.260± 0.015 Å) in the solid *o*-bromobenzoyl acetylene it would be expected that the hydrogen bond in the solid benzoyl acetylene would be comparatively weak. In fact the calorimetric evidence suggests that it is rather a strong hydrogen bond. Though one might expect the hydrogen bonds in the solute - solvent complexes to become stronger as association increases, the enthalpy tends to fall off in going from benzene to mesitylene as electron donor. However, all the values are reasonably close to one another and are in the range expected. The entropy change on association is seen to be greatest for benzene and to fall off as methyl groups are added to the ring. This suggests that the formation of a complex with benzene produces a higher degree of order in the solution than that obtained by any of the other solvents used. It has been suggested that the entropy term reflects the number of ways that the two components A and B can be oriented with respect to one another. On that basis benzene has many more possible orientations relative to benzoyl acetylene than has mesitylene.

IV. 3. INFRARED SPECTROSCOPY

Infrared spectroscopy can be applied to the detection and estimation of hydrogen bonding in a number of ways. The vibrational mode investigated in this report was the ethynyl hydrogen stretching vibration of benzoyl acetylene and phenyl acetylene. The frequency, half band width and the integrated absorption intensity of the above band all change on hydrogen bond formation. Of these three effects the latter is the most prominent and the most suitable for quantitative treatment.

The two acetylenic compounds, named above, were studied in a wide variety of solvents, the frequency, half band width and the maximum intensity of the ethynyl hydrogen stretching vibration being noted for each solvent. In the inert solvents, n-hexane and cyclohexane, the vibrational mode studied gave a relatively narrow band showing no trace of any bands which could be attributed to complex formation. The appearance of the band in phenyl acetylene was somewhat more complex than that of the similar band in benzoyl acetylene owing to a Fermi resonance between the ethynyl hydrogen stretching vibration and a weak combination band. However, it was considered, that in the two solvents mentioned the acetylenic compounds were present only as monomers. The spectra of benzoyl acetylene and phenyl acetylene in these solvents were therefore taken as the standard from which all deviations, due to hydrogen bonding, were measured.

In the solvents ethyl, isopropyl and tert-butyl ether it was expected that the degree of association between them and the acetylenes would decrease, through the series, owing to steric hindrance. It was, in fact, observed that there was a decrease in the intensity of the "bonded" peak accompanied by an increase in the intensity of the "free" peak in going from ethyl to tert-butyl ether as solvent. A similar effect was also observed for phenyl acetylene in the solvents pyridine, α- picoline and 2:6 lutidine where the bonding was to the nitrogen atom of the ring. It was also of some interest to compare the spectra of phenyl acetylene in tetrahydrofuran and in furan. In the former solvent where the ethynyl hydrogen was undoubtedly bonded to the oxygen in the ring, the "free" and the "bonded" peaks were well separated as in ethereal solutions. In the latter solvent, however, the ethynyl hydrogen could bond to either the oxygen in the ring or to the "pi" electron cloud. In fact one observes a single broad peak similar to those found where bonding is definitely to a "pi" electron system. This was further confirmed by the apparent increase in association, as evidenced by an increasing half band width, in going to 2-methyl furan and then to 2:5 dimethylfuran as solvents. If the bonding had been to the oxygen the methyl groups would be expected to reduce the association due to steric hindrance. Thiophene also acted as an electron donor through its "pi" electron system giving results which compared well with those obtained for benzene.

The most sensitive method of detecting hydrogen bonding using the infrared technique involves studying the change in the integrated absorption intensity of the band. Most quantitative approaches to hydrogen bonding have used the intensity of the "free" or the "bonded" peak at the absorption maximum ($\varepsilon_{max.}$). This method is not very satisfactory since it does not take into account the contributions to the intensity resulting from band broadening, itself symptomatic of hydrogen bonding. Also, where the "free" and the "bonded" peaks overlap or coalesce, as in the present work, it is impossible to determine the intensity of the "free" or the "bonded" peaks accurately. A more accurate and generally applicable method was to determine the true integrated absorption intensity (A) of the band which is defined thus:-

$$A = (1/cl) \int \log_e(I_o/I)_\nu d\nu \quad ...... (32)$$

the integral being measured over the limits of the absorption band. I_0 and I are the incident and the transmitted intensities of monochromatic radiation of frequency ν; c is the concentration of the solute in moles per litre of solvent and l is the path length in cms. In actual practice, owing to the use of finite slit widths, one measures the apparent integrated absorption intensity (B). Ramsay[130] has shown that, for peaks with a half band width approximately five times greater than the slit width, the difference between the true and the apparent integrated absorption intensities is negligible. It is therefore possible to use the measured intensities as though they were in fact the true integrated absorption intensities. The base line from which the area under the peak is measured is normally obtained by running a solvent - solvent spectrum. Petrash[131] has shown that this was necessary only when other absorption bands were situated in the neighbourhood of the spectral region being studied. If the band envelope was allowed to fall to practically zero intensity, then it was possible to take as the base line, a line joining the integration limits of the curve. The equation used in determining the association constant has already been dealt with by other workers[126,127].

When the experimental results were plotted as indicated in the previous section (Fig.19) a considerable scatter in the points was observed. To obtain the best straight line through the points the technique of least squares refinement was employed. One then obtained values for the association constant (K_n), the integrated absorption intensity when association was complete (A_{AB}) and for the degree of association. Since the term $x_B/(A - A_A)$ involves a difference between the integrated absorption intensity at a particular mole fraction of the active solvent (A) and in pure cyclohexane (A_A), the greatest errors are for those solvents in which the mole fraction of the active solvent (x_B) is small. When the degree of association was small as in the case where chlorobenzene was the electron donor, the error was also large. This was because the chlorine drew electrons away from the ring thus lowering its electron donating capacity. As a result, when the system benzoyl acetylene - chlorobenzene - cyclohexane was investigated, the error was such as to render the results meaningless. Also, in the aromatic electron donating solvents studied, the results most subject to error were those obtained for benzene. The experimental points obtained for that solvent showed considerable scatter; in particular the result obtained for 0.1 mole fraction of benzene in cyclohexane is definitely dubious. This was emphasised by the fact that if this point was neglected the value of the association constant was doubled.

a) Where all points were considered:-

$K_n \simeq 0.31 \pm 0.13\ (\mathrm{m.f.})^{-1}$; $A_{AB} \simeq 1.86 \pm 0.52\ \mathrm{l.moles^{-1}cm.^{-2}}$;

Degree of Association $\simeq 0.24 \pm 0.10$.

b) Where the point at $x_B \simeq 0.1$ is neglected

b) $K_n = 0.61 \pm 0.08$ (m.f.)$^{-1}$; $A_{AB} = 1.36 \pm 0.09$ l.moles^{-1} cm.$^{-2}$;

Degree of Association = 0.38 ± 0.05.

It was of interest to note that the above change brought the benzene result much more into line with the value obtained by nuclear magnetic resonance spectroscopy. The results obtained for the other solvent systems, though they also showed scatter, were accepted as being reasonable.

In the series benzene to mesitylene the association constant and the degree of association both increased. This fitted in with the expectation that the methyl substituents increased the electron donating capacity of the "pi" electron cloud. The relation between the degree of hydrogen bonding and the number of methyl groups was not linear rising sharply at first and then more slowly. This would appear to indicate a form of competition between the inductive effect and the steric effect of the methyl groups, the former assisting and the latter opposing association. The integrated absorption intensity when association was complete (A_{AB}) tended to fall in going from benzene to mesitylene. The results obtained for benzoyl acetylene and phenyl acetylene in n-butyl ether compared reasonably well with those obtained for the same electron acceptors in ethyl ether.[1]

The position of equilibrium in the systems studied, as expressed by the association constants, was such that between one half and two thirds of the benzoyl acetylene was associated with the solvent. The values of the association constants ranged from 1 - 3 (m.f.)$^{-1}$ and a comparison with those obtained recently by Gramstad[132] for phenol in tributylamine ($K_n^{20^\circ}$ 29.2 (m.f.)$^{-1}$) and in pyridine ($K_n^{20^\circ}$ 59.8 (m.f.)$^{-1}$) indicated that one was dealing with a weak form of hydrogen bonding. A point of interest was that benzoyl acetylene complexes through the "pi" electron systems of aromatic rings as readily as through the lone-pair electrons of ethereal oxygens. Benzoyl acetylene actually complexes to a greater extent with p-xylene and mesitylene than with n-butyl ether. Similar results were found for chloroform in acetone[40] ($K_n^{28°}$ 1.8 (m.f.)$^{-1}$) and in benzene[109] ($K_n^{28°}$ 1.06 (m.f.)$^{-1}$). It thus appeared that the position of equilibrium was determined mainly by the nature of the electron acceptor, the electron donor playing a subsidiary role. In other words the degree of hydrogen bonding depended primarily on the acidity of the A-H group. The ability of the electron donor to alter the degree of association is strictly limited by the willingness of the acidic hydrogen to accept its electrons. However the electron donating capacity of the ethereal oxygen is similar to that of the "pi" electrons of an aromatic ring. This probably results from the ease of access to these electrons and the ability of the "pi" electron system to become polarized.

The similarity in the association constants for benzoyl acetylene in the ethereal and the aromatic solvents was belied by the frequency shifts of the "bonded" peaks in the two types of solvent. In n-butyl ether as solvent the "bonded" peak was shifted by as much as 50 cm.$^{-1}$ to lower frequency and was easily distinguished from the "free" peak. In the aromatic solvents the "free" and "bonded" peaks were so close together as to be indistinguishable. This further verified the belief that the frequency shift cannot be related to the degree of hydrogen bonding over a wide range of solvents. Only when the electron donors and acceptors are of similar type will the frequency shift indicate the degree of hydrogen bonding. It would appear to be indicative of hydrogen bonded systems, in which the aromatic "pi" electrons were the donating group, that the frequency shift is very small.

In calculating the association constants at different temperatures the principal assumption made was that the integrated absorption intensity of the ethynyl hydrogen stretching vibration, if association was complete, (A_{AB}) did not change with temperature. It was shown experimentally that the integrated absorption intensity in pure cyclohexane (A_A) was invariant with change in temperature. Equation (27) permitted the determination of the association constant at a known mole fraction (x_B) of the electron donor and at a known temperature. Using the standard Clausius - Clapeyron equation a linear relation was obtained between the logarithm of the association constant and the reciprocal of the absolute temperature. Considerable scatter was observed in the experimental points and a least squares refinement was required to obtain the best straight line through the points. The slope of the line gave an estimate of the enthalpy of association which was taken to be the strength of the hydrogen bond in the complex. The results appeared to indicate that the strength of the hydrogen bond increased from benzene to mesitylene.

The results obtained by this method were suspect owing to the inherent inaccuracy of the method and to their magnitude. Gramstad[132] obtained enthalpies of about 7 kcals/mole for phenol in nitrogen bases and Joesten and Drago[60] found enthalpies of 5 - 6 kcals/mole for phenol in various ethers. However, in complexes involving chloroform Huggins, Pimentel and Shoolery[40] obtained enthalpies of 2.5 kcals/mole in acetone and 4.0 kcals/mole in triethylamine. Creswell and Allred determined the enthalpy of chloroform in benzene[109] to be 1.97 kcals/mole and of fluoroform in tetrahydrofuran[41] to be 2.59 kcals/mole. The above results would lead one to expect values for the enthalpy of association in a complex of benzoyl acetylene with an aromatic solvent to lie in the range 2 - 4 kcals/mole. In fact the only result to lie in that range is the enthalpy of the benzene - benzoyl acetylene complex which is probably unreliable. The results obtained undoubtedly suffer from the inherent inaccuracies involved in the method of obtaining the association constants.

Though the results do not compare as well as could be hoped with the enthalpies obtained by calorimetric means they are at least of the same order of magnitude. It is to be expected that the results obtained calorimetrically will be the most accurate. The greatest deviation between the results obtained by the two methods is found for the benzoyl acetylene - mesitylene system. It is also of interest to note that the infrared technique claims that the lowest enthalpy of association is that for the system benzoyl acetylene - benzene while it is given the highest enthalpy by the calorimetric method. While the enthalpies obtained by the infrared method agree with the expectation that the strength of the hydrogen bond in the complex.would become greater on going to more highly methylated benzenes, the calorimetric results appear to disagree with this expectation. The position with regard to the comparison of hydrogen bond strengths obtained by differing techniques is, as a result, rather unsatisfactory.

IV. 4. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance was applied to this investigation of hydrogen bonding partly to supplement the data obtained by infrared techniques and partly to confirm that data. The chemical shift of the ethynyl proton resonance signal in various solvents was used as a means of estimating the degree of association of benzoyl acetylene in that solvent. It has been suggested by Buckingham, Schaeffer and Schneider[133] that the chemical shift of the solute molecules is affected by a number of factors i.e.

$$\delta = \delta_G + \delta_B + \delta_a + \delta_w + \delta_c + \delta_E \quad \ldots\ldots \ (33)$$

where δ_G is the chemical shift measured in the gas phase.

δ_B is the chemical shift due to the bulk diamagnetic susceptibility.

δ_a is the chemical shift arising from the solvent magnetic anisotropy.

δ_w is the chemical shift due to Van der Waals interactions between solute and solvent molecules.

The above contributions are important for all solute molecules in solution but if, in addition, the solute molecule is polar then two further terms have to be included:-

δ_c which is the shift due to specific interactions between the solute and the solvent, i.e. complex formation.

And δ_E the shift arising from the reaction field of the solvent. The latter effect arises from neighbouring polarised solvent molecules producing an electric field at the polar solute molecule resulting in a change in the electronic configuration and the screening of the solute.

In all systems studied cyclohexane was used both as an inert solvent and as the internal reference. Since the shape, molar volume and the dielectric constant of cyclohexane and the aromatic solvents are similar the contributions to the chemical shifts from the Van der Waals forces and the reaction field can be ignored. The use of an internal reference also eliminated the contribution of the bulk diamagnetic susceptibility of the solvent. This left only two contributions to the chemical shift arising from the presence of the solute in the solvent. These were

δ_a, the shift due to the solvent magnetic anisotropy and δ_c, the shift arising from complex formation. If δ_c were zero, implying complete randomnization then δ_a should also be zero since both the solute and the cyclohexane in the active solvent would experience the same magnetic environment. If, however, δ_a were not zero, in other words there was a specific interaction between the solutes and the active solvent resulting in preferred mutual orientations, then δ_a would not equal zero. δ_c, which arises from small perturbations of the electronic charge distribution of the solute molecule due to the electric fields of neighbouring molecules, was usually negative. δ_a, due to the magnetic anisotropy of the active solvent, was, especially in aromatic solvents, large and positive. In aromatic solvents the ethynyl proton resonance signal shifted upfield indicating δ_a to be much greater than δ_c. This suggests that small chemical shifts of the solute proton arising from complex formation in aromatic solvents are effectively amplified because of the large magnetic anisotropy of the active solvent. Schneider[134] has also shown that the differing shapes of the solute and the solvent molecules cannot account for the chemical shift observed. It was assumed that the shifts obtained were due entirely to complex formation between the benzoyl acetylene and the active solvent.

