HYDROGEN BONDING IN PRIMARY AROMATIC AMINES

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SUMMARY

The existence of an intramolecular hydrogen bond in ortho-substituted phenols has been well established. However, the corresponding ortho-substituted anilines do not show the same marked variation in their physical and chemical properties and in 2-nitro-aniline there has been some doubt as to the presence of the expected chelate structure.

The NH stretching frequencies of the amind group in 109 ortho-substituted aromatic amines have been studied as the fundamental and first overtone bands both before and after deuteration. The separation of ν (0-2)NH_2 into two members has been suggested as being due to intramolecular hydrogen bond formation. However, although the shape and the separation of the absorption bands can be related to the strength of the hydrogen bond, the cause of this splitting is still uncertain. The appearance of two NH stretching frequencies in the mono-deuterated amine is regarded as the most sensitive test for unilateral hydrogen bond formation. Repulsive interactions can also bring about a similar doubling but it is usually possible to decide on the nature of the interaction by a consideration of the NH_2 stretching frequencies. Mono-deuteration of 2,6-disubstituted anilines has shown that the amine group remains symmetrically placed with respect to both substituents. Contrary to assumptions which have been made by other workers, the NH_2 stretching frequencies in these symmetrically substituted anilines do not conform to the relationship established for meta and para anilines. A reason for this departure has been advanced and the direction of the departure can be related to the presence of repulsive or attractive interactions.

No estimate has been made of the strength of the hydrogen bonds formed but they are considered to be much weaker than those in the corresponding phenols.

ACKNOWLEDGMENTS

The Author would like to record his sincere appreciation of the guidance, help and inspiration given to him by his supervisor, Professor A.N. Hambly, during this investigation.

The help of other members of staff is also acknowledged.

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1 - INTRODUCTION

1.1 Definition of a Hydrogen Bond:

Pimentel and McClellan (1960a) have defined a hydrogen bond in the following terms:- "A hydrogen bond exists between a functional group A-H and an atom or group of atoms B in the same or different molecule when -

(a) there is evidence of bond formation (association or chelation);

(b) there is evidence that this new bond linking A-H and B specifically involves the hydrogen already bonded to A."

Although a definition of this nature is practicable when the hydrogen bond is strong, as evidenced by its effect on the physical and chemical properties of the system involved, it becomes a matter of what criterion is to be used as being sufficient evidence of bonding when the bond is weak and less specific interactions play a more important role.

Hydrogen bonds have been classified into two broad classes, depending on whether the bond is formed between two groups in different molecules or in the one molecule. The former class, intermolecular hydrogen bonds, can be divided into several sub-classes in which the hydrogen bonded complex is dimeric or polymeric and exists in a linear, cyclic or three-dimensional network. It was this type of bond that was first postulated by Latimer and Rodebush (1920) to account

for the properties of liquid water, and it has since been found in numerous other organic and inorganic systems in the solid, liquid and gaseous states.

The other class, intramolecular hydrogen bonds, although by its nature more limited in occurrence, has far reaching effects on the properties of compounds. Because the two participating groups are restricted to the one molecule, they must have a suitable steric relationship to one another. It is not surprising therefore to find intramolecular hydrogen bonds being formed in molecules in which the groups are α, ortho, peri or cis to one another. In general a five, six or seven membered ring is formed on bond formation, with the six membered ring being the most favoured because of the easier retention of approximate linearity of the A–H···B bond (Hunter, 1954). However in macro-molecules, such as proteins, the ring size can be much greater.

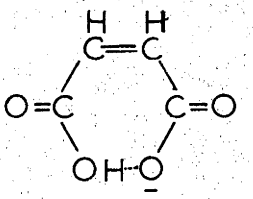
1.2 Electronegativity and the Nature of the Hydrogen Bond:

A hydrogen bond, while being much stronger than the van der Waals attractive forces between molecules, is much weaker than ordinary covalent bonds, rarely having a bond energy in excess of nine kilocalories. The bond is formed between a hydrogen atom and an atom containing an unshared electron pair, and the strength of the bond formed is best correlated to the acidity of the hydrogen atom and the

basicity of the acceptor atom. Of course if the hydrogen atom is too acidic and the acceptor atom too basic the hydrogen will be transferred as a proton to form a covalent bond with the acceptor atom in a simple acid-base reaction.

Hydrogen bonding has been depicted as an electrostatic interaction, and Coulson (1957) has reviewed much of the evidence for such a presentation. However, although electrostatic interactions must contribute to hydrogen bonding, a representation solely on this basis might be expected to yield a correlation of hydrogen bonding ability with electronegativity (Pauling, 1960). For example, one would expect the alkyl fluorides to be better hydrogen bond acceptors than alcohols and ethers, and these to be better than amines. The actual order, however, appears to be the reverse of this with the more basic atoms leading to the stronger hydrogen bond (Gordy and Stanford, 1940,1941; Hammett, 1940a; Curran, 1945). The unusually strong bond in the bifluoride ion is no exception to this generalization, since in this case, it is not a bond existing between two highly electronegative fluorine atoms, but between a fluorine atom and the much less electronegative fluoride ion. Recently Allerhand and Schleyer (1963) have shown that the halide ion forms a stronger hydrogen bond than the same covalently bound halogen. The same is true of other

strong hydrogen bonds. In the hydrogen maleate ion (I) the



I

bond is established between the undissociated carboxyl group and the singly bound, negatively charged oxygen of the ionised carboxyl group. This oxygen is certainly much less electronegative than the carbonyl oxygen and yet it is the one involved in the hydrogen bond.

The electronegativity aspect of hydrogen bonding can be approached from another point of view. While fluorine is the most electronegative of the normal atoms, units more electronegative, i.e. having a greater attraction for electrons, are easily obtained. These are the positive ions. The least electronegative of the positive ions will correspond to that of the most electropositive metal, francium. Although the value of the electronegativity of the francium ion is not known, the electronegativity of the caesium ion is found to be 1.84 compared to fluorine 3.72; yet no hydrogen bonding involving positive ions has been reported.

Electronegativity, however, plays some part in the

formation of hydrogen bonds. Hydrogen fluoride, owing to the greater electronegativity of fluorine compared to hydrogen, has a dipole moment with an electron distribution

$$\overset{\delta+}{H} - \overset{\delta-}{F}$$

If a fluoride ion approaches, it will experience the maximum of electrostatic attraction and the minimum of electrostatic repulsion if it comes along the F–H internuclear line towards the hydrogen end. As it moves nearer, the bonding electrons will be increasingly displaced towards the fluorine atom, and the less shielded proton will be attracted towards the approaching fluoride ion. The formation of the hydrogen bond is thus associated with a weakening of the original covalency. At the same time the approaching fluoride ion, which initially has a spherically symmetrical electronic distribution, will become increasingly polarised as a pair of electrons with opposite spins is displaced towards the proton. The remaining electrons will adopt a most stable configuration on the far side of the fluorine nucleus. The resultant of these two processes is that the fluoride ion loses some of its ionic character and the fluorine of the hydrogen fluoride molecule begins to acquire the characteristics of a fluoride ion. At equilibrium, in this particular case, the two fluorines are symmetrically related to the hydrogen (Westrum and Pitzer, 1949; Peterson and Levy, 1952).

It is evident therefore that if the hydrogen which forms the bridge is part of a covalent structure it must be attached to an electronegative atom so that the hydrogen can acquire a positive charge and the atom to which the bridge is established must be polarisable and capable of forming a covalent bond with a proton.

1.3 Effect of the Hydrogen Bond:

Perhaps the most widely investigated compounds, containing intramolecular hydrogen bonds, would be the 1.2 disubstituted aromatics. Although ortho substituted phenols and benzoic acids have been subjected to an extensive study by physical and chemical methods, the corresponding ortho substituted anilines have not been so exhaustively investigated until recent years.

There have been recent reviews (Badger, 1957; Pimentel and McClellan, 1960b) on the general aspects of the detection of hydrogen bond by studying changes in the physical properties of molecules. Hambly (1961) has reviewed the more specific topic of hydrogen bonding in ortho substituted anilines and concludes that the intramolecular hydrogen bond from the aromatic primary amine group to an ortho substituent is very much weaker than in the corresponding phenols, and that it is in many cases only by refined studies of the infra-red spectrum that the existence of intramolecular bonds can be

demonstrated.

When a strong to moderate intramolecular hydrogen bond is formed, the simple physical properties (boiling point, melting point, steam volatility, solubility) are markedly different to those exhibited by the corresponding para isomer, and the presence of a hydrogen bond can be postulated with some degree of certainty. With the weaker interactions, however, it becomes necessary to use alternative techniques. It was soon recognised by earlier workers that hydrogen bonding had profound effects on the infrared spectrum and that in compounds, such as ortho nitro phenol, the absorption due to the O–H stretching vibration disappeared altogether (Hilbert et al., 1936). This was later realised to be a manifestation of the general effect of a shift in the X–H stretching frequency to lower frequencies on the formation of a hydrogen bond and, in the case quoted, the O–H absorption had moved to a lower frequency where it had become confused with the C–H absorptions. Because of instrumental difficulties most of the investigations were carried out in the region of the 1st (5000 - 7000 cm^{-1}) and 2nd (7500 - 10000 cm^{-1}) overtones of the hydrogenic stretching vibrations. Rodebush et al. (1939) found that although phenols gave satisfactory results, the anilines had proved to be disappointing compounds to study.

However it has generally been agreed that infra-

red spectroscopy is the most satisfactory method for detecting hydrogen bonds and with the advent of spectrometers of greater resolving power, a large volume of work has appeared on the detection of hydrogen bonds and the correlation of the stretching frequencies with other properties of the molecule concerned.

Pimentel and McClellan (1960c) have summarised the effects of hydrogen bonding upon the vibration frequencies of the A–H bond participating in hydrogen bonding as follows –

1. A–H stretching mode:– The stretching mode is shifted to lower frequencies and there is an increase in half width and intensity which is often affected by a change in temperature, concentration or solvent.
2. A–H bending modes:– The bending mode is shifted to higher frequencies but the relative shift is much less than that for the stretching mode, and changes in half width and intensity are slight.