In a solution of benzoyl acetylene in an active solvent an equilibrium of the following type exists:-

$$A + B \rightleftharpoons AB$$

The association constant for the equilibrium being given by

$$K_{11} = (AB)/(A)[B] \qquad \ldots\ldots (34)$$

where ( ) = the concentration in moles/litre

[ ] = the concentration in mole fractions.

In the solution the total amount of ethynyl compound added $(A)_o$ was made up as follows:-

$$(A)_o = (A) + (AB) \qquad \ldots\ldots (35)$$

If one assumed that $\delta = 0$ for the ethynyl compound in pure cyclohexane and that δ_{AB} was the shift if association was complete then :-

$$(A)_o \delta = (A)\delta_A + (AB)\delta_{AB}$$

and since $\delta_A = 0$

$$\delta = (AB)\delta_{AB}/(A)_o \qquad \ldots\ldots (36)$$

Combining equations (34) and (36)

$$(A)_o \delta = K_n (A)[B]\delta_{AB}$$

and combining equations (34) and (35)

$$(A)_o = (A) + K_n(A)[B] = (A)\ (1 + K_n[B])$$

Therefore

$$(A)_o \delta = K_n (A)_o [B]\delta_{AB}/(1 + K_n[B])$$

and $[B]/\delta = 1/K_n\delta_{AB} + [B]/\delta_{AB}$

i.e. $x_B/\delta = x_B/\delta_{AB} + 1/K_n\delta_{AB}$ $\qquad \ldots\ldots (29)$

The above equation will give a straight line graph from which the association constant K_n and the term δ_{AB} can be obtained.

Owing to the relative insensitivity of the apparatus the concentration of benzoyl acetylene (0.1 moles/l. of solvent) was greater than that used for the infrared investigations. However an infrared study of benzoyl acetylene in cyclohexane at concentrations up to 0.3 moles/l. of solvent showed no trace of self association. The straight line graphs obtained using this technique were superior to those obtained by infrared methods. This could be attributed partly to the fact that chemical shifts can be obtained much more quickly and accurately than band areas and partly to obtaining at least ten experimental values for each point. The results obtained by the two techniques are listed in Table 29.

Table 29

Solvent	Infrared		N.M.R.	
	K_n (m.f.)$^{-1}$	Deg. of Assoc.	K_n (m.f.)$^{-1}$	Deg. of Assoc
Benzene*	0.31 ± 0.13	0.24 ± 0.10	1.14 ± 0.03	0.53 ± 0.02
Toluene	1.39 ± 0.28	0.56 ± 0.14	1.67 ± 0.04	0.63 ± 0.02
P-Xylene	2.43 ± 0.31	0.71 ± 0.11	2.27 ± 0.02	0.69 ± 0.01
Mesitylene	2.96 ± 0.81	0.75 ± 0.26	2.57 ± 0.04	0.72 ± 0.02
n-Butyl ether	1.77 ± 0.09	0.64 ± 0.04	2.12 ± 0.06	0.68 ± 0.02

* Alternative values for benzene :-

K_n = 0.61 ± 0.08 (m.f.)$^{-1}$; Degree of Association = 0.38 ± 0.05

The association constants were determined much more accurately by nuclear magnetic resonance spectroscopy. In these systems, neglecting the benzene system for the moment, there was a reasonable comparison between the results obtained by the two methods. This correspondence between the two sets of results assures one that both methods are measuring the same physical properties of the system. The discrepancy in the results obtained for the benzoyl acetylene - benzene system by the two methods has already been explained in terms of the inaccuracy of the infrared results. The justification for neglecting the experimental result at 0.1 mole fraction of benzene in the infrared results is that this brings them more into line with those obtained by nuclear magnetic resonance spectroscopy.

Both the infrared and the nuclear magnetic resonance results show an increase in the association constant as the aromatic solvents become more highly methylated. This increase is not linear however and there is probably a steric effect competing with the inductive effect of the methyl groups. It was also noticeable that, as the number of methyl groups attached to the ring was increased the terms A_{AB} and δ_{AB} both decreased. Both methods indicated that a 1:1 complex was formed between the benzoyl acetylene and the active solvent. In all cases the electron acceptor was the ethynyl hydrogen of the benzoyl acetylene or of the phenyl acetylene. In the n-butyl ether solvent both the appearance of the spectrum in the infrared and the direction of the shift in the nuclear magnetic resonance treatment indicated that the ethynyl hydrogen was bonding to the ethereal oxygen. The upfield shift obtained for the solutions in the aromatic solvents indicated that bonding was to the "pi" electron system of the ring. In these investigations the nuclear magnetic resonance method was found to be superior, both with regard to speed and accuracy, to the infrared approach.

A rather different form of solute - solvent interaction has been investigated using nuclear magnetic resonance spectroscopy. This resulted from work carried out by Hatton and Richards[51] on propargyl chloride in a variety of solvents. They observed that both the ethynyl and the methylene proton resonance signals shifted, usually in the same direction. Table 30 gives a list of the values obtained by the above authors.

Table 30

Propargyl Chloride - Solvent Effects

Solvent	Ethynyl Proton τ p.p.m.	Methylene Proton τ p.p.m.
Cyclohexane	7.81	6.13
Acetone	6.94	5.77
Dioxan	7.07	5.87
Acetonitrile	7.20	5.83
Nitrobenzene	7.10	5.79
Nitromethane	7.27	5.82
Thiophene	7.92	6.38
Benzene	8.12	6.58
Toluene	8.16	6.62

Both the ethynyl and the methylene proton resonance signals are seen to shift in the same sense in going from cyclohexane to some other solvent. Where the bonding could be clearly attributed to lone pair electrons of strongly electronegative groups the ethynyl proton resonance signal was always shifted to lower field to a greater extent than was the methylene proton resonance signal. In such cases the shift in the methylene proton signal was probably due purely to a solvent effect, the bonding group being the ethynyl hydrogen. The most interesting effects were observed in the aromatic solvents where both proton resonance signals moved upfield. In particular, the methylene resonance signal shifted upfield to a greater extent than did the ethynyl resonance signal (Table 31).

Table 31

The Effect of Aromatic Solvents on Propargyl Chloride

Solvent	Ethynyl Proton Shift p.p.m.	Methylene Proton Shift p.p.m.
Thiophene	0.11	0.25
Benzene	0.31	0.45
Toluene	0.35	0.49

Hatton and Richards[51] attached no significance to this difference, assuming the formation of a weak complex in which the axis of the propargyl chloride was parallel to the plane of the aromatic ring. However it was considered feasible to explain the differences in terms of a complex in which the methylene protons, owing to activation by neighbouring groups, bonded to the aromatic ring.

It was shown that when methylene protons were involved in a complex with benzene the chemical shift observed depended on the nature of the neighbouring groups i.e.

$$C \equiv C < Cl < C \equiv N$$

Whether the association results from hydrogen bonding or from dipole - induced dipole effects produced by the solute dipole is difficult to determine. Both forms of association would be strongly influenced by temperature. Abrahams[112] investigated the formation of complexes between toluene and methyl iodide or iodoform. In both cases he concluded that the dipole axis of the solute molecule lay along the hexagonal axis of the ring with the protons oriented towards the ring. Iodoform, like chloroform was believed to be hydrogen bonded to the ring as was methyl iodide. This belief was based on the observation that the high field shifts of the protons in the methyl halide were not significantly affected by varying the halogen atom (i.e. varying the solute dipole moment). This fitted in with the fact that hydrogen bonding is not simply related to the solute dipole moment.

However Schneider[134] has related the proton resonance shift of a number of alkyl halides to the dipole moment and the molecular volume of the solute. He also postulated that bonding between alkyl halides and benzene was due to a dipole - induced dipole attraction between the two molecules. The correlation between the chemical shift experienced by the methyl protons in going from neopentane to benzene and the dipole moment and molecular volume is somewhat poor. In particular the fact that the shifts of methyl bromide and methyl iodide were almost identical does not fit at all with Schneider's postulate. The methylene protons may therefore form a legitimate hydrogen bond to the aromatic "pi" electrons in benzene.

In 1:4 dichlorobut-2-yne there are two identical methylene groups and the results obtained and graphed on the basis of a 1:1 complex give a curved line. When the equation was extended to include a 1:2 complex of the acetylene and benzene a straight line was obtained. In this modified equation δ_{AB} was assumed to be identical for both complexes and this appeared to be justified by the results obtained.

The results obtained for propargyl chloride indicated that the δ_{AB} for the methylene protons was nearly twice that observed for the ethynyl proton. The results for the methylene protons gave a straight line graph indicating the presence of a 1:1 complex but the graph obtained for the ethynyl proton was slightly curved. This curvature was not pronounced and was probably due to the low values of the shift being measured. At low chemical shifts the difference between the shift of the uncomplexed solute protons and those of the cyclohexane is no longer negligible and could account for the deviation from a straight line. The association constants obtained for both types of proton were identical within the limits of experimental error indicating that only one complex existed in solution. In this complex the methylene protons were closer to the ring than the ethynyl proton, the molecule lying at an angle across the ring.

Using the ring current theory it was possible, using the chemical shift, to determine the distance of the ethynyl proton from the plane of the ring. The method on which the calculation was based was due to Johnson and Bovey[135]. The value of the chemical shift used in these calculations was that of the δ_{AB} term, representing the additional field seen by the solute proton in the complex as compared with the uncomplexed solute proton. Since this shift was measured relative to cyclohexane in the aromatic solvent and since the cyclohexane protons were also shifted in the benzene, the high field shift of the cyclohexane protons in aromatic as compared with isotropic solvents had to be added. Abrahams[112] obtained a value for this high field shift for cyclohexane in going from cyclohexane to benzene as solvent of 0.43 p.p.m. As a result the true chemical shift of benzyl acetylene in benzene as compared with cyclohexane was 1.55 p.p.m. This gave a distance for the ethynyl proton from the ring of 3.19 Å if it lay on the hexagonal axis of the ring. This distance was greater than the Van der Waals contact of 2.9 Å and therefore cannot be taken too seriously. The error may have arisen from positioning the ethynyl hydrogen over the centre of the ring. Since the "pi" electron cloud forms a circular loop of electron density round the edge of the ring the proton might be expected to lie above the edge of the ring. Assuming this position, the distance of the ethynyl proton of benzoyl acetylene from the plane of the benzene ring was found to be 2.8 Å. This result can only be considered as being of a semi-quantitative nature.

IV. 5. X-RAY DIFFRACTION

The C-H ····O hydrogen bond was studied in the crystalline state, partly to verify that it did exist and partly to determine the average number of hydrogen bonds formed per molecule. The latter factor was important in understanding the calorimetric results. Little work has been carried out on this form of hydrogen bond in the solid state and as a result its length was not known with any accuracy. Hassel[118,119] studied the complex of ethyl ether and bromodichloromethane in two dimensions and obtained a value for the C-H···· O distance of 3.1 Å. Though Sutor[120,121] has published a list of molecules containing short C-H ····O contacts no confirmatory evidence has been given to indicate that these were in fact hydrogen bonds. The X-ray study of o-bromobenzoyl acetylene indicated that the molecules were linked by hydrogen bonds to form a zig-zag chain. The individual molecules were linked through a hydrogen bond between the ethynyl hydrogen and the carbonyl oxygen. The two - dimensional Fourier map (Fig.24) indicates the nature of the linkage. The molecule itself was almost planar and the hydrogen bond was linear. The final value obtained for the C-H ····O hydrogen bond distance was 3.260 ± 0.015 Å which, if one takes the ethynyl C-H bond length to be 1.06 Å, gives an actual hydrogen bond length of 2.20 Å. This was considerably less than the Van der Waals contact distance of 2.6 Å. The data also indicated that there was, on average, one hydrogen bond per molecule. The length of the bond (3.26 Å) indicates that it should be comparatively weak being comparable, at least on the basis of length, with the N-H ····N (3.35 Å), the O-H ····Cl (3.18 Å) and the N-H ····Cl (3.20 Å) hydrogen bonds. In addition, the value obtained compared well with that of Hassel[118,119] and those postulated by Sutor[120,121].

IV. 6. CONCLUSION

Benzoyl acetylene is capable of hydrogen bonding through its ethynyl hydrogen to a variety of electron donors. Of most interest was the bonding to the "pi" electron systems of aromatic molecules. Infrared and nuclear magnetic resonance measurements were carried out to determine the association constants of benzoyl acetylene in a series of methylated benzenes. Though both methods gave comparable results the nuclear magnetic resonance method was both faster and more accurate. The more methyl groups attached to the ring the greater was the degree of association with the benzoyl acetylene. This increase was not linear possibly owing to competition between the inductive and the steric effects of the methyl groups. It was also noted that the degree of association of benzoyl acetylene with the aromatic solvents and with n-butyl ether was quite similar. This suggested that the electron donating capacity of both types of molecule was approximately the same.

The strengths of the hydrogen bonds studied was determined by infrared methods and by calorimetric means. The results obtained by the two methods were of the same order of magnitude but were not otherwise similar. The calorimetric results tended to oppose the idea that the more methyl groups attached to the benzene, then the stronger would be the hydrogen bonds, whereas the infrared results appear to agree with our expectations. The most accurate results were those obtained by calorimetry. Also determined were the free energy and the entropy of association, the latter indicating that association in benzene as solvent produced the highest degree of order.

A combined infrared and X-ray investigation of *o*-bromobenzoyl acetylene indicated that the molecules in the solid were linked through hydrogen bonds. A value for the C-H ····O hydrogen bond distance of 3.260±0.015 Å was obtained this being the first reliable measurement of a definite hydrogen bond of that type.

Propargyl chloride and 1:4 dichlorobut-2-yne were shown to associate with benzene through their methylene protons, the latter forming both a 1:1 and a 1:2 complex with the benzene. The methylene protons were considered to be activated by neighbouring groups in the molecule.

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APPENDIX

1) Figure 16 : Temperature versus Time for mixing Potassium Chloride with Water.

2) Figure 18 : (a - 1) Benzoyl Acetylene - Benzene - Cyclohexane Infrared Spectra at 28°-29°C.

In pure cyclohexane ---------- ;

In 0.4 m.f. benzene -·-·-·-·-·- ;

In 0.7 m.f. benzene ·········· ;

In 1.0 m.f. benzene ―――――――― .

(a - 2) Benzoyl Acetylene - Toluene - Cyclohexane Infrared Spectra at 28°-29°C.