Further, the changes produced by intramolecular hydrogen bonds are in general less than those produced by intermolecular hydrogen bonds.

The present work will describe the I.R. spectroscopic methods that have been used to detect intramolecular hydrogen bonds in ortho substituted aromatic amines and to point out their limitations when applying them to the investigation of weak hydrogen bonds.

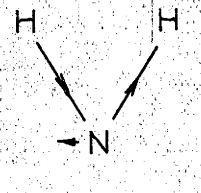
2 - SPECTROSCOPIC DETECTION OF HYDROGEN BONDS

2.1 Fundamental NH_2 Stretching Frequencies:

The infra-red absorption spectrum of primary amines in dilute solution of non-polar solvents has two bands at ca. 3400 and ca. 3500 cm^{-1}, corresponding respectively to the in-phase (symmetric) and out-of-phase (antisymmetric) vibrations I and II.

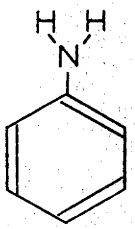


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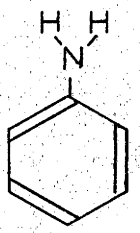


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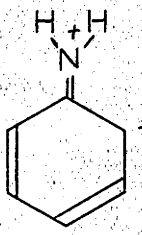
The frequency of these absorptions is dependent upon the configuration of the nitrogen atom. In the aliphatic amines, which possess a pyramidal arrangement, the absorptions are at lower frequencies than in aniline which is somewhat more planar. The resonance structures involved in aniline can be depicted as III, IV, V, VI and VII (Hine, 1962).



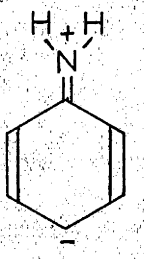
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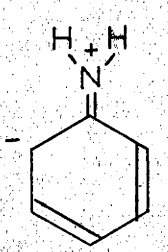
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V



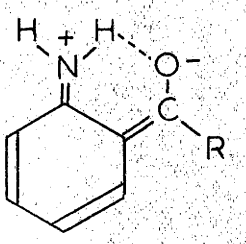
VI



VII

The contribution of structures V, VI and VII to the total structure gives the resonance hybrid a smaller density of unshared electrons on the nitrogen atom, which is therefore less basic than in the aliphatic amines or ammonia. It thus becomes a better donor but poorer acceptor of a hydrogen bond. Furthermore the resultant C–N bond will have a degree of sp^2 character, which will tend to pull the hydrogens into the plane of the aromatic ring. If an electron withdrawing group is substituted in the 2 or 4 position, the amount of sp^2 hybridisation will be increased, bringing the amino hydrogens still more into coplanarity, and at the same time shortening the N–H bonds. The effect then on the infra-red spectrum of the NH_2 stretching frequencies will be to shift them to higher values.

When a hydrogen bond is formed by one of the amino protons, the N–H bond will increase in length and become weaker. Simultaneously the electrons in this bond will move towards the nitrogen atom, decreasing its electronegativity and thus weakening the other bond. When the amino group is conjugated to a suitable <u>ortho</u> substituent, such as in VIII,



VIII

the excess negative charge is transferred to the acceptor atom, enhancing the strength of the original bond but decreasing the bond order of the carbonyl group. The nett result will be a lowering of the NH_2 stretching frequency as well as a lowering of the carbonyl stretching frequency.

The lowering of the NH_2 frequencies produced will be different for the individual stretching modes. Wolff and Staschewski (1962) have used the method of Kohlrausch (1938) to calculate the variation in the stretching frequencies of the NH_2 group when one bond remains at a fixed strength while the force constant of the other is varied by hydrogen bond formation or other causes (Figure 2.1). The effect of unilateral bonding will be to uncouple the two motions so that the higher frequency moves towards the mean of the coupled motions. The other vibration will show a much larger displacement to lower frequencies. For strong hydrogen bonds the two motions may be almost completely uncoupled and be characteristic of the free and bonded N-H linkages. The lowering of frequencies by hydrogen bonding may, however, be offset by an increase in frequency due to a change in hybridisation on the nitrogen atom brought about by an electron-attracting, acceptor group.

Bellamy and Williams (1957) have pointed out that as the antisymmetric and symmetric frequencies depend basically on the same force constant, they must be directly related to

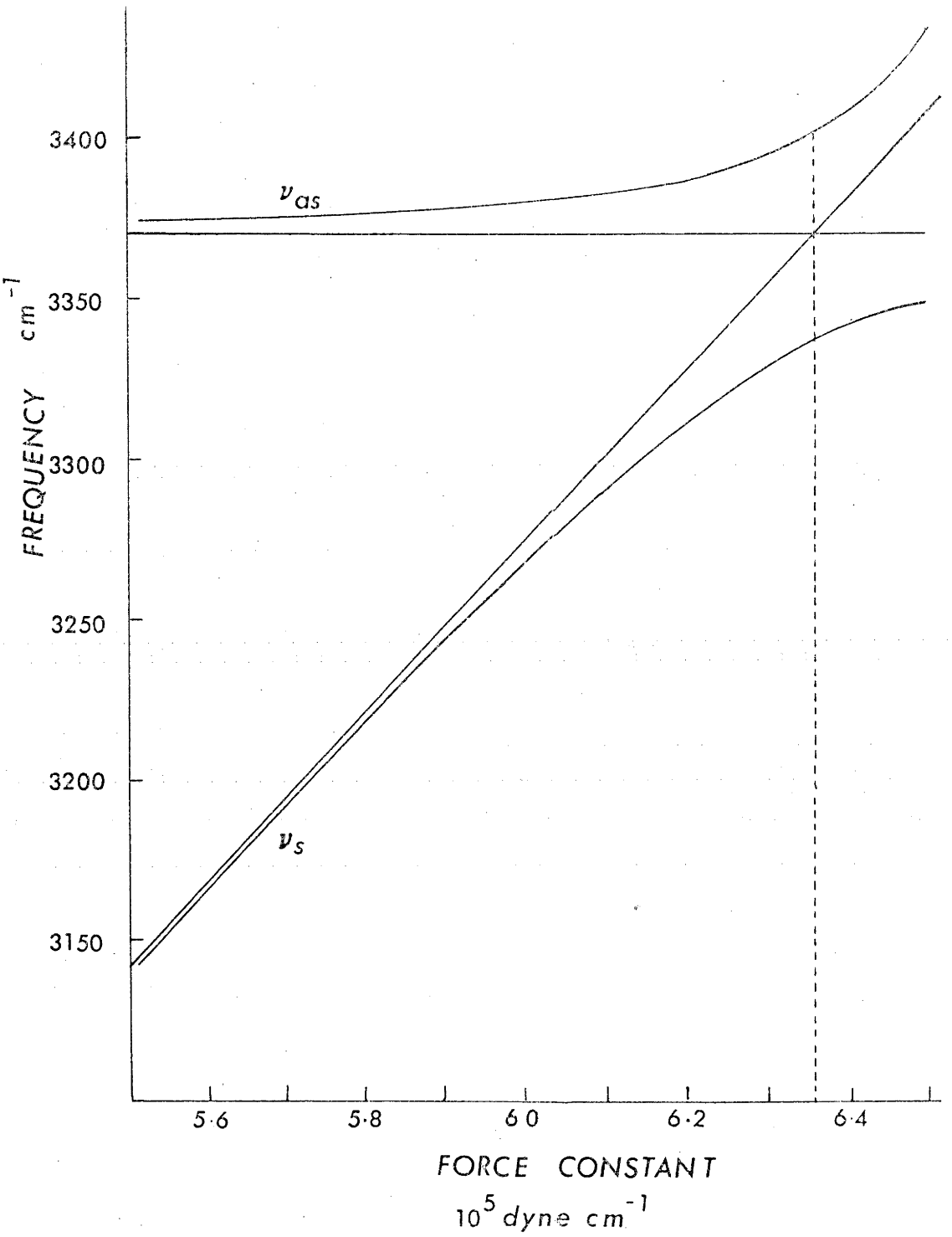


Fig. 2.1 - Effect of unilateral hydrogen bonding on NH_2 stretching frequencies (after Wolff and Staschewski, 1962). The broken line corresponds to two NH bonds of equal strength ($F = 6.34 \times 10^5$ dyne cm^{-1}). The strength of one bond is kept constant at this value while the other is varied as shown on the abscissa.

one another. They revieved the high resolution data available at that time and for a range of sixty-four primary amines in which mass and coupling effects were negligible, they found the equation

$$\nu_s = 0.876\,\nu_{as} + 345.33 \qquad (2.1)$$

is obeyed in all cases with a standard deviation of 4.8 cm^{-1}. Further they pointed out that the relationship must be expected to fail in situations in which one NH link is hydrogen bonded and the other is not. They assume that once the equality of the NH links is restored the relation is again obeyed and the method therefore offers a sensitive test for the non-equivalence of NH linkages in primary amines. Krueger and Thompson (1959), with the more restricted case of meta- and para-substituted anilines, found that the results were better represented by

$$\nu_s = 0.682\,\nu_{as} + 1,023 \qquad (2.2)$$

with a standard deviation of less than 1 cm^{-1}. A similar relationship has been also deduced for primary amide by Puranik and Ramiah (1961) which is

$$\nu_s = 1.1214\,\nu_{as} - 542.5 \qquad (2.3)$$

Krueger (1962a) has interpreted the lower slope of the aniline correlation as opposed to the amine and amide correlation as being evidence for a systematic change of sp^3/sp^2 character of the amino group in the aniline series as the electron

withdrawing or donating power of the substituent alters. Moritz (1962) regards the increased slope of the amide correlation as probably being related to a dipolar field effect on the N-H bond which is *cis* to the carbonyl group (Moritz, 1960).

Hambly (1961), for a large number of *meta*- and *para*-substituted anilines examined at high resolution, obtained the relationship

$$\nu_s = 0.7033\ \nu_{as} + 948.2 \qquad (2.4)$$

with a standard deviation of 1.4 cm^{-1}. The effect of unilateral hydrogen bonding on the amino group will, as stated earlier, lower ν_s more than ν_{as}. For a given value of ν_{as}, the calculated value of ν_s from equation 2.4 will be greater than the observed value, i.e. unilaterally hydrogen bonded anilines will show a negative departure from this relationship. The assumption has been made (Richards and Walker, 1961) that the extent of this deviation could be correlated with the strength of the hydrogen bond formed. This assumes that other *ortho* interactions will be negligible with respect to the influence of the hydrogen bond. While this may be true for strong hydrogen bonds, it is not true for those that are weak, and other methods must be used before it is possible to assign unambiguously a small departure from equation 2.4 as being evidence for hydrogen bonding.

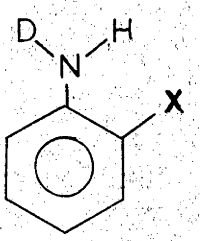
2.2 Partial Deuteration:

When only one of the amino hydrogens in aniline is replaced by deuterium the two NH_2 absorptions disappear to be replaced by a single absorption approximately mid-way between the original absorptions. This absorption can be assigned to the N-H stretching mode of the NH(D) group. Dyall and Hambly (1958) observed without comment that when 2-nitro-aniline was partially deuterated, two absorptions separated by 31 cm^{-1} were found.

The spectrum of aniline, when both of the hydrogens of the amino group are replaced by deuterium, exhibits several marked changes. The two absorptions due to the NH_2 stretching vibrations are replaced by a complex pattern in the 2600 cm^{-1} - 2400 cm^{-1} region (Evans, 1960; Calfanio and Moccia, 1957). These absorptions are due to the ND_2 stretching vibrations. $\nu_{as}\ ND_2$ is generally broad and sometimes doubled and $\nu_s\ ND_2$ is usually, but not always, a complex multiplet. The additional bands have been ascribed to Fermi resonance between the ND_2 vibrations with weak combination bands of the aromatic ring vibrations (Hambly, 1961; Califano and Moccia, 1957). Evans (1960) suggests that the unknown resonating level to be a combination of two modes which both apparently involve considerable C-N bond stretching and ND_2 bending. These modes occur at 1303 cm^{-1} and 1150 cm^{-1} respectively.

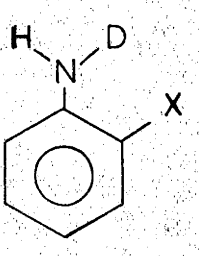
The usual discussions of the structure of aniline emphasise that delocalisation of the lone pair electrons of the nitrogen atom will occur to an extent sufficient to give appreciable double-bond character to the C_{ar}-N bond, and at least imply that there will be a tendency for the aniline molecule to assume an all-planar structure. However, there is considerable indirect evidence which suggests strongly that, although the lone-pair electrons of the nitrogen are delocalised to a certain degree, this delocalisation is not as great as to produce a completely planar molecule and that the NH_2 group has a configuration between that in methylamine and that in formamide where the C-N bond order is estimated to be larger than in aniline. Formamide has recently been shown to be non-planar (Costain and Dowling, 1960). An estimate by molecular orbital methods (Daba and Suzuki, 1961) of the C-N bond order in the ground state of the aniline molecule gives it the value of 1.4. The estimated bond order of the C-N bond would imply that there would be appreciable restriction to rotation of the NH_2 group. Evans (1960) estimates it to be of the order of 4.5 k.cal/mole. The results of Daba and Suzuki for the ground state of aniline suggest a delocalization energy associated with the C-N bond of about 8 k.cal/mole. This figure has been taken (Davies, 1962) as a reasonable estimate of the order of magnitude of $\Delta E^{\neq}$ for the rotation of

the amino group in aniline. If the amine nitrogen group is mono-deuterated there will be a sufficient barrier to rotation so that the NHD group will be able to adopt two configurations with respect to an ortho-substituent.



NH "cis"

IX



NH "trans"

X

This is akin to the situation which was said by Pauling (1936) to exist in ortho halo-phenols. Moritz (1960) has explained the presence of the two NH bands in Nd_1,2-nitro-aniline as arising from forms IX and X, and suggests that this is a sensitive method for the detection of a hydrogen bond between the ortho-substituent and the amino group. The separation of the two bands gave reasonable agreement with the strengths of the hydrogen bonds estimated by other methods. The conditions necessary for two NH frequencies corresponding to the cis and trans conformation of the NHD group are -

(a) the amine group must retain its steric relationship to the ortho-substituent for a time that is long compared to the vibration period of the N-H bond.

(b) the asymmetry of the environment must produce a sufficient difference in vibration frequencies to permit resolution of the absorption bands which have a finite band width varying with type of substituent.

This test however will not be specific for hydrogen bonds alone, and is only an indication that there is a sufficient difference in the environment of the two hydrogens to give [illegible] separate NH stretching frequencies.

2.3 Overtone Vibrations:

In contrast to the extensive investigation which has been made of the NH_2 fundamental stretching region in recent years, the first overtone has received little attention. Bell (1925,1926,1927) was responsible for the first relatively intensive investigation of this region, and from the spectra of aniline, N-methyl aniline and NN-dimethyl aniline, he concluded that absorptions at 1.04 and 1.47μ were due to NH vibrations. Ellis (1927,1928) reached similar conclusions and showed that when the results in the near infra-red were combined with the fundamental NH vibration at 2.8μ there was a hyperbolic relationship between the frequencies, showing that these absorptions were overtones of the fundamental vibration. These early studies were on the pure liquid anilines and the resultant spectra were poorly resolved.

Wulf and Liddel (1933,1935) produced the first well-

resolved, solution spectra of a large number of ring-substituted anilines in this region. In contrast to the two absorptions observed for the fundamental stretching vibration of the NH_2 group, there were three and sometimes four bands observed in the overtone. A shoulder on the low frequency side of the main absorption was common to all the aromatic compounds studied but was absent in primary aliphatic amines. They describe this as being due to coupling between the amine group and the adjacent CH groups. They support this argument by pointing out that it is more pronounced in aniline and its meta and para derivatives than in the ortho or 2,6-disubstituted anilines. Ortho-nitro-aniline and methyl anthranilate displayed a feature not common to the other ortho-substituted anilines. The intense low frequency band was split into two members and this was attributed to a coupling between the NH_2 and the adjacent carbonyl or nitro group.

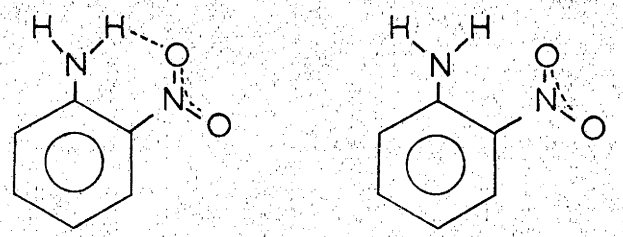
Kaye (1954) has assigned the more pronounced bands in the m-toluidine spectrum as being due to NH bands. An absorption at 1.975μ is described as being a combination band involving the stretching and bending modes of the NH_2 group. The bands at 1.498μ and 1.460μ are assigned to ν_s(0-2) and ν_{as}(0-2) for the NH_2 group respectively.

In attempts to use these absorptions for quantitative estimation of anilines, Whetsel et al. (1958) reported the

spectra of 30 ortho, meta- and para-substituted anilines in the 0.8 to 2.1μ region. They observed that in addition to ortho-nitro-aniline and methyl anthranilate, ortho-methyl-sulphonyl- and ortho-methylthio-aniline exhibited a splitting of the symmetric stretching frequency in both the first and second overtone bands. As this splitting occurred in cases where moderate to strong hydrogen bonding to the ortho-substituent could reasonably be expected, and not in other instances, they suggested that this was due to bonded and non-bonded forms of the N-H group, with the high frequency member corresponding to the non-bonded form.

Krueger (1963) has calculated the anharmonicity factors, "x", for both members of these ν_s(0-2) bands and concludes on this basis that the reverse is the case. Whereas the low frequency member has a small positive anharmonicity factor of the same order as that found for the meta- and para- substituted anilines, the high frequency absorption has in the case of ortho-amino-acetophenone and methyl anthranilate a negative value and in the other instance a very small positive value. From the relative intensities of these two bands he has calculated the percentage of the amines existing in the bonded and non-bonded forms. In the case of o-amino-acetophenone and ethyl anthranilate he chooses to assign the low frequency absorption at approximately

6580 cm^{-1} to a combination band and claims that these compounds existed completely in the bonded form. He suggests that as the high frequency component of the symmetric doublet has an abnormal anharmonicity constant, it is due to a bonded NH, whereas the low frequency component arises from the free NH group in an equilibrium of the type XI.



XI

However he reports that 2-tert.-butyl-aniline and 2,5-di-tert.-butyl-aniline show a splitting which is almost as great as for ortho-nitro-aniline, and it is difficult to conceive how these compounds would have an equilibrium as shown.

Hambly (1961) has suggested that the doubling could be due to a tunnelling through a potential barrier, similar to that which has been suggested to occur with some intermolecular hydrogen bonding (Barrow and Bell, 1959; Barrow, 1960). In general there are two positions which the proton can occupy in the bond A-H•••B, one closer to the atom A, the other closer to atom B. These two positions can be represented as

A-H•••B A•••H-B

One of these usually has a much lower energy than the other so that there is no splitting of zero and first vibrational levels and the fundamental frequency is single. There will be some vibrational level at which the energy of the A–H•••B system becomes similar to the energy for the ground state for A•••H–B, and if the symmetries of the levels are appropriate they will interact and produce a double energy level. Barrow deduces that if the pK_a value for the acid A–H, as determined in aqueous solution, is 5 units greater than the acid H–B, then there will be a doubling of the fundamental frequency as observed in non-polar solvents. If the pK_a values differ by 15 units then splitting will occur in the second vibrational level and though the fundamental vibrational transition is single, the first overtone will be doubled. If the suggestion of Barrow is applicable to this case, the doubling of $\nu_s(0\text{–}2)$ would provide definite evidence for a hydrogen bond in the ground state of the molecule.