In pure cyclohexane ---------- ;

In 0.3 m.f. toluene -·-·-·-·-·- ;

In 0.6 m.f. toluene ·········· ;

In 1.0 m.f. toluene ―――――――― .

(b - 1) Benzoyl Acetylene - P-Xylene - Cyclohexane Infrared Spectra at 28°-29°C.

In pure cyclohexane ―――――――― ;

In 0.3 m.f. p-xylene -·-·-·-·-·- ;

In 0.7 m.f. p-xylene ·········· ;

In 1.0 m.f. p-xylene ―――――――― .

(b - 2) Benzoyl Acetylene - Chlorobenzene - Cyclohexane Infrared Spectra at 28°-29°C.

In pure cyclohexane ――――――――;

In 0.4 m.f. chlorobenzene -·-·-·-·-·- ;

In 0.7 m.f. chlorobenzene ·········· ;

2) Figure 18 : (b - 2) In 1.0 m.f. chlorobenzene ———————— .

(c - 1) Benzoyl Acetylene - Mesitylene - Cyclohexane

Infrared Spectra at 28°-29°C.

In pure cyclohexane - - - - - - - - ;

In 0.3 m.f. mesitylene -·-·-·-·-·- ;

In 0.7 m.f. mesitylene ·········· ;

In 1.0 m.f. mesitylene ———————— .

(c - 2) Benzoyl Acetylene - n-Butyl ether - Cyclohexane

Infrared Spectra at 28°-29°C.

In pure cyclohexane - - - - - - - - ;

In 0.4 m.f. n-butyl ether -·-·-·-·-·- ;

In 0.7 m.f. n-butyl ether ·········· ;

In 1.0 m.f. n-butyl ether ———————— .

3) Figure 19 : Graphs of $x_B/(A - A_A)$ against x_B .

(a) Benzoyl Acetylene - Benzene - Cyclohexane.

(b) Benzoyl Acetylene - Toluene - Cyclohexane.

(c) Benzoyl Acetylene - P-Xylene - Cyclohexane.

(d) Benzoyl Acetylene - Mesitylene - Cyclohexane.

(e) Benzoyl Acetylene - n-Butyl ether - Cyclohexane.

(f) Phenyl Acetylene - n-Butyl ether - Cyclohexane.

4) Figure 20 : Infrared temperatures studies of hydrogen bonded complexes.

(a - 1) Benzoyl Acetylene in 0.5 m.f. benzene.

At 27°C ———————— ; At 50°C - - - - ; At 70°C ······

(a - 2) Benzoyl Acetylene in 0.8 m.f. toluene.

At 28°C ———————— ; At 50°C - - - - ; At 70°C ·······

4) Figure 20 : (b - 1) Benzoyl Acetylene in 0.5 m.f. p-xylene.

At 29°C —— ; At 50°C ----- ; At 70°C ······

(b - 2) Benzoyl Acetylene in 0.5 m.f. mesitylene.

At 27.5°C —— ; At 50°C ---- ; At 70°C ·····

(c) Benzoyl Acetylene in 0.5 m.f. n-butyl ether.

At 27.5°C —— ; At 50°C ----- ; At 70°C ·····

5) Figure 21 : Graphs of x_B/δ against x_B.

(a) Benzoyl Acetylene - Benzene - Cyclohexane.

(b) Benzoyl Acetylene - Toluene - Cyclohexane.

(c) Benzoyl Acetylene - P-Xylene - Cyclohexane.

(d) Benzoyl Acetylene - Mesitylene - Cyclohexane.

(e) Benzoyl Acetylene - n-Butyl ether - Cyclohexane.

6) Figure 22a : Graph of x_B/δ against x_B for the system,

1:4 Dichlorobut-2-yne - Benzene - Cyclohexane.

7) Figure 22b : Graph of $\delta/x_B(\delta_{AB}-\delta)$ against x_B for the system,

1:4 Dichlorobut-2-yne - Benzene - Cyclohexane.

8) Figure 23 : Graphs of x_B/δ against x_B

(a) Methylene protons of Propargyl Chloride in Benzene

(b) Ethynyl proton of Propargyl Chloride in Benzene.

9) Figure 24 : Two - dimensional electron density projection of

o-bromobenzoyl acetylene.