The position is not clear as to whether any of these explanations is a complete description of the condition which brings about the splitting of $\nu_s(0\text{–}2)$ NH_2. However the assumption can be made that any doubling of the overtone of the symmetric vibration frequency is an indication of an appreciable interaction, whether it be a repulsion or a hydrogen bond between the <u>ortho</u> group and the amino group.

Whetsel et al. (1953) deduced a linear relationship between $\nu_s(0\text{-}2)$ and $\nu_{as}(0\text{-}2)$ for <u>meta</u> and <u>para</u> anilines. The equation

$$\nu_s(0\text{-}2) = 0.876\ \nu_{as}(0\text{-}2) + 345.5 \qquad (2.5)$$

which had a standard deviation of 5 cm^{-1}, failed, as did the corresponding equation for the fundamental region to hold for <u>ortho</u>-substituted anilines in which bonding was expected between the amine group and the substituent.

3 - EXPERIMENTAL

3.1 Spectrometers:

The spectra were recorded with a Perkin Elmer Model 112 single beam, double pass spectrometer. For the 8000 cm^{-1} to 4000 cm^{-1} region the instrument was fitted with a lithium fluoride prism, a tungsten filament source and a lead sulphide photoconductive detector. In the 4000 cm^{-1} - 2000 cm^{-1} range, the source was changed to a "globar" rod and the detector to a thermocouple. Below 2000 cm^{-1} the lithium fluoride prism was replaced by one of calcium fluoride.

To reduce the interference produced by the absorption spectra of atmospheric water vapour and carbon dioxide, the monochromator was continuously purged with a stream of dry nitrogen.

The overtone spectra of the nitro-anilines in carbon tetrachloride and methyl anthranilate and 6-methyl,2-nitro-aniline in various solvents were recorded with a Beckman DK 2. A. spectrometer.

3.2 Calibration:

The positions of the absorption bands were measured as a distance from an arbitrary reference point; these measurements were made in centimetres and with the aid of a vernier it was possible to estimate the position of a peak to within 0.01 cm. The distances in centimetres were then

converted to the frequency in wavenumbers by the appropriate calibration graph. The method and standards used for obtaining the required calibration curves are described below.

The emission lines from a mercury arc provide several excellent calibration points between 9000 cm^{-1} and 4000 cm^{-1}. However they are too widely spaced to provide a sufficient number of points to give a satisfactory calibration. A thin film of suitable refractive index and thickness will give an interference pattern with $\Delta\nu$ the distance between adjacent maxima (or minima) given by

$$\Delta\nu = \frac{1}{2t}.n. \qquad (3.1)$$

where n is the refractive index of the film of thickness t. Mica, which can be cleaved into very thin layers, has been found (Kaye, 1954) to be adequate for producing an interference pattern with a suitable trough to peak height. By interpolating this series of absorptions between the mercury emission lines, a suitable calibration curve can be obtained. For a material to be suitable for calibration by this means it is essential that its refractive index remain constant over the range under consideration. With mica this appeared to be the case as the frequency difference between successive absorptions remained unchanged.

As a check on the day-to-day reproducibility of this calibration, the spectrum of a 1% solution of ortho-nitro-

aniline in carbon tetrachloride was recorded with each group of samples. To keep distances measured along the chart to a minimum the sharp combination band of chloroform at 8229 cm^{-1} was used as the reference point from which all measurements were made.

The results were reproducible to ± 5 cm^{-1} and were in reasonable agreement with the values obtained by Krueger (1963) and Whetsel et al. (1953) where the same compounds were examined.

The calibration of the region from 3600 cm^{-1} to 3400 cm^{-1} is still in an unsatisfactory state for spectrometers of medium to low resolution because of the non-availability of a suitable standard. Ammonia gas is generally used as a calibrant but is not particularly satisfactory as the frequencies of the absorption are resolution sensitive (Thompson, 1961). A typical trace of the ammonia spectrum at the resolution of the spectrometer is shown in Figure 3.1. The assigned values for the frequencies are generally weighted means of the frequencies obtained at higher resolution. Measurements were made relative to a sharp peak in the 2.6μ water band at 3854.0 cm^{-1}. Reproducibility of sharp peaks was ± 1 cm and the results were in agreement with other workers (Krueger, 1962; Moritz, 1960).

The vibration-rotation spectrum of hydrogen bromide

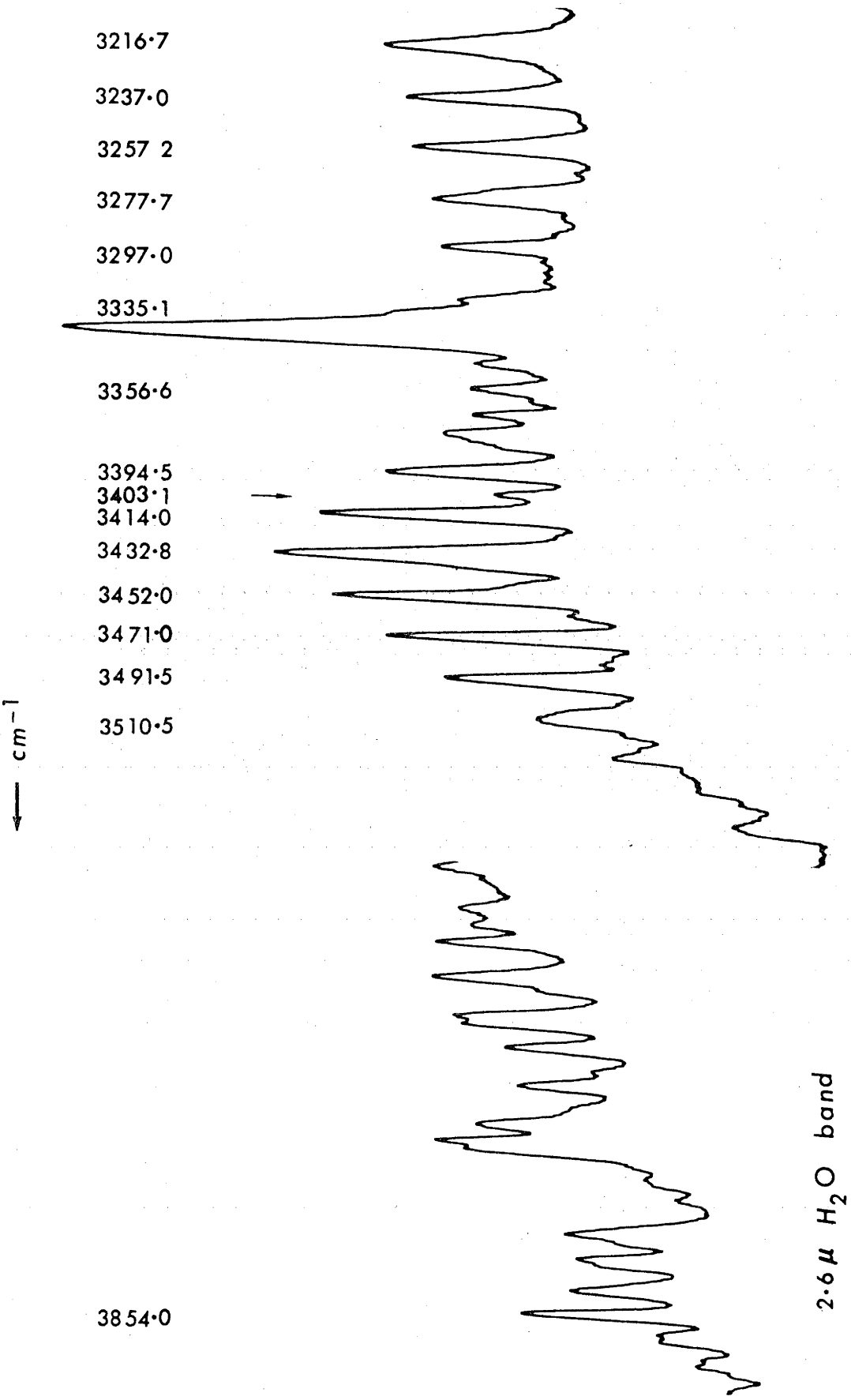


Fig. 3.1 - Ammonia calibration spectrum (3,600-3,200 cm^{-1}).

gas, prepared from bromine and tetralin (Vogel, 1961), was used as the calibrant for the region 2700 cm^{-1} to 2400 cm^{-1}. The values assigned to the individual bands are those given by Thompson (1961). Measurements were made relative to the centre of the carbon dioxide band at ca. 2348 cm^{-1}. Reproducibility for this region was ± 1 cm^{-1}.

Because of the single beam operation of the spectrometer, spectra in the 2000 cm^{-1} - 1200 cm^{-1} region are superimposed upon the absorption spectra of the 6μ water band. Over a narrow range, the change in frequency with wavelength was regarded as being linear, and the frequencies of the absorption bands under consideration were obtained by direct interpolation between adjacent peaks of the water band. The frequency values assigned to absorptions in the water band were those of Jones (1956,1957). Reproducibility was better than ± 1 cm^{-1}.

3.3 Concentration Effects:

There have been many attempts to determine whether aniline is associated in the pure liquid. N.M.R. evidence points to the non-existence of intermolecular hydrogen bonding as dilution of aniline with a non-polar solvent has no effect on the chemical shift of the amino proton (Rao et al., 1962; Yamaguchi, 1961). The effect of concentration on the N-H stretching frequencies, however, is quite marked. Upon

diluting aniline both the antisymmetric and symmetric stretching frequencies move to higher values until at a concentration below 0.1M they remain constant (Dyall and Hambly, 1958). This variation of frequency has been ascribed to a general dielectric effect rather than to intermolecular hydrogen bonding. Dyall and Hambly have reported that, although the bands in the spectra of liquid aniline are quite broad, there is no evidence of a doubling corresponding to "free" and "bonded" NH groups. In the present work, at the higher resolution obtainable with a lithium fluoride prism, a noticeable shoulder on the high frequency side of both the stretching vibrations has been observed. On dilution this band increases in intensity until at a concentration of 3M the low frequency band becomes the shoulder and the high frequency band the main absorption. At still lower concentrations the shoulder disappears completely and the two bands remaining stay unchanged by further dilution. This type of behaviour is typical of what one would expect to observe if there was association between the aniline molecules.

Two other anilines, ethyl anthranilate and <u>para</u> trifluoromethyl aniline, were also investigated and the effect of concentration on their NH_2 stretching frequencies is shown in Figure 3.2.

The behaviour of <u>para</u> trifluoromethyl aniline is

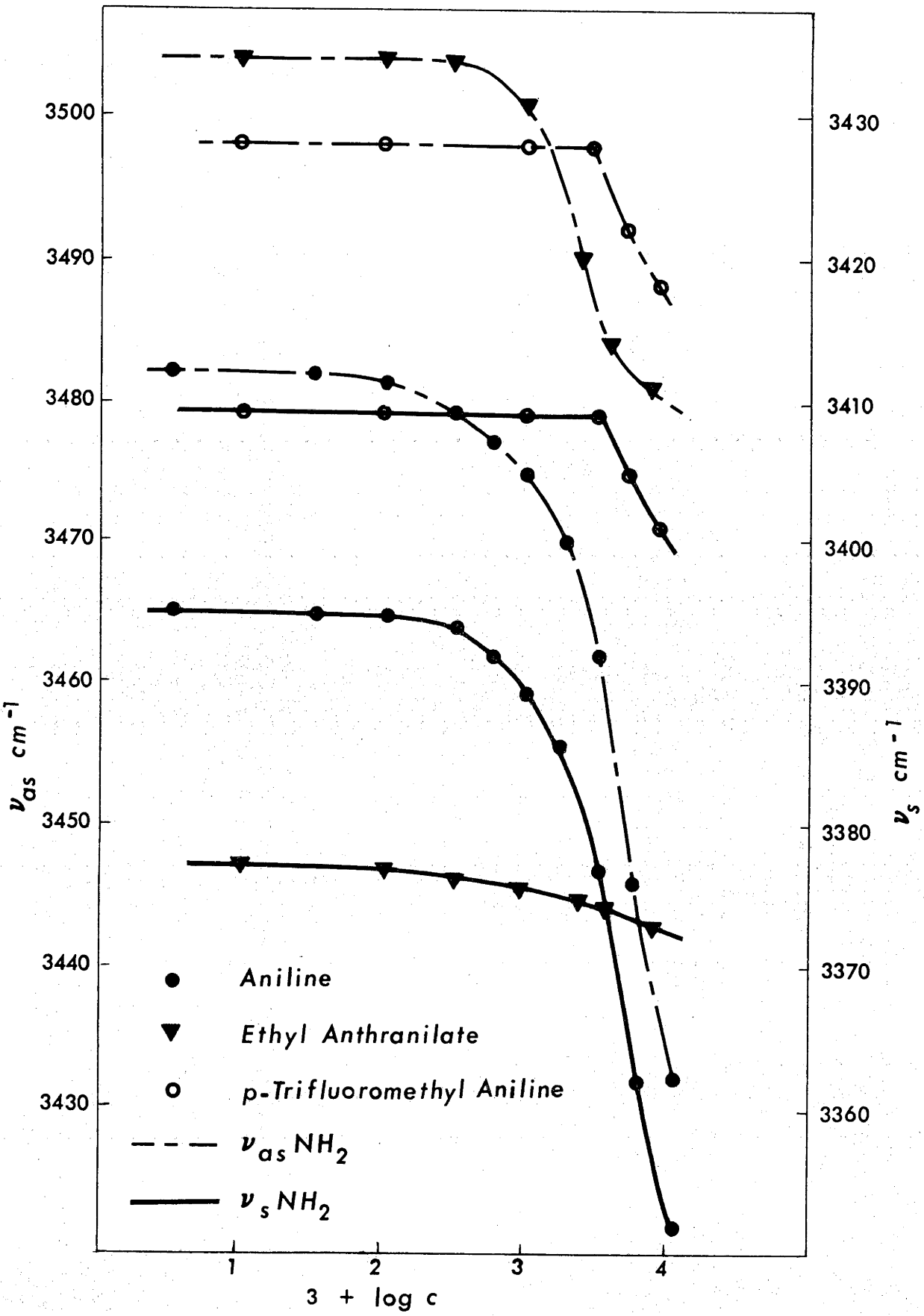


Fig. 3.2 - The effect of concentration on the NH_2 stretching frequencies.

quite different from that of aniline. The change in frequency on dilution is much less and the symmetric and antisymmetric absorption bands are single at all concentrations. It would be expected that the strong electron withdrawing trifluoromethyl group in the para position would make the amino nitrogen a better donor for a hydrogen bond. However at the same time it would make it a correspondingly weaker acceptor, thus giving an overall lessening of the possibility of a hydrogen bond being formed between the two amino groups. The possibility of a hydrogen bond between the amine group and the trifluoromethyl group cannot be overlooked, but in the corresponding ortho isomer it has been shown (this thesis, p. 57) that the trifluoromethyl group exerts a repulsive effect on the amine group and that there is no evidence for the formation of an intramolecular hydrogen bond.

In ethyl anthranilate the symmetric stretching frequency of the NH_2 group remains sensibly constant in contrast to the antisymmetric frequency. The concentration versus frequency plot shows the behavicur of the main absorption. However the antisymmetric band is single for the liquid film, double at concentrations of ca. 5M with a shoulder on the high frequency side, becomes single again at lower concentrations and then becomes double at concentration of 1M with the shoulder appearing on the low frequency side of

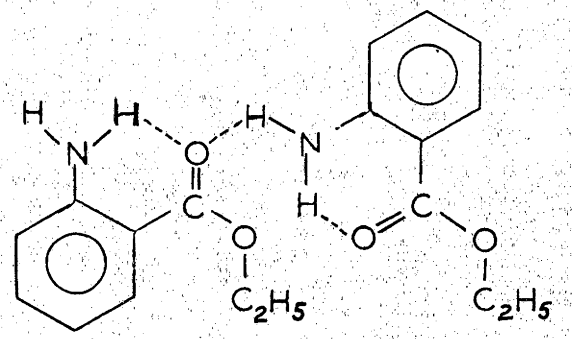
the absorption. At still lower concentrations the absorption becomes sharp, single and has a constant frequency.

This behaviour can be explained in terms of an intermolecular hydrogen bond being formed by the remaining "free" amino hydrogen to one of the oxygen atoms.

In the liquid film probably all the molecules are associated by a week intermolecular hydrogen bond into dimers or higher polymers. On dilution these week hydrogen bonds are broken very easily so that the NH absorption gives evidence of "free" and "bonded" NH groups. Further dilution gives equal intensity of these NH absorptions and the individual bands cannot be resolved. On diluting further the "free" band dominates with the "bonded" NH absorption becoming the shoulder until at concentration below 0.1M the amine exists solely as the monomer.

If the intermolecular hydrogen bond is formed to the carbonyl oxygen, the bond order of the C-O linkage will be reduced, resulting in a shift of the carbonyl frequency to a lower value. This would result in two carbonyl absorptions, one corresponding to the intramolecularly hydrogen bonded and the other to the bilaterally hydrogen bonded (inter- and

intra-) oxygen (I).



I

The spectrum of ethyl anthranilate at various concentrations was recorded and the results are given in Table 3.2. The absorption was doubled at high concentrations but became single below a concentration of 1M, which was in agreement with the behaviour exhibited by the NH stretching frequencies of the same compound. To ensure that the frequency values would be strictly comparable, the anilines were studied as dilute (< 0.01M) solutions in carbon tetrachloride.

3.4 Deuteration:

The replacement of the active hydrogens in amines, alcohols or carboxylic acids with deuterium has generally been achieved by repeated evaporation of the sample from a solution of deuterium oxide or in the case of water insoluble compounds from deuterium oxide/dioxan mixtures or from deuterated alcohols. To prevent back exchange from traces of moisture in solvents and absorbed on the apparatus, it is necessary to

work in a drybox and to take special precautions with the drying of all materials likely to come in contact with the deuterated sample. A further complication with compounds in which intramolecular hydrogen bonding can occur is their volatility in steam during the evaporation process.

The development of a rapid method by Fales and Robertson (1962) of deuterating natural products in structural investigations, by adding a drop of deuterium oxide to the solution in the infra-red cell, has enabled this technique to gain wider applicability. In the present work, deuteration was accomplished by shaking the dilute, carbon tetrachloride solution of the aniline with deuterium oxide, removing the excess and drying the solution with anhydrous sodium sulphate. The residual deuterium oxide present was insufficient to give any OD absorption at approximately 2600 cm^{-1}, and to shift any of the absorption bands under consideration. When treating water soluble compounds, which distribute preferentially into the "aqueous" layer, it was necessary to "salt" out the amine with dried sodium chloride before adding the sodium sulphate. By this technique it was possible to retain the concentration of the sample at approximately its original level. In order to obtain partial deuteration, in which only one of the amine protons is replaced by deuterium, a mixture of 75% D_2O to 25% H_2O gave satisfactory results. An alternative procedure

for partial deuteration was to mix the original solution of the aniline with a solution of the fully deuterated aniline at the same concentration in a ratio of 2:3. The mixture equilibrated rapidly to give a solution of partially and fully deuterated amine but with very little of the non-deuterated material

TABLE 3.1

Effect of Concentration on the NH_2 Stretching Frequencies (cm^{-1})

Aniline

Concentration (moles/litre)	ν_{as}	ν_{s}
10.97	(3456 sh. (3432	(3365 sh. (3352
10.05	(3458 sh. (3432	(3370 sh. (3354
5.66	(3472 sh. (3446	(3381 sh. (3362
3.18	(3462 (3443 sh.	(3377 (3350 sh.
1.79	(3470 (3448 sh.	(3386 (3352 sh.
1.00	3475	3369
0.56	3477	3392
0.32	3470	3394
0.10	3481	3395
0.032	3482	3395

cont'd.