Figure 16

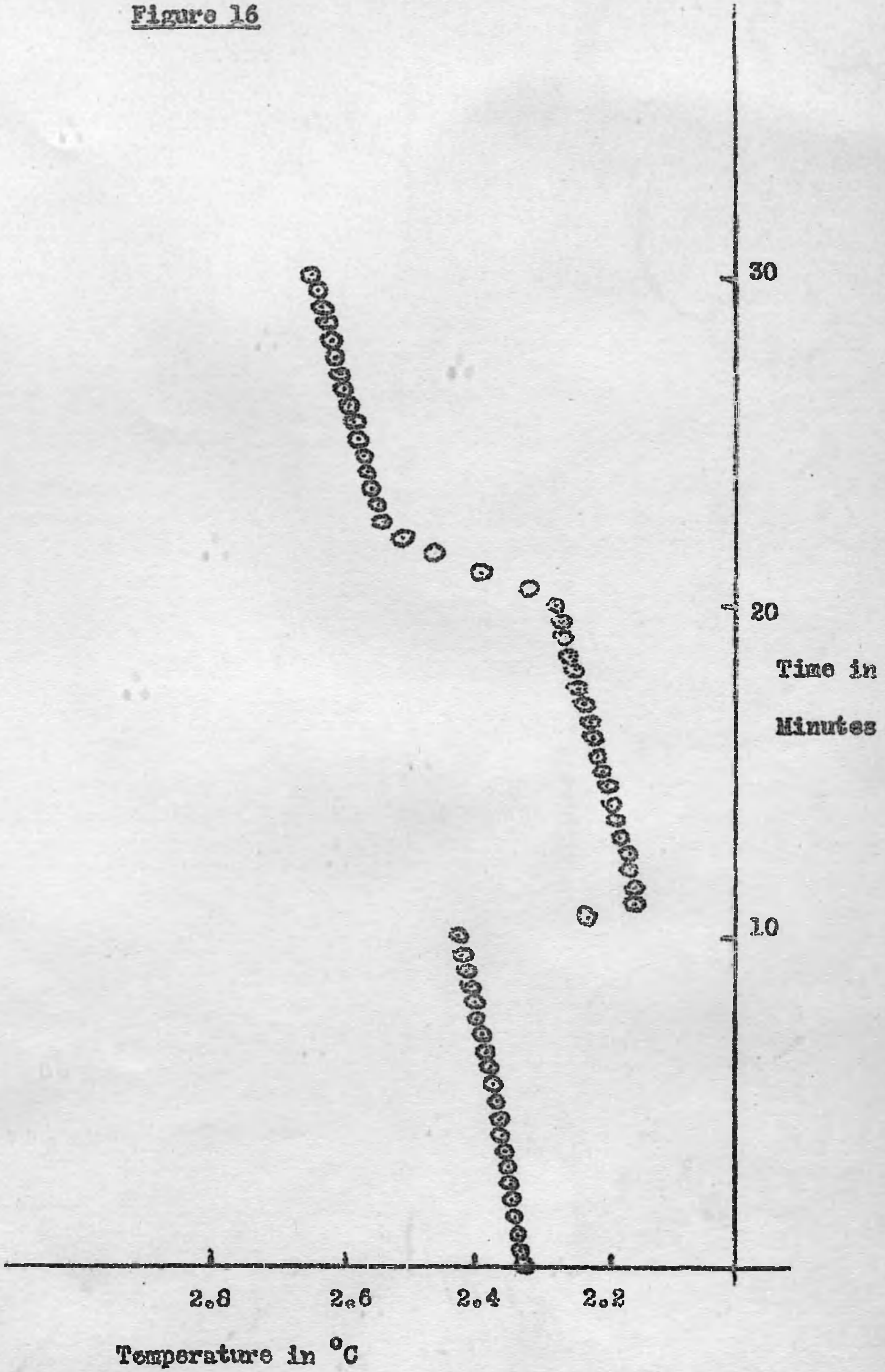


Figure 18

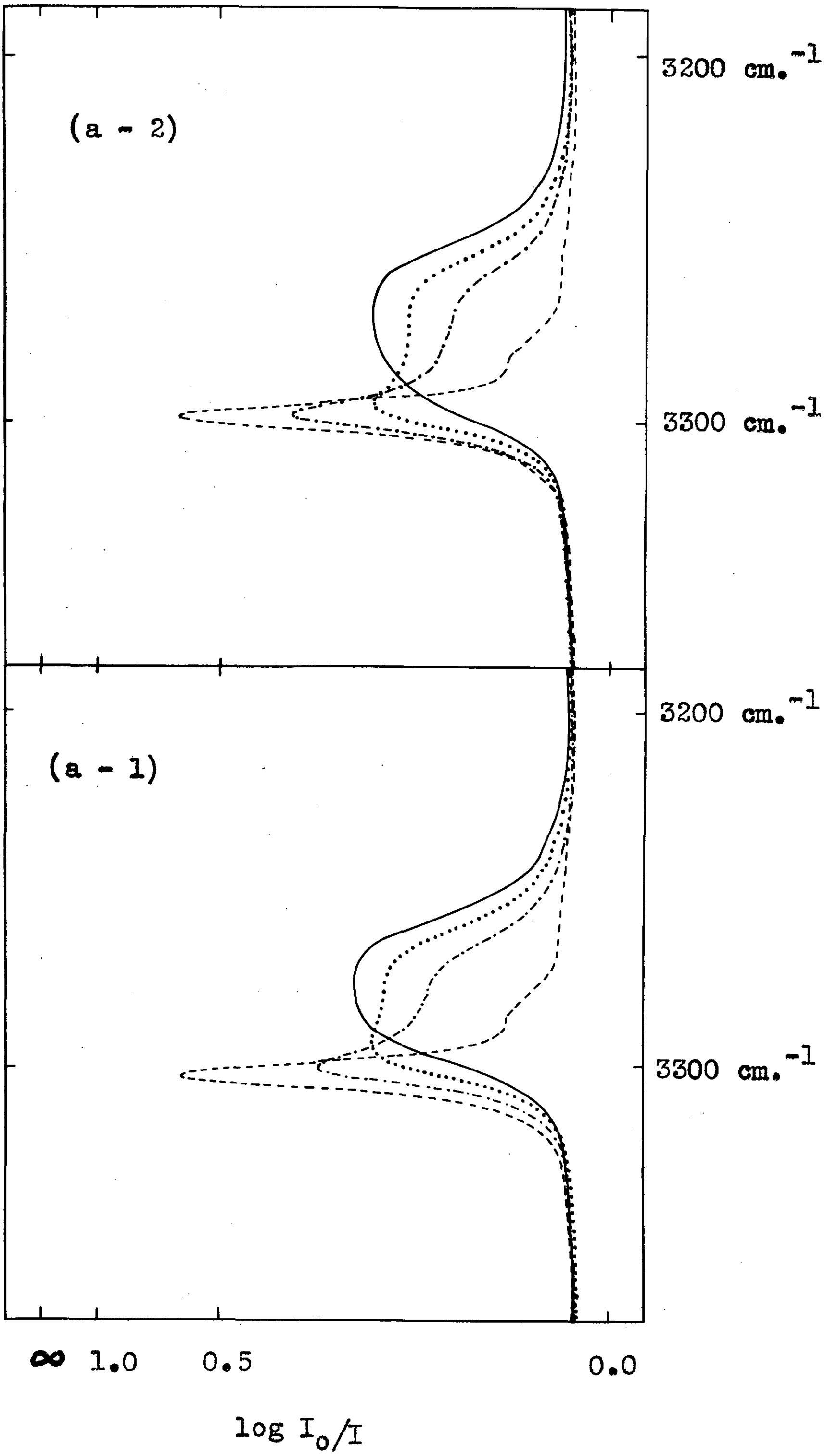


Figure 18

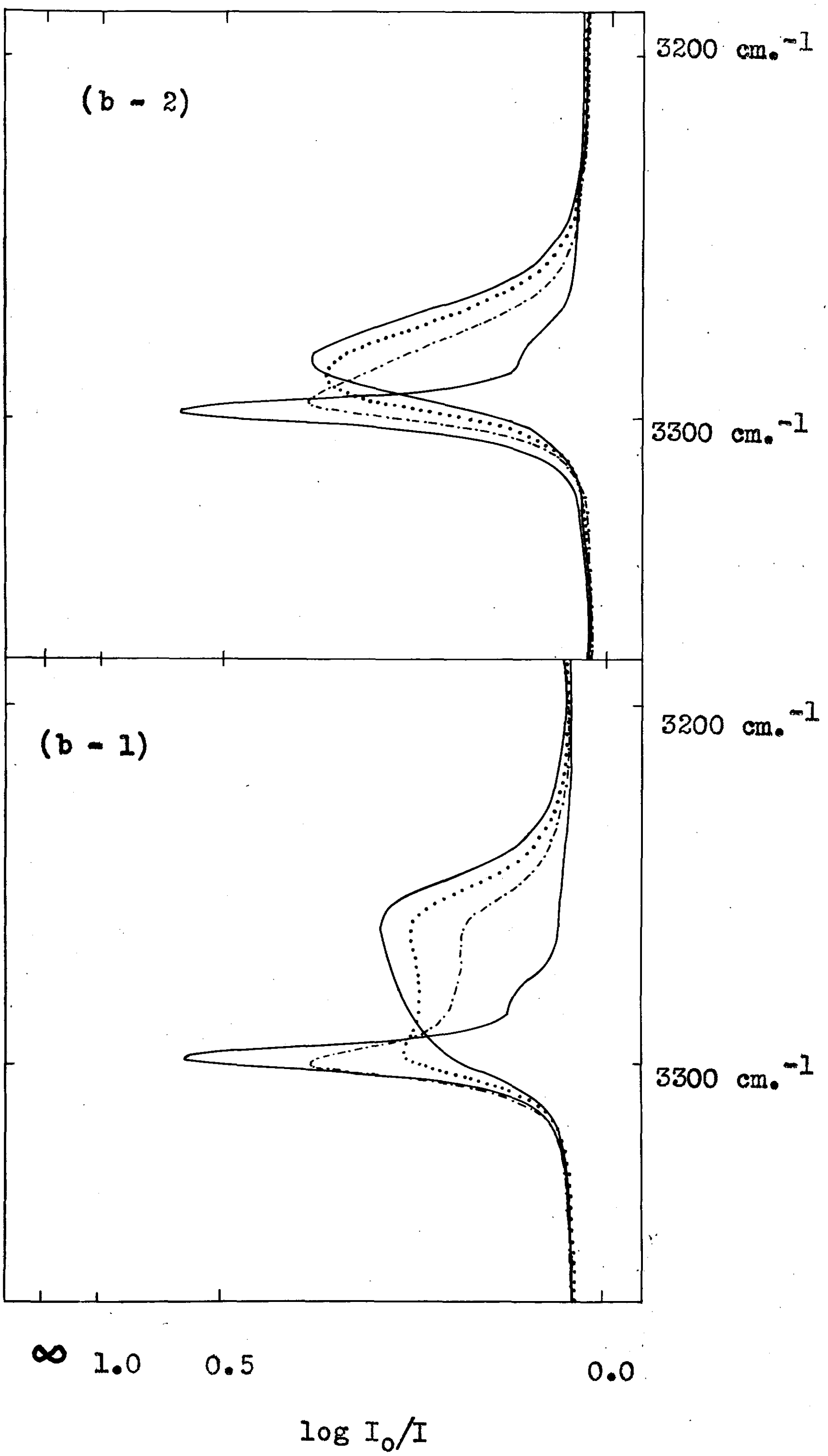


Figure 18

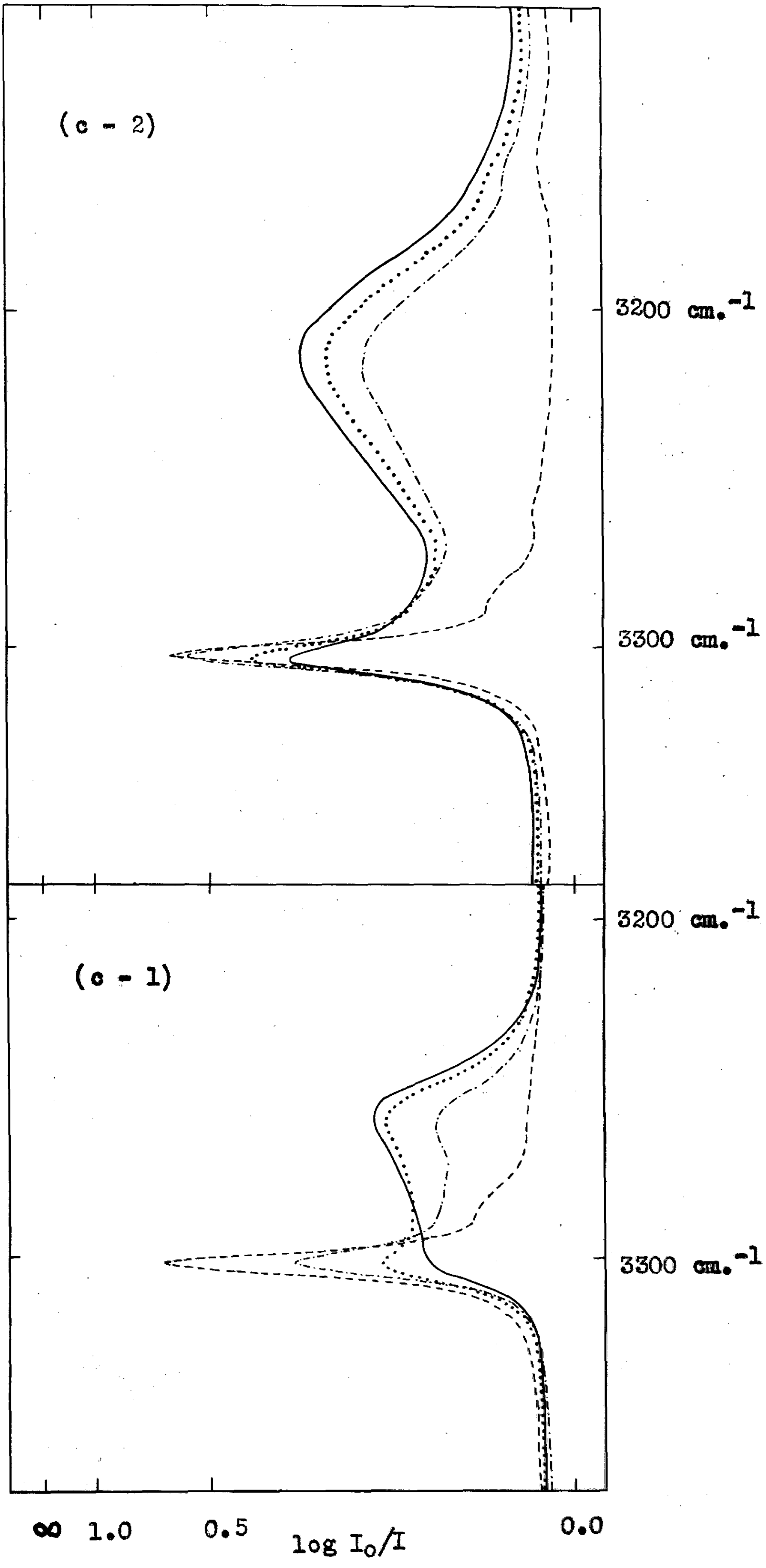


Figure 19(a)

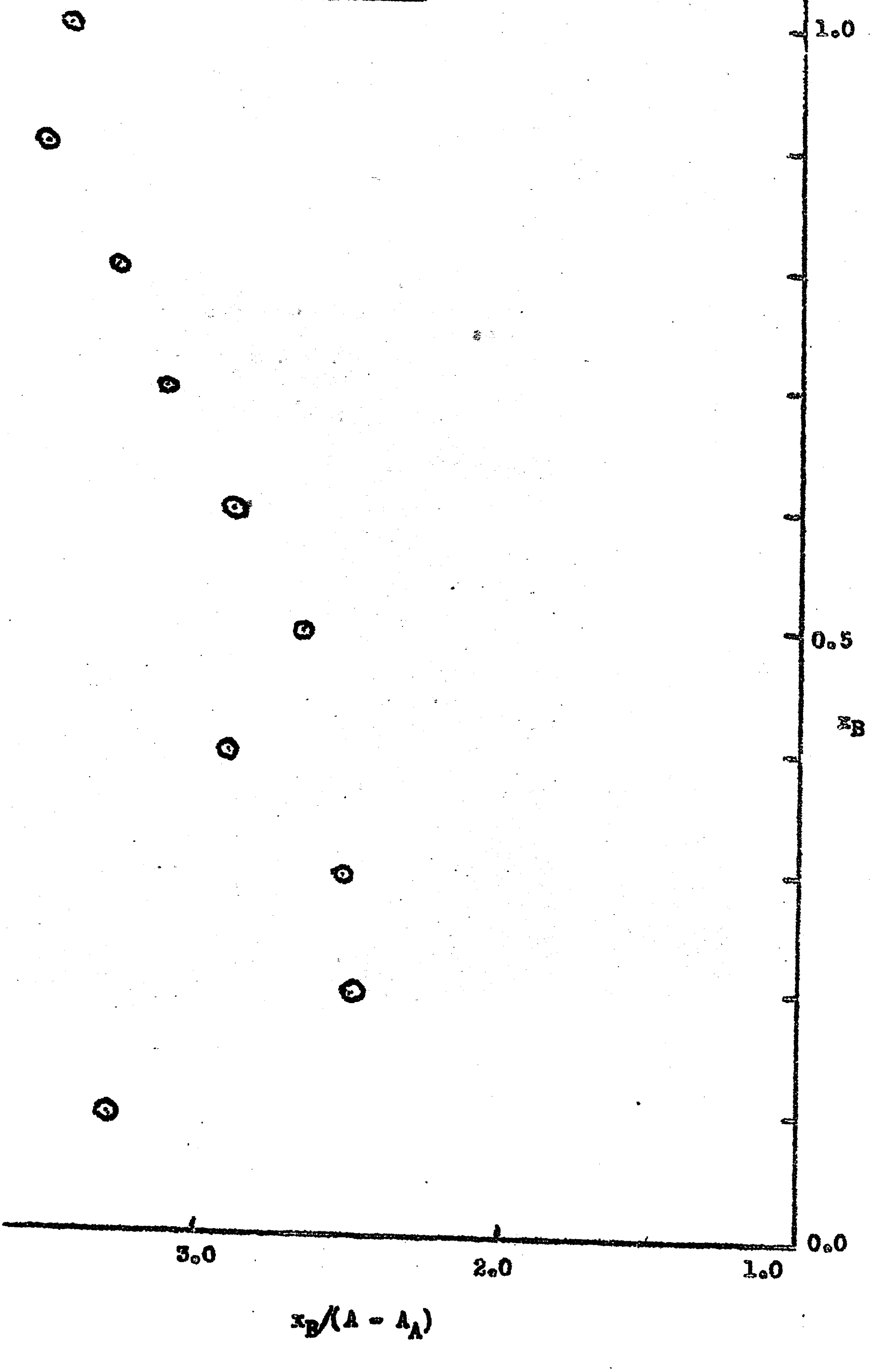


Figure 19(b)

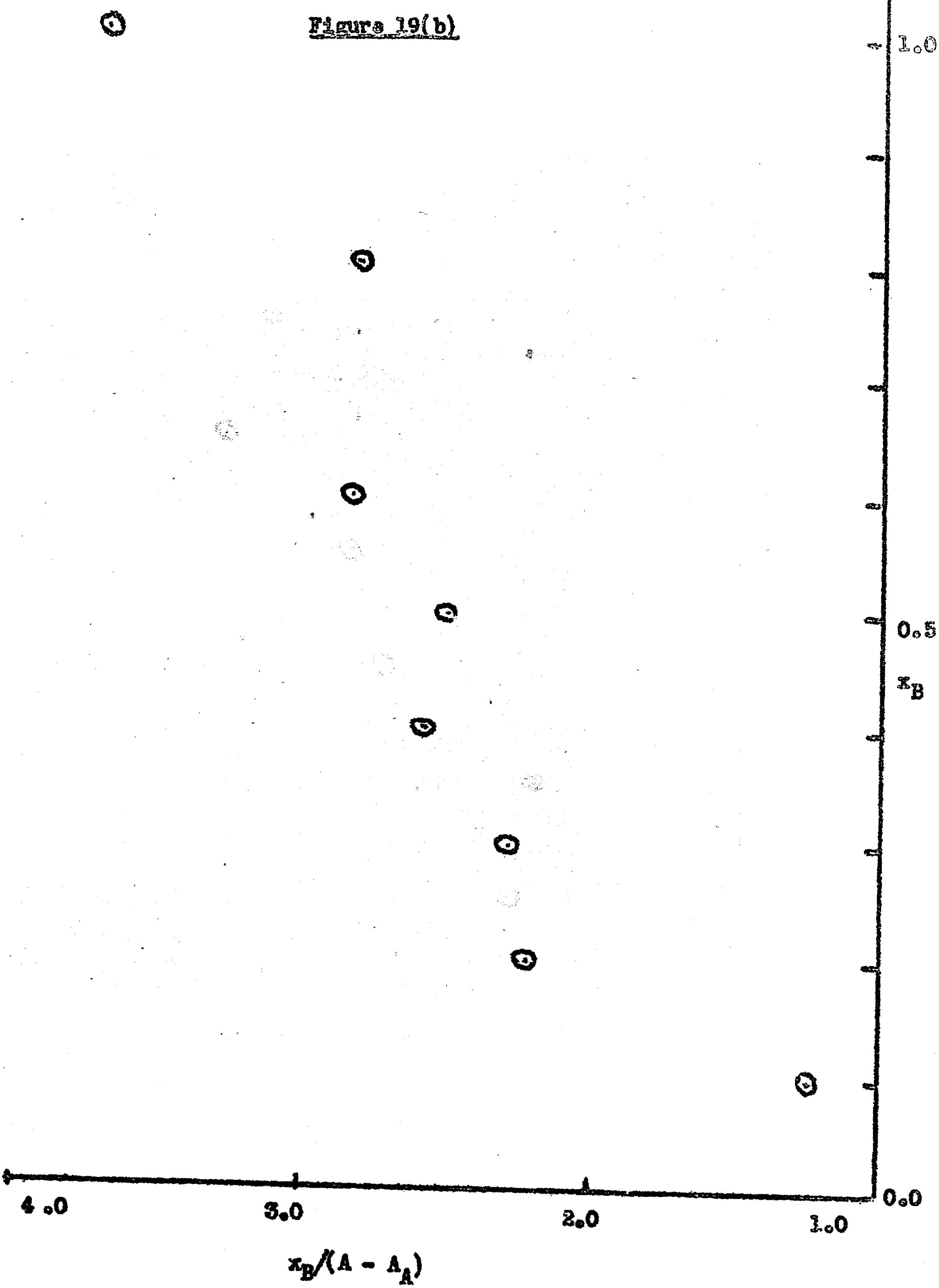
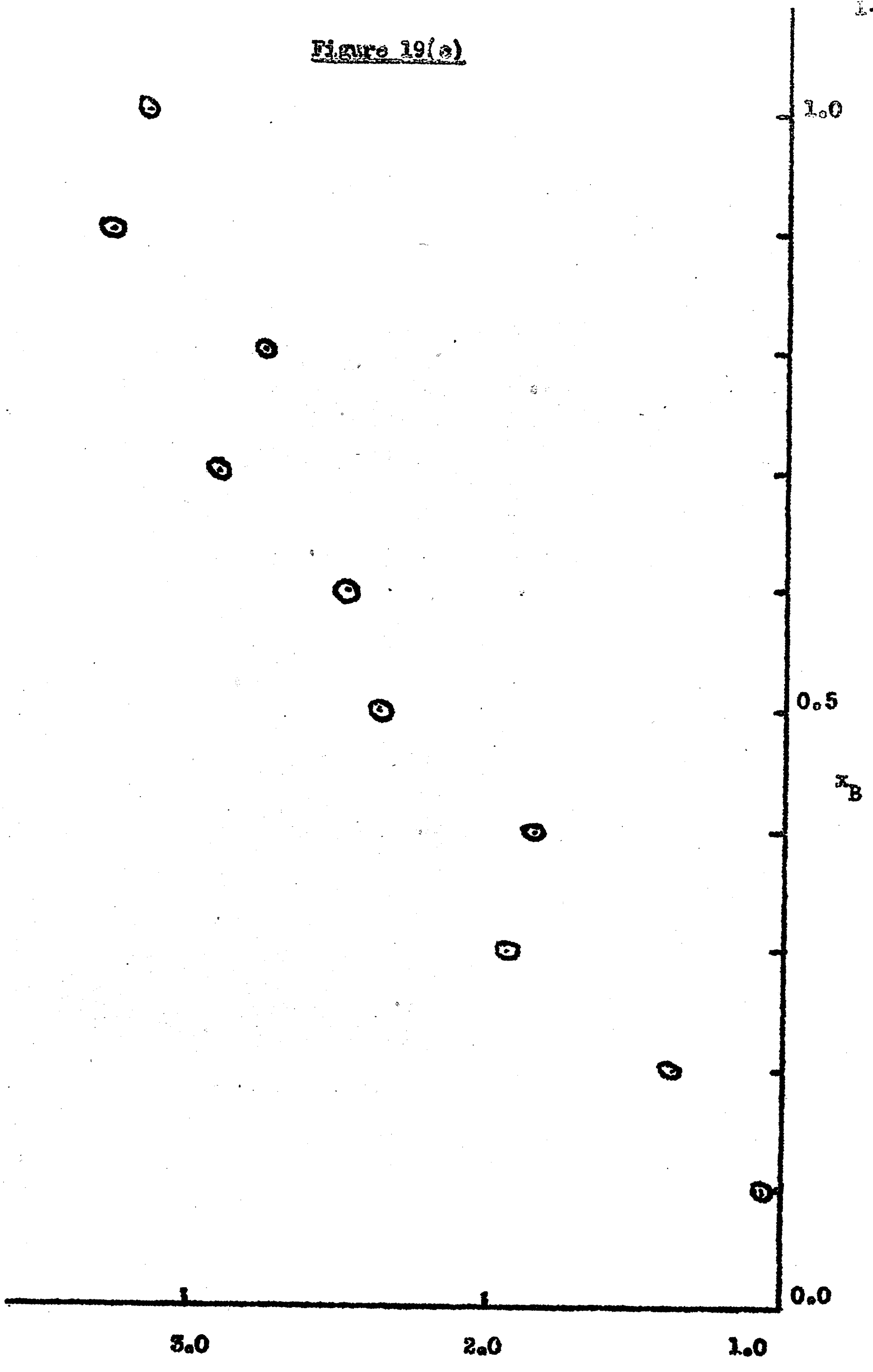