TABLE 3.1 cont'd

para-Trifluoromethylaniline

Concentration (moles/litre)	ν_{as}	ν_{s}
8.068	3488	3401
4.984	3492	3405
2.990	3498	3409
1.994	3498	3409
1.495	3499	3409
0.997	3499	3409
0.100	3499	3409

Ethyl Anthranilate

Concentration (moles/litre)	ν_{as}	ν_{s}
7.143	3481	3373
3.861	(3500 sh. (3484	3374
2.421	3490	3375
1.675	(3498 (3480 sh.	3375
0.974	(3501 (3481 sh.	3375
0.292	3504	3376
0.097	3506	3378
0.0097	3506	3378

sh. denotes shoulder

TABLE 3.2

Effect of Concentration on the C=O Stretching Frequency (cm^{-1})

Concentration (moles/litre)	$\nu_{C=O}$
7.143	(1690 (1679 sh.
2.874	(1692 (1685 sh.
1.724	(1692 (1686 sh.
1.035	1693
0.621	1693
0.103	1693

sh. denotes shoulder

4 - ortho ALKYL-ANILINES

4.1 Methyl Substituents:

Although the alkyl group cannot participate in hydrogen bonding, it is convenient to include the results for a series of ortho-alkyl-anilines as an indication of how interactions, apart from hydrogen bonding, can affect the infra-red spectrum and, in particular, the criteria which are to be used as being indicative of hydrogen bonding.

The experimental results for the fundamental NH_2 stretching frequencies are recorded in Table 4.1, together with the difference between the observed symmetric frequency and that predicted by equation 2.4. Figure 4.1 shows the plot of ν_s NH_2 versus ν_{as} NH_2, together with the line representing equation 2.4 for meta- and para-substituted anilines.

The frequencies of the first overtones of the NH_2 stretching vibrations and the difference between the observed overtone symmetric frequency and that predicted by equation 2.5 are recorded in Table 4.2. Two types of profile have been observed for the absorptions due to these vibrations, and these are represented in Figure 4.2a,b. The first type is typical of that observed for meta- and para-substituted anilines and for ortho-substituted anilines in which there is evidence of little or no interaction between the amine group

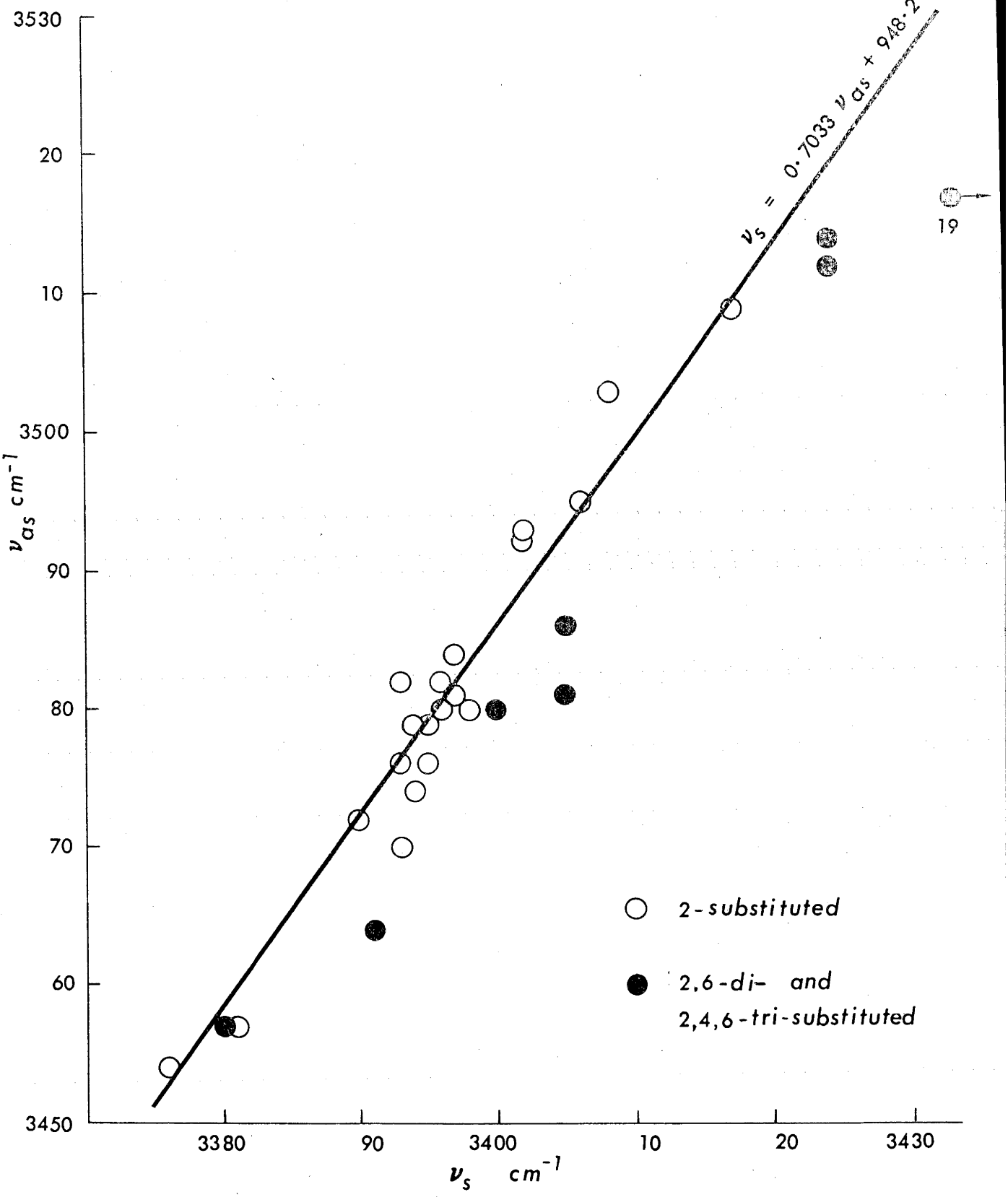


Fig. 4.1 - Relationship between the antisymmetric and symmetric stretching frequencies for the NH_2 group in 2-alkyl anilines.

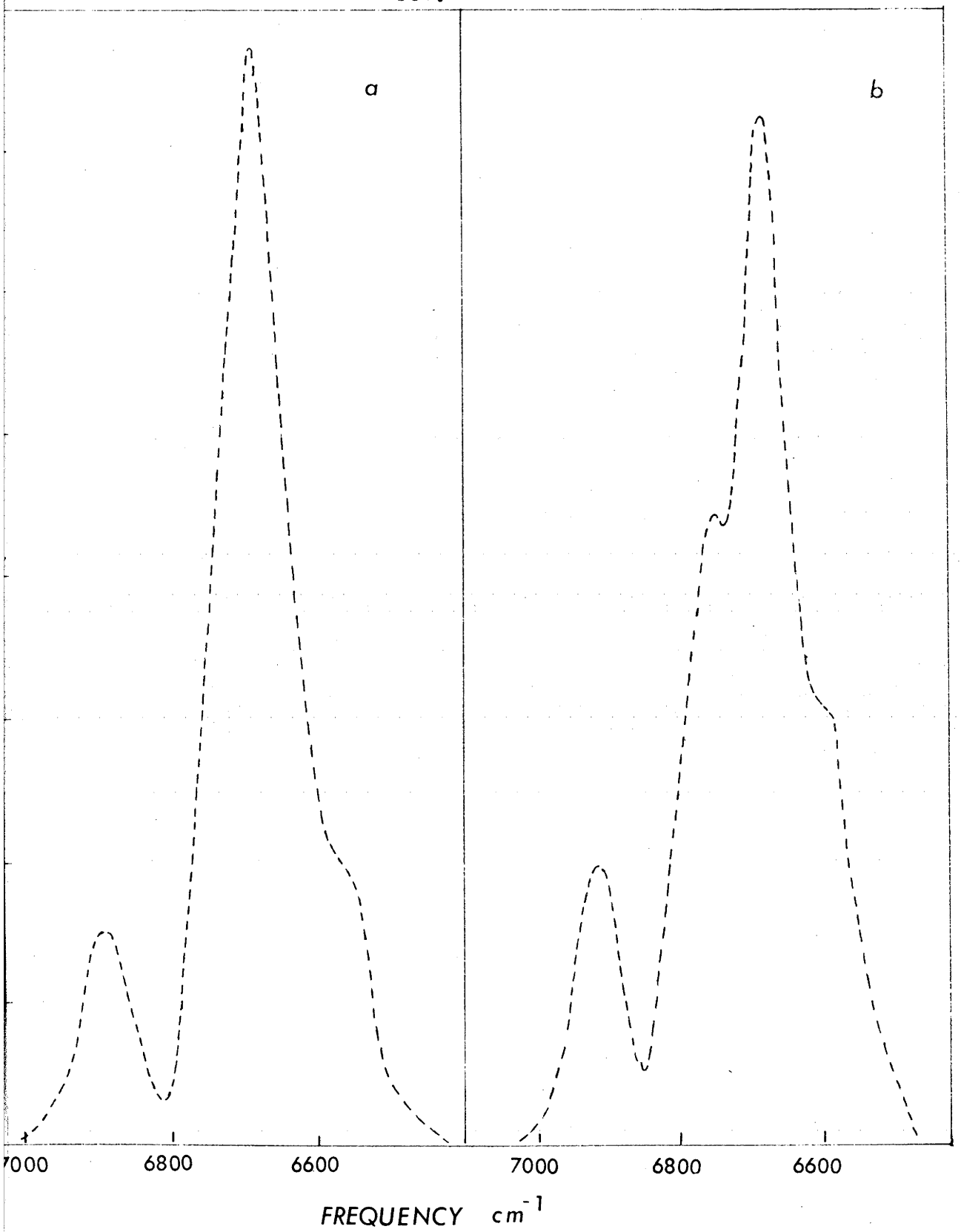


Fig. 4.2 - Absorption bands due to the first overtones of the NH_2 stretching vibrations of 2-alkyl anilines.

a, 2-methyl-aniline. b, 2-tert. butyl-aniline.

and the ortho substituent. Type 4.2b has been observed when there is an indication of a repulsive interaction on the amine group.

Several anilines were partially deuterated and the results for the stretching frequencies are recorded in Table 4.3. The appearance of multiple absorptions for the ND_2 symmetric stretching vibration has been attributed (Califano and Moccia, 1957; Hambly, 1961) to Fermi resonance between a weak combination band of the aromatic system and $\nu_s\ ND_2$.

The ten primary anilines with a single ortho-methyl group all conform to equation 2.4 with a standard deviation of 1.0 cm^{-1}. This agreement is not surprising as there is no evidence of any interaction between the methyl and hydroxyl groups in the corresponding ortho-substituted phenols (Puttman, 1960; Krueger and Thompson, 1959). One case of particular interest is that of 2-methyl,4-amino-aniline for which, at the resolution available, the presence of a methyl produces so little interaction with the adjacent amine group, that only two absorption bands are found for the stretching vibrations of the NH_2 groups. The six compounds with an ortho-methyl substituent that were studied in the overtone region produced spectra of type 4.2a and conformed to equation 2.5, the standard deviation being 2.0 cm^{-1}. Deuteration of ortho-

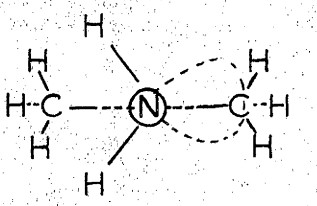
toluidine gave only a single NH and a single ND stretching frequency, the interaction between the substituent methyl group and the amino hydrogen being insufficient to enable differentiation between the *cis* and *trans* forms.

Six anilines with 2,6-dimethyl substituents were examined and for five the value of the symmetric NH_2 stretching frequency was higher than that predicted from equation 2.4. This result is in contradiction to the assumption by Richards and Walker (1961) that, in the absence of hydrogen bonding, *ortho*-substituted anilines will conform to this relation. Bellamy and Williams (1957) also postulate that, when the two NH links are equivalent, there will be no deviation, and support this idea with the results from some co-ordination compounds.

Wepster (1958), in an investigation of the ultra-violet spectra of a series of di-*ortho*-substituted alkyl-anilines, including 2,6-di-*tert*.-butyl aniline and 2,4,6-tri-*tert*.-butyl aniline, found no evidence of significant steric inhibition to mesomerism. Further he points out - "that these results leave no doubt that, in the less heavily substituted amines like 2,6-di-methyl aniline, there is no steric inhibition at all."

Because of the pyrimidal nature of the amine grouping, any rotation through a small angle will increase the repulsion

between one of the amine hydrogens and the adjacent ortho-group. Further, it has been shown that in piperazine the lone pair on the nitrogen exerts a greater repulsion on the axial hydrogens of the adjacent methylene groups than does the hydrogen on the nitrogen. The preferred conformation of the molecule is with this hydrogen in the axial position. Rotation of the amine group in di-ortho-substituted anilines will introduce this additional hindrance to adopting a configuration such as in I



I

It is probable therefore that the change in the NH_2 stretching frequencies, and consequent departure from equation 2.4, is caused by an alteration in configuration of the amine group other than that produced by rotation of the group. If the effect of electrostatic repulsion between the NH_2 and an adjacent group is to raise the frequency, then the opposing effect of electron release by the alkyl group, which tends to lower the frequency, will, in the case of a single methyl group, cancel this increase. Such a single methyl group

can thus give agreement with the ν_{as}/ν_{s} relationship. When there are methyl groups in both the two and six positions, the direct interaction between the hydrogen atoms predominates, giving rise to an effect which could be described as "anti-hydrogen bonding".

Because of the lowering of the bond order of the C-N link by the electron releasing para-amino group, the one 2,6-di-methyl aniline complying with equation 2.4, 2,6-di-methyl,4-amino-aniline, would have the 1-amino group in a more completely pyrimidal conformation, which would lessen the amine-methyl interaction. The decreased frequency shift caused by this lowering of repulsion, would make the frequency of the interacting NH_2 group approach that of the para-NH_2 group. At the resolution available with the spectrometer, the absorptions due to the stretching vibrations of the two groups would appear as two composite bands with frequency values intermediate to the true values for the individual groups and consequently any deviation from equation 2.4 would be small.

Di-amino-durene on the other hand showed evidence of increased interaction between the amine groups and the adjacent methyl groups, exhibiting an increased departure from the equation relating ν_{as} and ν_{s}. Scale models show that the presence of the two extra methyl groups prevent the amine groups and the methyl groups from taking up a position of minimal [illegible] interference, as they can do in the other

2,6-di-methyl anilines.

The two 2,6-di-methyl anilines examined in the overtone region agree with the predictions of equation 2.5 and gave spectra of type 4.2a. The failure to differentiate these compounds from those with a single methyl group would indicate that the anharmonicity factors must be sufficiently different to annul the deviations found in the fundamental region.

Mono-deuteration of diamino-durene in common with other 2,6-di-methyl aniline resulted in only a single NH absorption.

4.2 Other Alkyl Substituents:

In the series ortho-ethyl,-isopropyl,-tert.-butyl aniline there is no marked difference between the calculated and observed values of the symmetric NH_2 stretching frequency. This result is surprising as, although it could be argued that the effect of the ethyl and isopropyl groups would be the same as methyl because an α hydrogen atom can still be directed towards the amine group, the rapid increase in size of the tert.-butyl group would be expected to give quite a marked departure.

Nd_1,2-tert.-butyl-aniline gives definite evidence of an asymmetry in the environment of the amino hydrogens as two absorptions, separated by 45 cm^{-1}, are observed for the cis and trans NH vibrations. This would indicate that the period of any vibration or libration of the amine group to bring the

hydrogens in turn into the region of influence of the tert.-butyl group must be long compared with the frequency of vibration of the NH_2 group, since the two NH bands are sharper than the NH_2 bands of 4-tert.-butyl aniline. The reason why the dissimilarity of the NH linkages is not evident in the NH_2 stretching frequencies is not clear.

Ethyl aniline on mono-deuteration gave a single NH absorption band, hence either there are no isomeric mono-deutero compounds or the difference in the NH linkages is not sufficiently great to permit resolution of the separate absorption bands which have a finite band width varying with the type of substituent (Krueger and Thompson, 1959; Moritz, 1961).

The overtone spectra for 2-ethyl and 2-isopropyl aniline were of the type 4.2a and the results fitted equation 2.5 within the standard deviation. 2-tert.-butyl-aniline gave absorptions of type 4.2b. The high frequency shoulder on $\nu_s NH_2(0-2)$ has a large positive departure (+51) from equation 2.5 whereas the main band has a much smaller negative deviation (-18).

The evidence of a repulsive interaction between the tert.-butyl group and the amino group is not surprising as Goddu (1960) has shown that in a series of 2-tert.-butyl phenols there are two absorptions corresponding to the O-H stretching vibrations of the hydroxyl group in the cis and

trans configurations. The main absorption occurs at ca. 3610 cm^{-1} which is similar to the "free" O-H stretching vibration in other ortho-substituted phenols. The second absorption occurs at a higher frequency (ca. 3640 cm^{-1}) and is approximately one-tenth the intensity of the low frequency band. Goddu, in the absence of positive evidence, prefers to call them the high and low frequency forms of the O-H vibration.

The stretching force constant for the N-H bonds in tri-tert.-butyl aniline can be calculated from the symmetric and antisymmetric stretching NH_2 frequencies (Linnett, 1945; p. 119 this thesis). Krueger (1962) has made an error in calculating both the stretching force constant and HNH angle for this compound. The value of the stretching force constant is greater than that found for the other anilines studied, and is much higher than in any other substituted anilines with substituents possessing a similar additive sum of the substituent constant σ.(Hammett, 1940 b; Taft, 1956). For example, para-phenylene-diamine has $\sigma = -0.66$ and $k = 6.47 \times 10^5$ dyne/cm whereas 2,4,6-tri-tert.-butyl-aniline has $\sigma = -0.6$ and $k = 6.70 \times 10^5$ dyne/cm. From this it is reasonable to assume that a repulsive interaction increases the force constant which would make it reasonable to assign the high frequency absorption of the OH vibration in 2-tert.-butyl-phenol and the NH vibration in Nd_1-2-tert.-butyl-aniline to the cis configuration.

4.3 2-Phenyl-Aniline:

Baker and Shulgin (1958) have shown that a phenolic hydroxyl group is able to form weak hydrogen bonds to a variety of unsaturated groups. They attribute to the π-electrons of the unsaturated groups, including the aromatic ring, the power of accepting such bonds. The spectrum of 2-phenyl-aniline in the fundamental NH_2 stretching region shows a double antisymmetric and a single symmetric absorption. The departure of ν_s from the prediction of equation 2.4 when using the high and low frequency values of ν_{as} is -4.0 and +4.6 respectively.

There is no evidence of cis and trans forms of the NHD group in the monodeuterated compounds, while the overtone bands are of the simple type 4.2a. No evidence for intramolecular bonding in this compound has been found.

4.4 Condensed Aromatic Amines:

The steric effect of the peri hydrogen atom has been often invoked to explain anomalies in the physical and chemical properties of 1-substituted naphthalenes and anthracenes. Although 1-amino-naphthalene and 1-amino-anthracene showed a slight positive deviation from equation 2.4, there was no evidence of a doubling of the NH absorption in the mono-deuterated compounds.

In conclusion, it appears that a group not capable of accepting a hydrogen bond can produce some spectral changes which

are similar to those produced when hydrogen bonding is present. However, when all three spectral methods are considered together, taking into account the nature of the groups concerned, it should be possible to deduce unambiguously whether the observations are the result of hydrogen bonding or of a repulsive interaction.