Figure 19(a)



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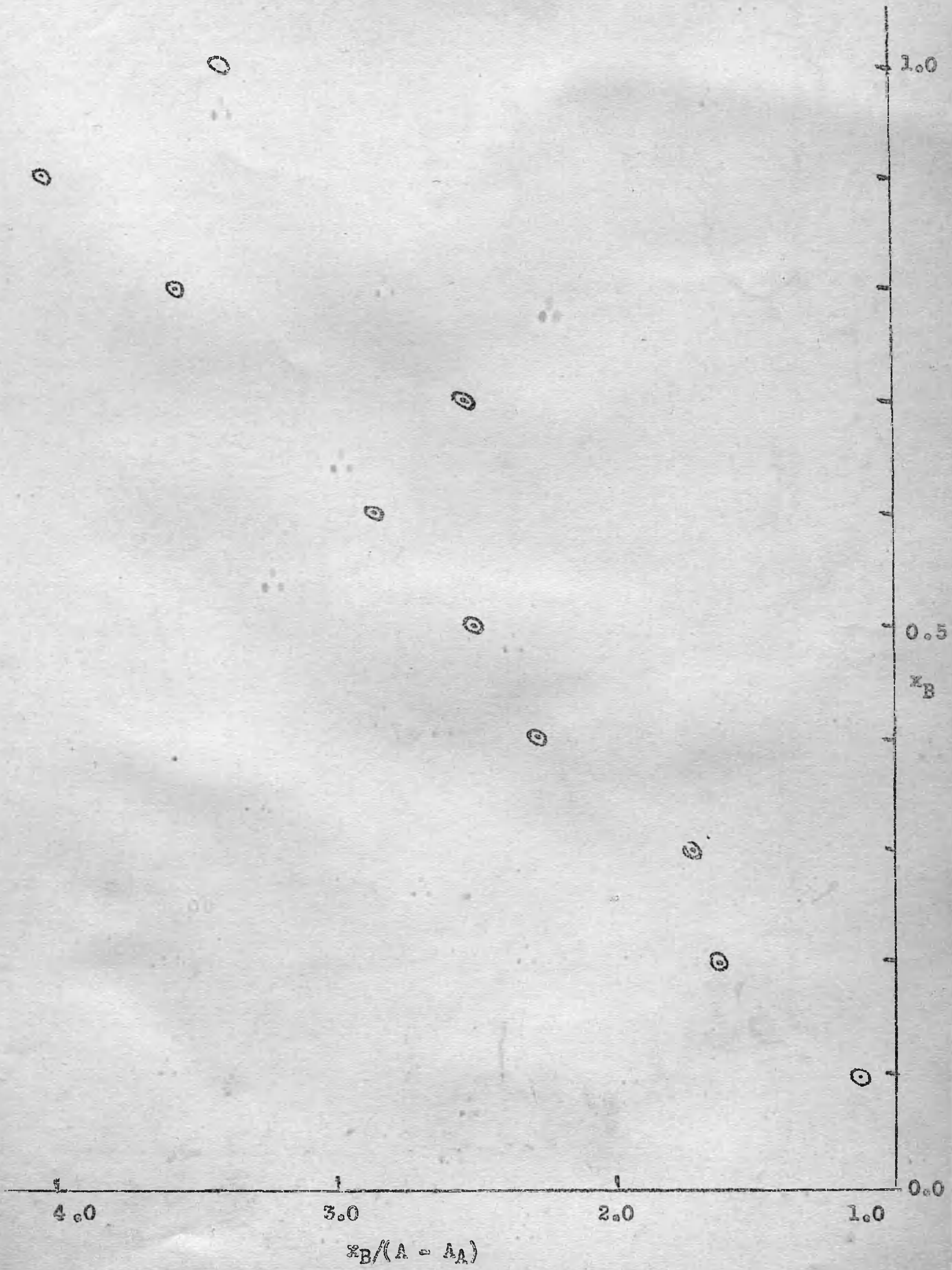
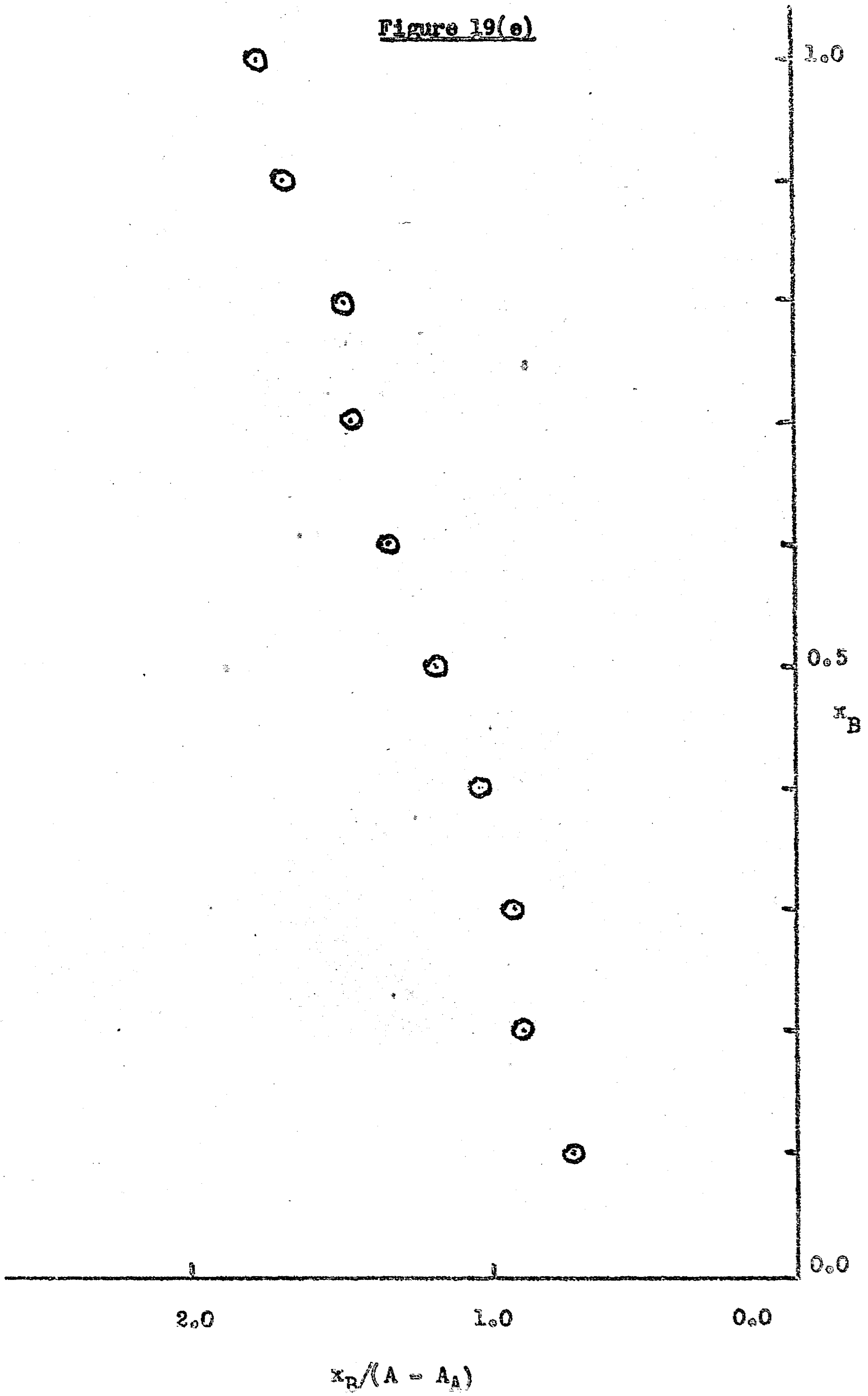


Figure 19(e)



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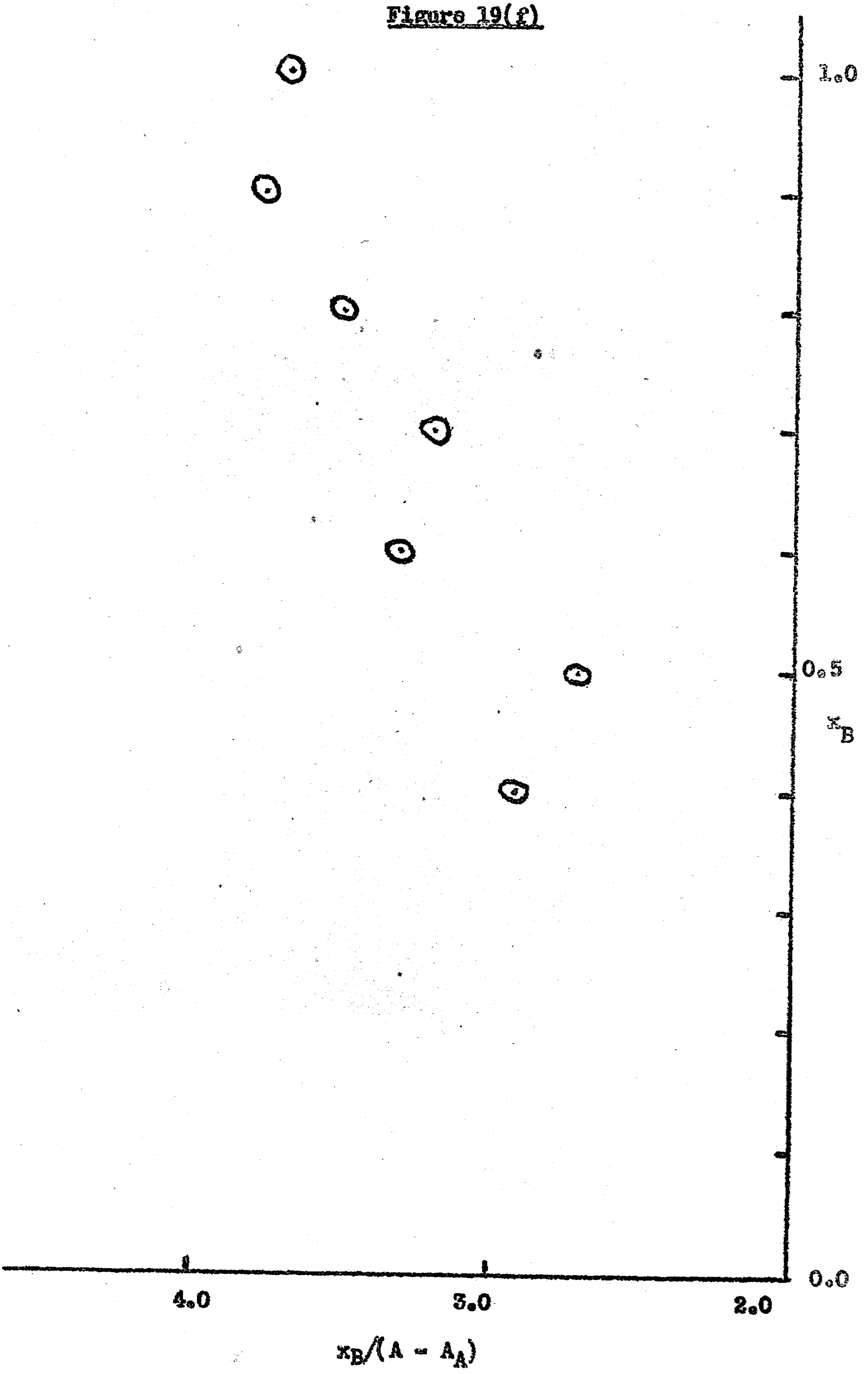

Figure 20

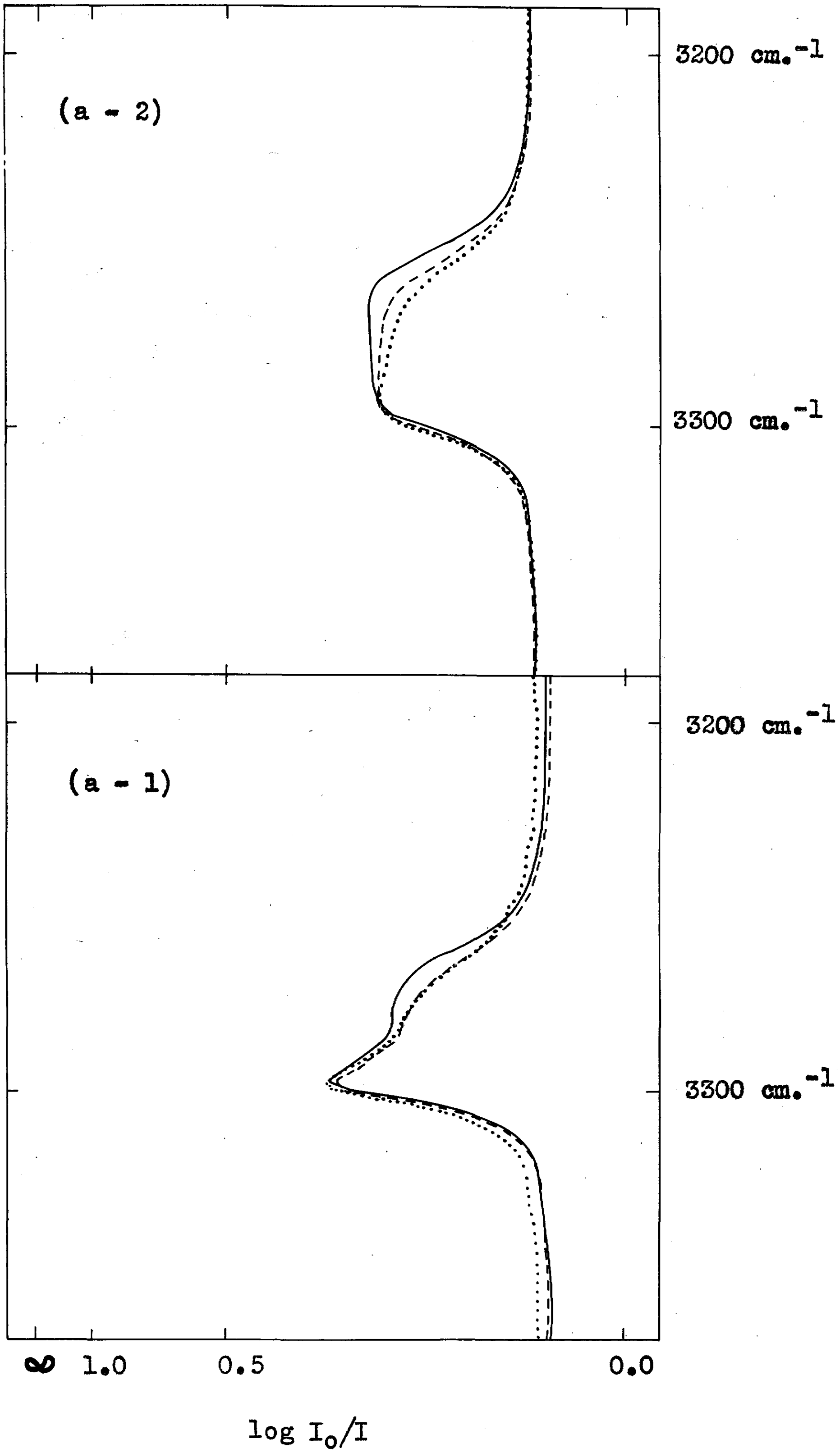

Figure 20

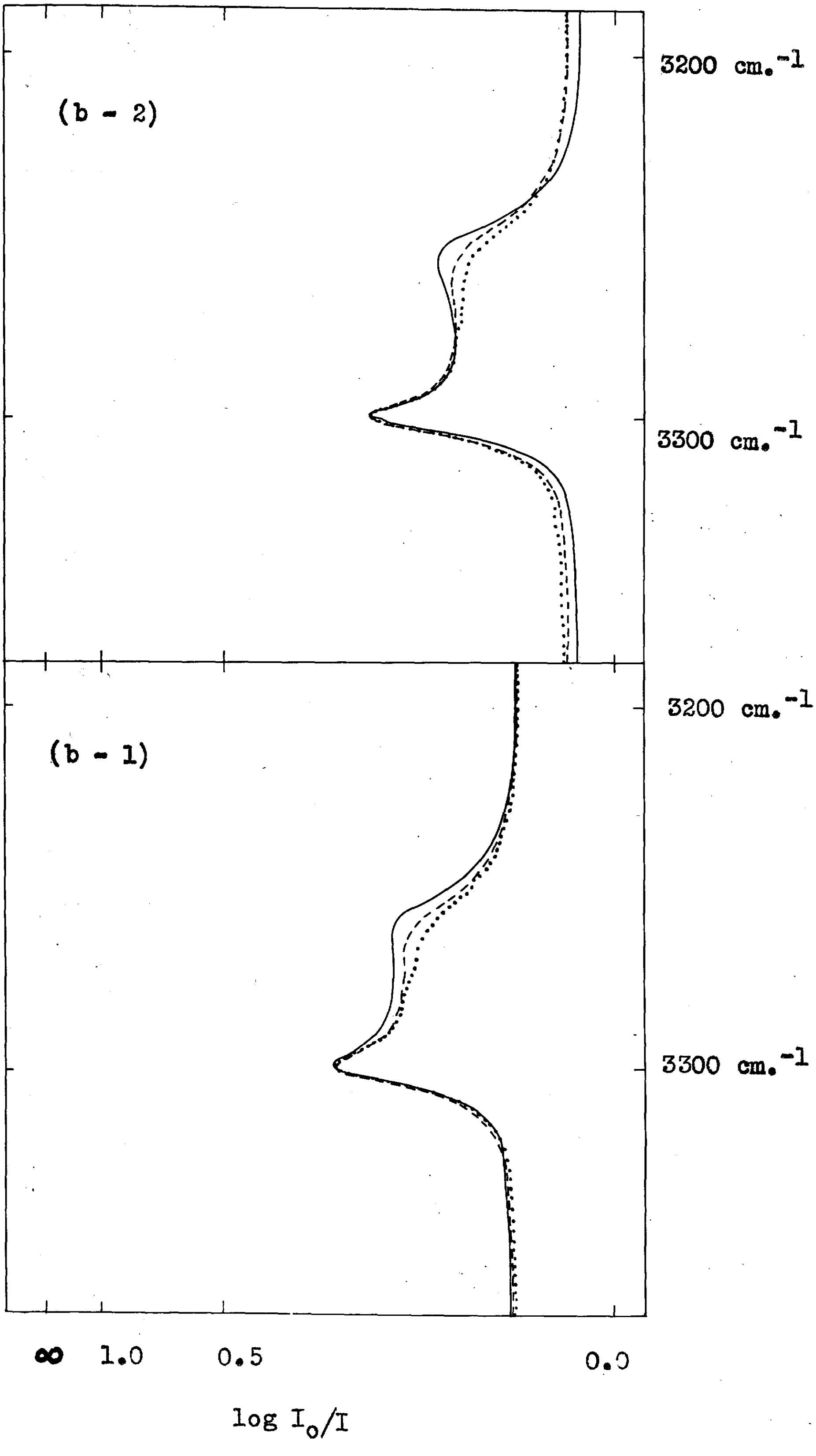

Figure 20

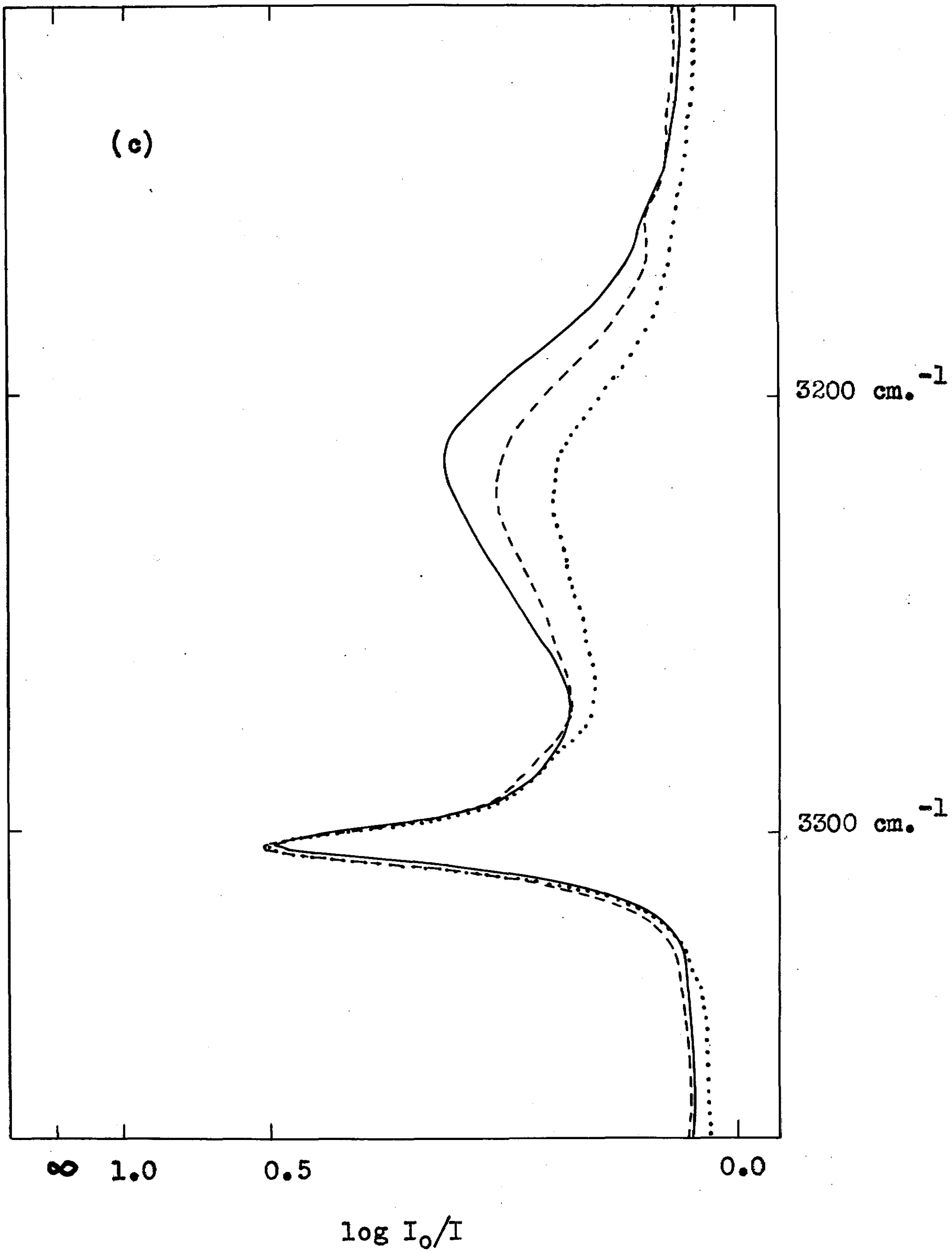

Figure 21(a)

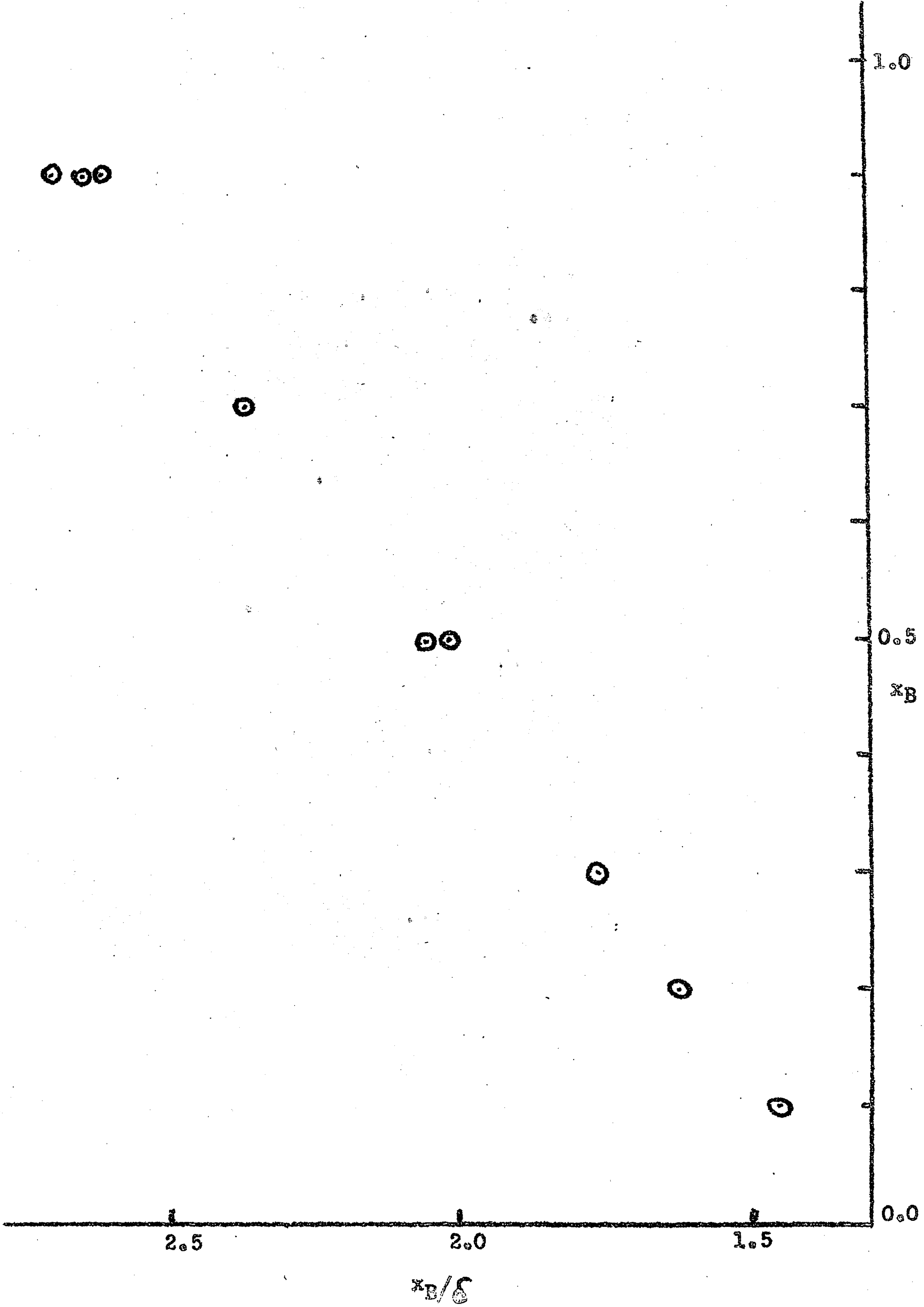

Figure 21(b)

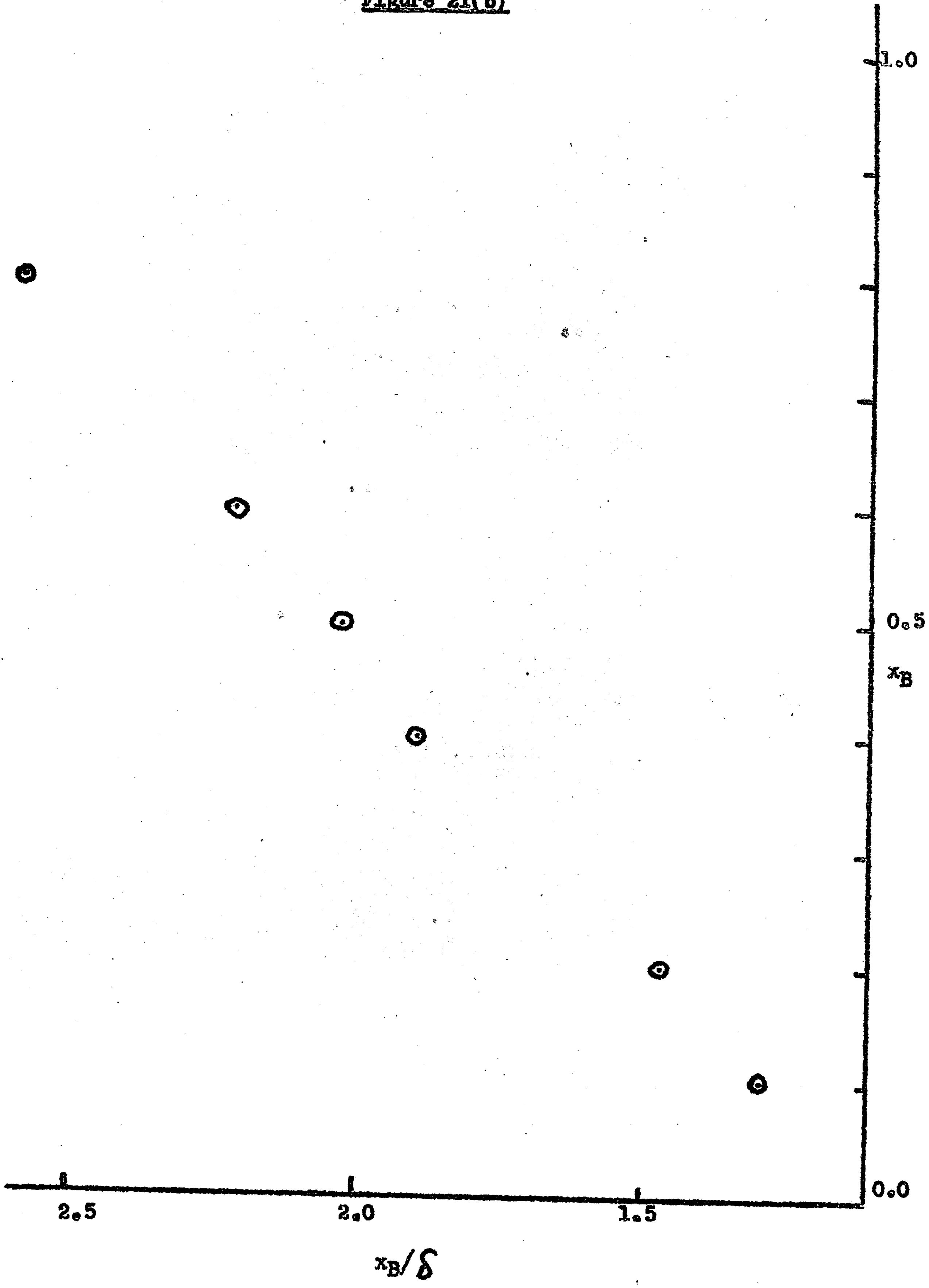

Figure 21(c)

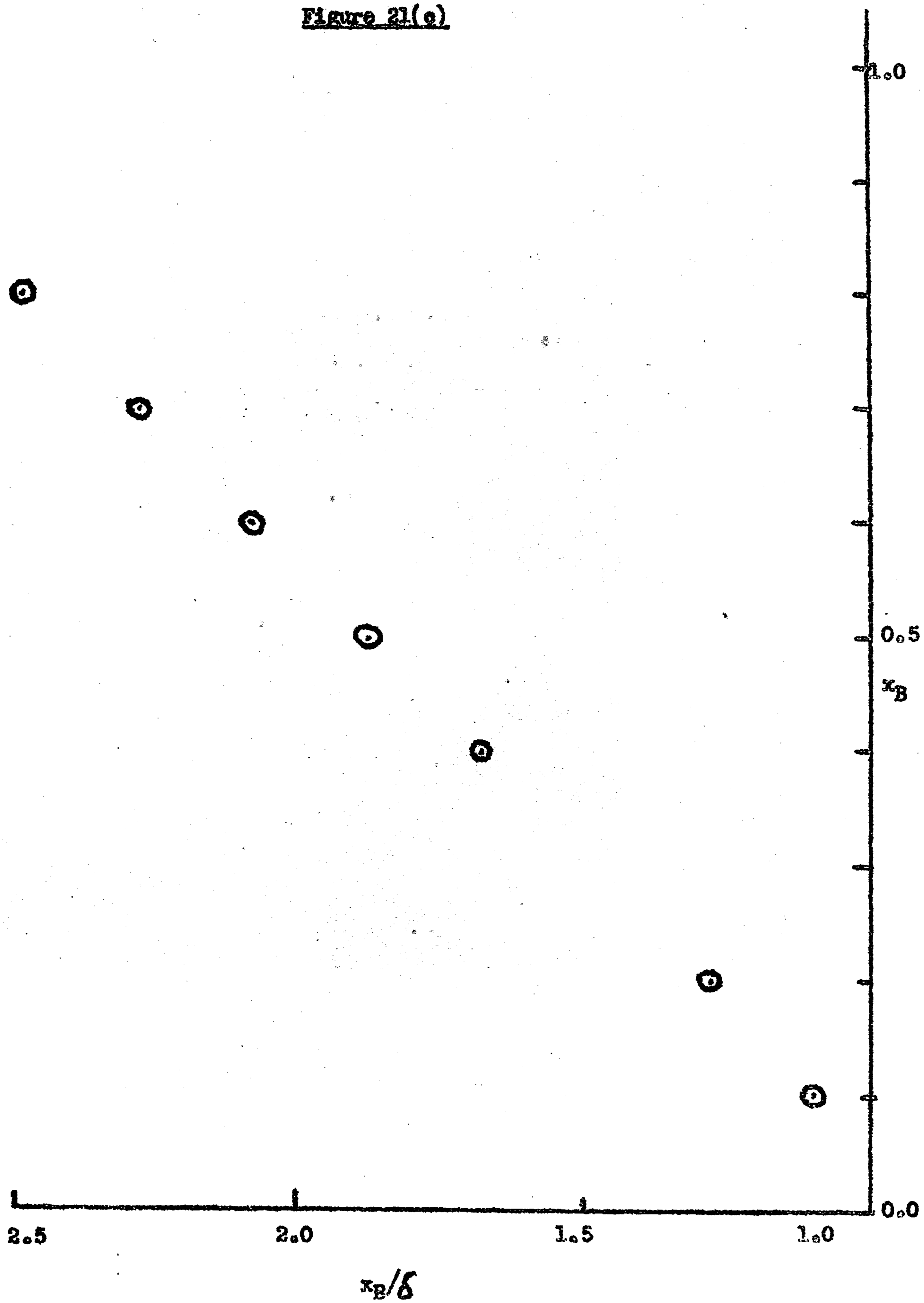

Figure 21(d)

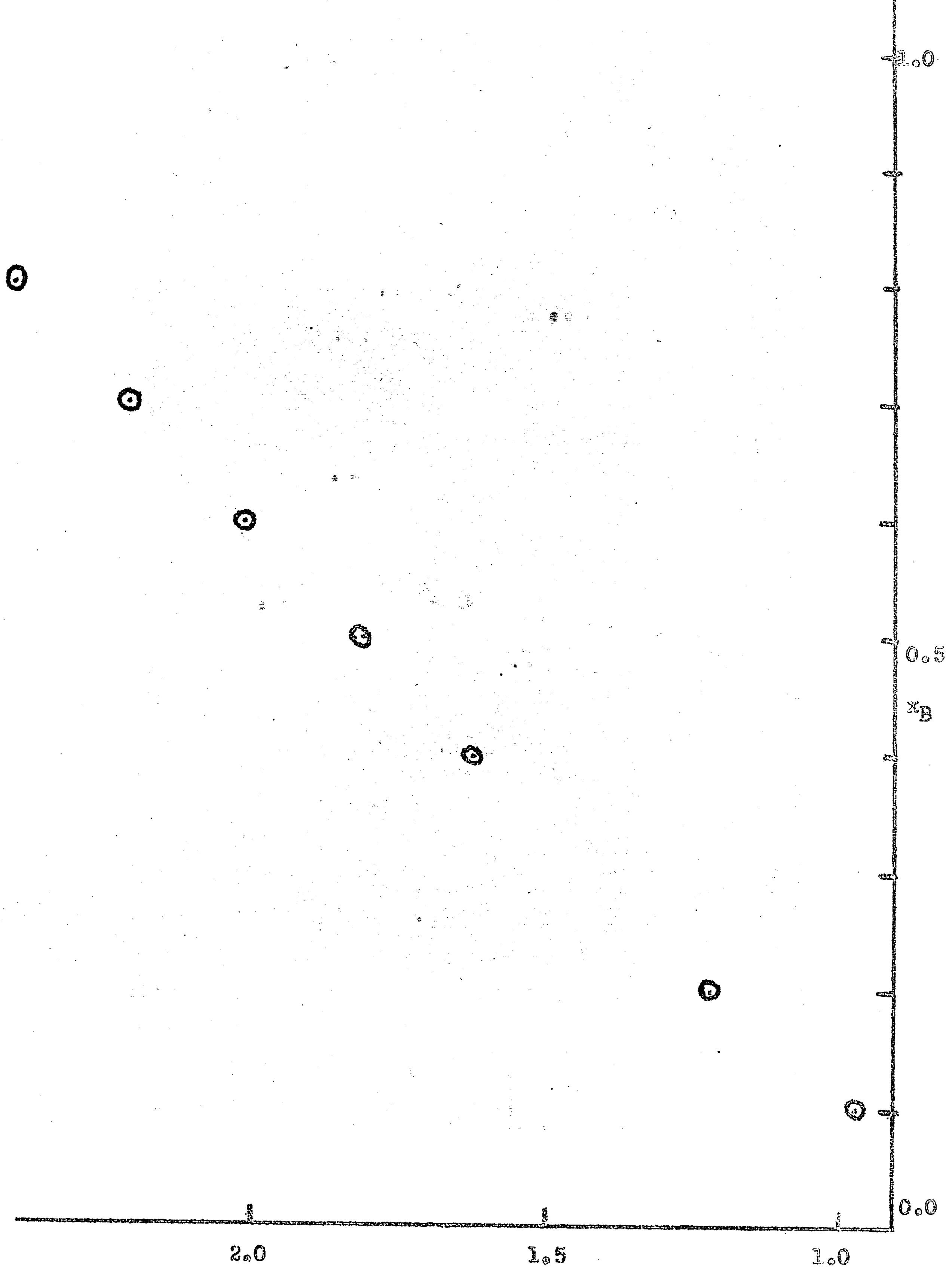

Figure 21(e)

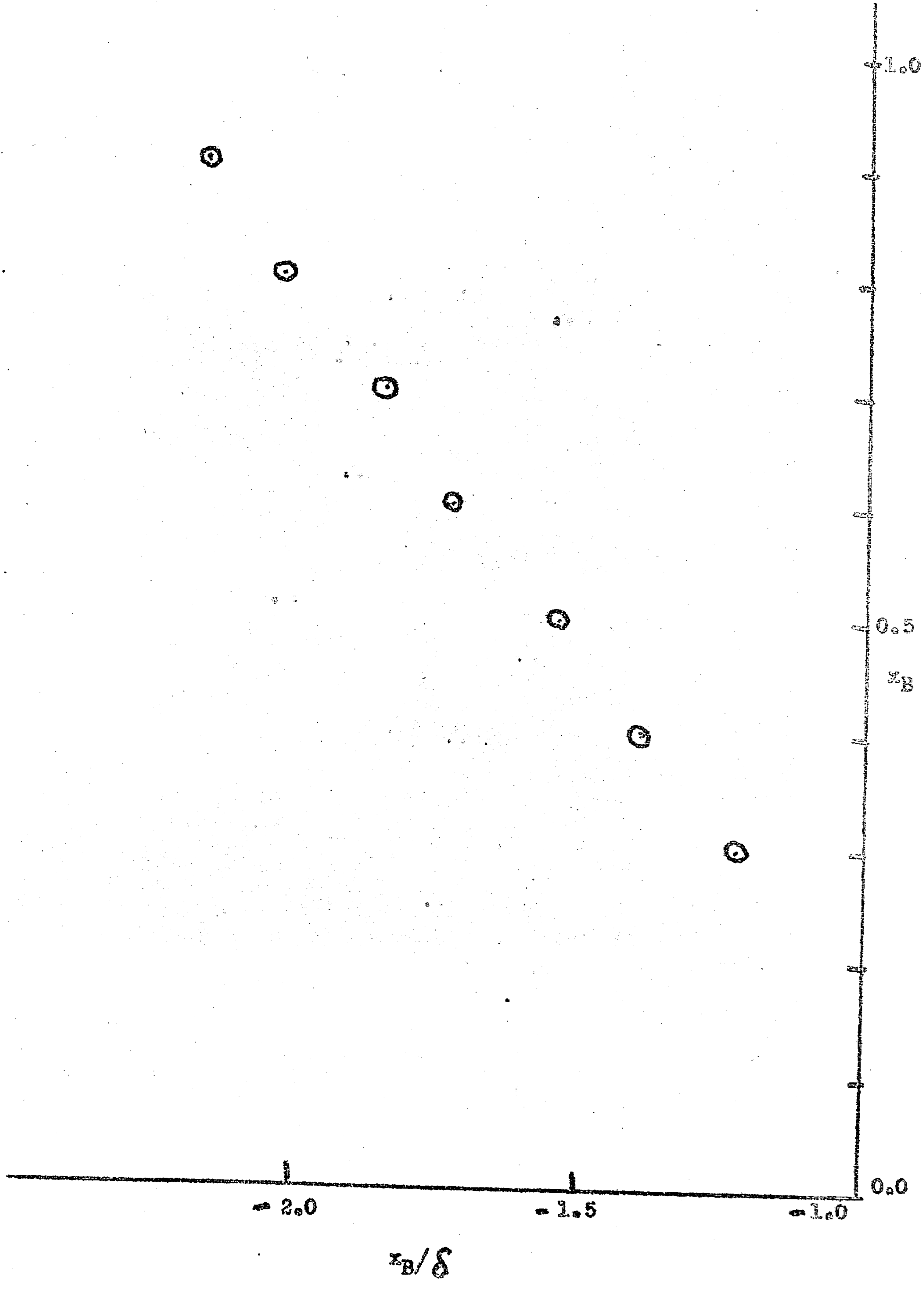

Figure 22(a)

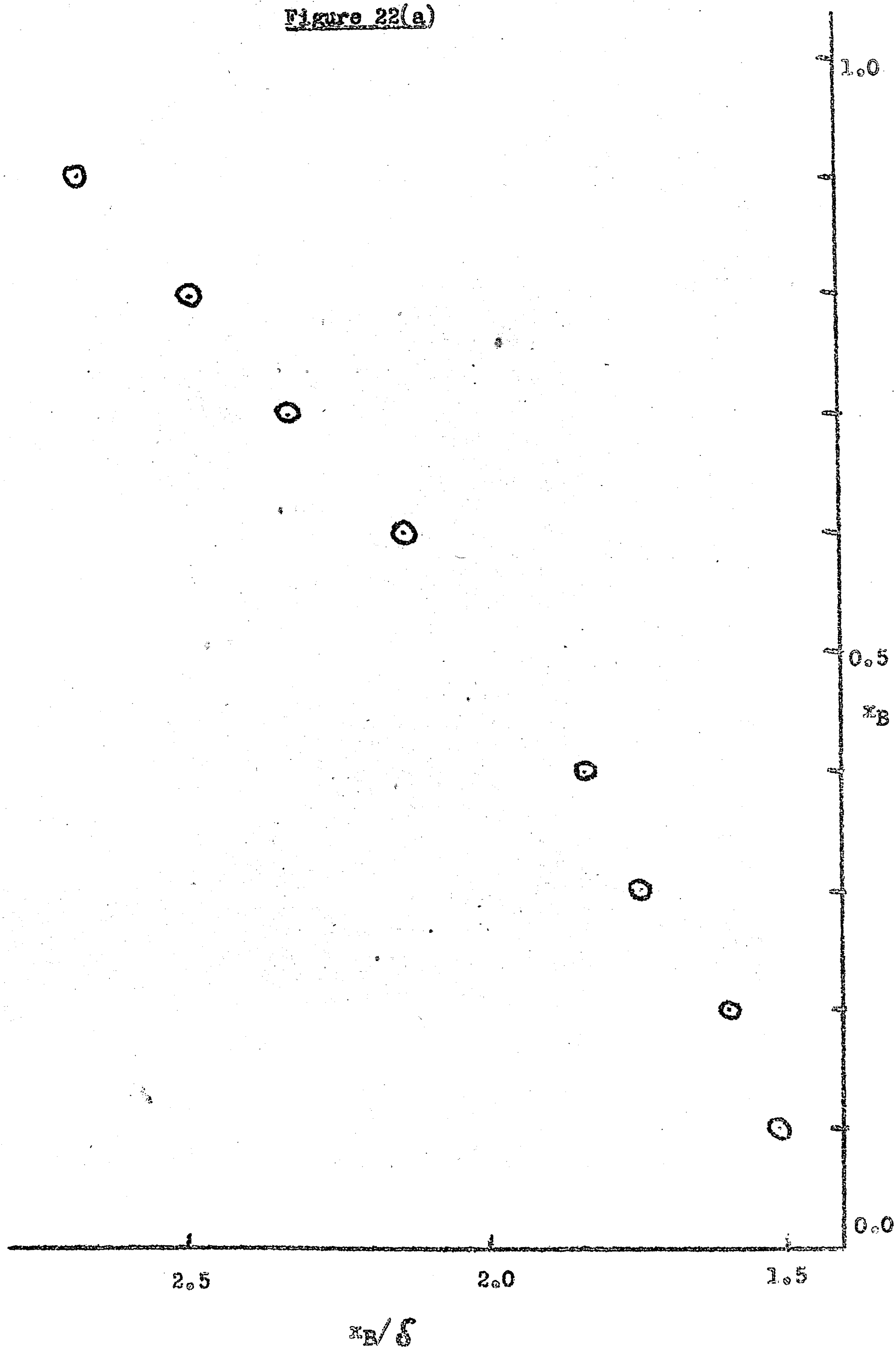

Figure 22(b)

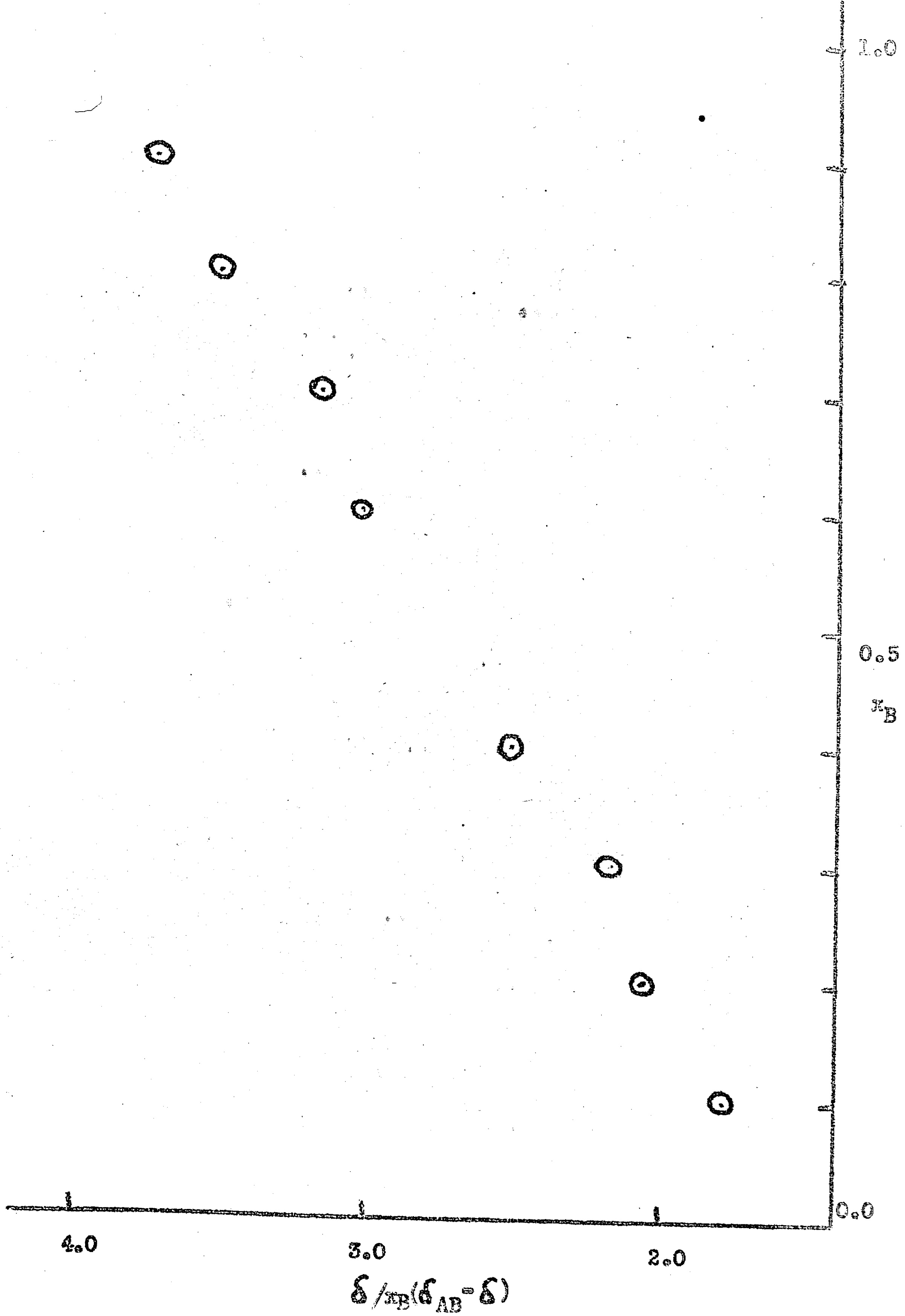

Figure 23(a)

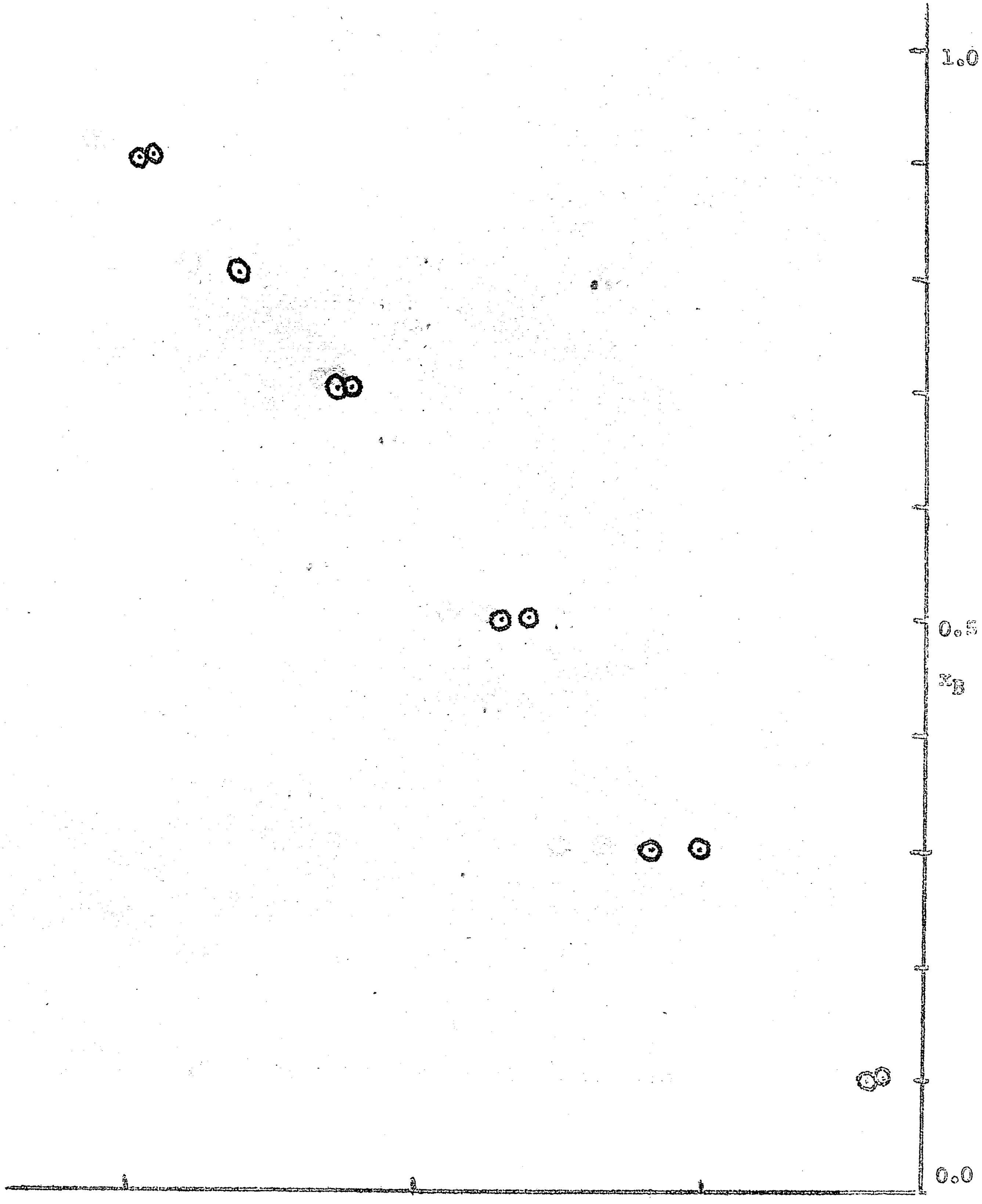

Figure 23(b)

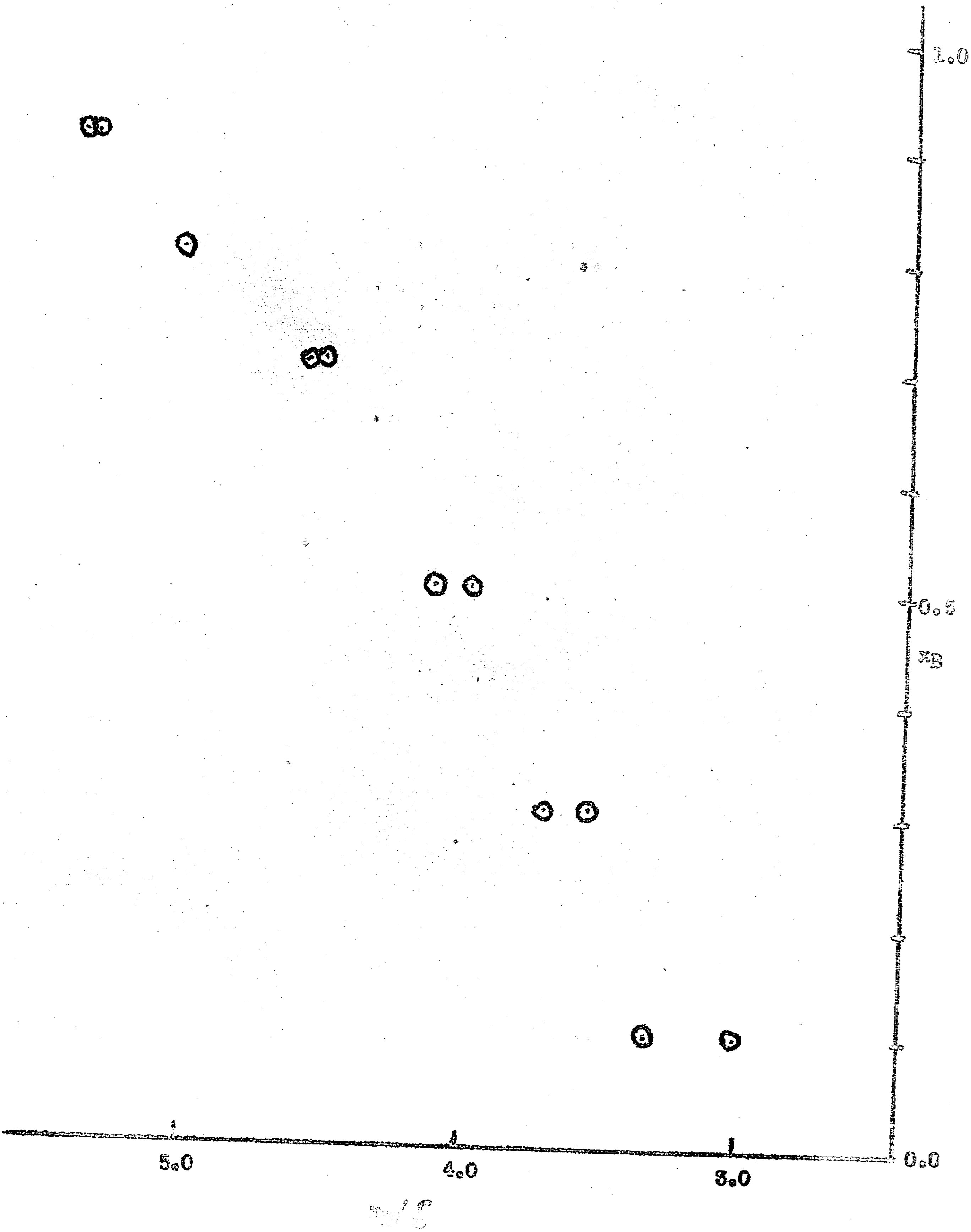

Figure 24