TABLE 4.1

Fundamental Stretching Frequencies of the NH_2 Groups in ortho-Alkyl-Anilines (cm^{-1})

Substituents	$\nu_{as}NH_2$	$\nu_{s}NH_2$	Deviation from Equation 2.4
1. 2-CH_3	3481	3396	-0.4
2. 2,6-di-CH_3	3480	3396	+0.3
3. 2,4-di-CH_3	3472	3390	+0.5
4. 2,5-di-CH_3	3479	3395	0.0
5. 2,6-di-CH_3	3486	3405	+5.1
6. 2-CH_3,5-iC_3H_7	3479	3394	-1.0
7. 2-CH_3,4-NO_2	3509	3417	+0.9
8. 2-CH_3,5-NO_2	3495	3408	-0.2
9. 2-CH_3,4-NH_2	3454	3376	-1.4
10. 2-CH_3,5-NH_2	3478	3393	+0.1
11. 2-CH_3,4-N(C_2H_5)	3456	3381	+2.2
12. 2,4,6-tri-CH_3	3480	3400	+4.3
13. 2,6-di-CH_3 - 3,5-di-NO_2	3512	3424	+5.9
14. 2,6-di-CH_3,4-NO_2	3514	3424	+4.4
15. 2-C_2H_5	3480	3398	+2.4
16. 2-C(CH_3)$_3$	3493	3402	-2.8
17. 2-C(CH_3)$_3$,5-Cl	3503	3408	-3.8
18. 2-CH(CH_3)$_2$*	3481	3397	+0.7
19. 2,4,6-tri-C(CH_3)$_3$*	3517	3442	+21.7
20. 2,4,6-tri-CH(CH_3)$_2$*	3481	3405	+11.3

cont'd

TABLE 4.1 cont'd

	Substituents	$\nu_{as}NH_2$	$\nu_{s}NH_2$	Deviation from Equation 2.4
21	2,6-di-$C(CH_3)_3$*	3490	3402	-2.8
22	1-naphthylamine	3476	3395	+2.2
23	2-naphthylamine	3482	3396	-1.1
24	1-amino-anthracene	3474	3394	+2.6
25	2-amino-anthracene	3484	3397	-1.4
26	Diamino-durene	3464	3391	+6.6
26a	2,6-di-CH_3,4-NH_2	3457	3380	+0.5
27	2-C_6H_5	(3482 (3470 sh.	3393	(-1.0 (+4.6

sh. denotes shoulder * Krueger (1962b)

TABLE 4.2

First Overtones of Stretching Vibration of NH_2 Group in

Ortho-Alkyl Anilines (cm^{-1})

Substituents	$\nu_{as}(2-0)NH_2$	$\nu_{s}(2-0)NH_2$	Deviation from Equation 2.5
1. 2-CH_3	6896	6693	+1
2. 2,3-di-CH_3	6896	6696	+4
4. 2,5-di-CH_3	6902	6698	+1
5. 2,6-di-CH_3	6905	6698	-2
6. 2-CH_3,5-iC_3H_7	6892	6686	-1
9. 2-CH_3,4-NH_2	6834	6644	+1
12. 2,4,6-tri-CH_3	6892	6690	+1
16. 2-$C(CH_3)_3$	6914	(6757 sh. (6668	(+51 (-18
17. 2-$C(CH_3)_3$,5-Cl	6933	(6773 sh. (6701	(+51 (-21
18. 2-$CH(CH_3)_2$*	6892	6686	+3
19. 2,4,6-tri-$C(CH_3)_3$*	6973	6767	+14
20. 2,4,6-tri-$CH(CH_3)_2$*	6891	6689	+1
27. 2-C_6H_5	6888	6679	-7

sh. denotes shoulder * Krueger (1963)

TABLE 4.3

Fundamental Stretching Frequencies of NH and ND Bonds in Deuterated and Partially Deuterated Anilines (cm^{-1})

Substituents	ν.NH(D)	ν.ND(H)	$\nu_{as}ND_2$	$\nu_{s}ND_2$
1. 2-CH_3	3436	2539	2600	(2489 (2457
12. 2,4,6-tri-CH_3	3440	-	-	-
15. 2-C_2H_5	3436	2538	2598	(2485 (2456
16. 2-$C(CH_3)_3$	(3470 (3425	(2562 (2531	2609	2492
17. 2-$C(CH_3)_3$, 5-Cl	(3476 (3433	(2571 (2537	2616	2494
22. 1-naphthylamine	3433	2538	2597	(2477 (2461
23. 2-naphthylamine	3438	2537	(2602 (2590 sh.	(2500 (2476 (2444
24. 1-amino-anthracene	3430	2535	2593	(2483 (2467 (2456
25. 2-amino-anthracene	3440	2540	(2641 (2600	(2487 (2466
26. Diaminodurene	3426	-	-	-
27. 2-C_6H_5	3436	2538	2600	(2489 (2455

sh. denotes shoulder

5 - ortho-ALKOXY-ANILINES

2-Methoxyphenol has a very weak intramolecular hydrogen bond (Lüttke and Mecke, 1938; Baker and Shulgin, 1958), and it would be expected that ortho-anisidine would show little or no interaction between the amino and methoxyl groups.

The spectra of nine ortho-alkoxy-anilines were recorded and the values of the NH_2 stretching frequencies are given in Table 5.1. Three of the amines, ortho-anisidine, 2-methoxy,3-chloro,5-nitro-aniline and 2-methoxy,1-naphthylamine were partially deuterated and their NH stretching frequencies are given in Table 5.2. The spectra of ortho-anisidine and ortho-phenetidine were recorded in the first overtone region and the values of $\nu_{as}NH_2(0\text{-}2)$ and $\nu_{s}NH_2(0\text{-}2)$ for these compounds are given in Table 5.3.

The NH_2 stretching frequencies of all compounds, with the exception of 2-methoxy,1-naphthylamine, did not comply with the ν_s/ν_{as} relationship, and the calculated values of ν_s were 6.0 ± 1.7 cm^{-1} greater than the observed values. As expected, 2-methoxy,3-chloro,5-nitro-aniline gave the largest deviation.

In ortho-anisidine it would be expected that the methoxyl group would lie in the plane of the benzene ring through conjugation of the oxygen lone pair with the electrons of the aromatic nucleus. The effect of conjugation will be to make the oxygen, electron-deficient and a poorer acceptor

of the hydrogen bond. However, when a bulky group is introduced in the meta position, the methoxy group will be forced to rotate and break its conjugation with the ring. The oxygen atom will then become a better acceptor of a hydrogen bond by virtue of its electron attracting inductive effect which will produce an increased electron density on the oxygen atom.

The results obtained on partial deuteration are in accord with this idea. Whereas Nd_1,ortho-methoxy-aniline gave a single NH absorption, Nd_1,2-methoxy,3-chloro,5-nitro-aniline showed a distinct doubling of the band, though the measured separation between the two frequencies was only 6 cm^{-1}. It would have been expected that 2-methoxy,1-naphthylamine would have shown evidence of increased amine/methoxyl interaction because of the steric effect of the peri hydrogen, however the partially deuterated compound gave no evidence of such an effect.

The spectra in the overtone region were of type 4.2a. Although Krueger (1963) reports a shoulder on the high frequency side of ν_s(2-0), the work in this thesis was done at lower resolution and it was impossible to obtain a sensible measure of the position of this shoulder. There is also a small difference (ca. 10 cm^{-1}) between his values of ν_{as}(0-2) for ortho-phenetidine and ortho-anisidine and those reported here. Probably this is due in part to the weakness and the width of the absorption band being measured.

The results in the overtone comply with equation 2.5, giving further evidence that there is no significant interaction in these compounds.

TABLE 5.1

Fundamental NH Stretching Frequencies of the NH_2 Group in Alkoxy-Anilines (cm^{-1})

Compound Number	Substituents	$\nu_{as} NH_2$	$\nu_{s} NH_2$	Deviation from Equation 2.4
28	2-OCH_3	3487	3395	-5.6
29	2-OC_2H_5	3486	3394	-5.9
30	2,5-di-OCH_3	3488	3397	-4.3
31	2,5-di-OC_2H_5	3487	3395	-5.6
32	2-OCH_3,4-NO_2	3515	3414	-6.3
33	2-OCH_3,5-NO_2	3502	3405	-6.2
34	2-OCH_3,3-Cl,5-NO_2	(3500 (3482 sh.	3402	(-7.7 (+5.0
35	2-OCH_3,1-naphthylamine	3473	3388	-2.7
36	Dianisidine	3485	3393	-6.2

sh. denotes shoulder

TABLE 5.2

Fundamental NH Stretching Frequencies of Partially Deuterated Alkoxy-Anilines (cm^{-1})

Compound Number	Substituents	ν_{NH}
28	2-OCH_3	3437
34	2-OCH_3,3-Cl,5-NO_2	(3452 (3446
35	2-OCH_3,1-naphthylamine	3426

TABLE 5.3

First Overtones of Stretching Vibrations of NH_2 Groups in Alkoxy-Anilines (cm^{-1})

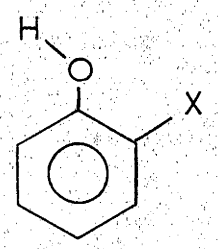
Compound Number	Substituents	ν_{as} (0-2)	ν_s (0-2)
28	2-OCH_3	6901	6695
29	2-OC_2H_5	6901	6696

6 - INTRAMOLECULAR HYDROGEN BONDING TO HALOGENS

6.1 o-Halogeno-Phenols:

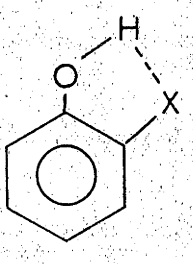
Although there has been an extensive study of ortho-halogeno-phenols in recent years, little systematic work has been done on the corresponding ortho-substituted anilines. The results for the phenols have been confusing and no conclusive evidence has been obtained for the relative strengths of the hydrogen bonds to the different halogen atoms.

The conclusion that the hydrogen bonds in the 2-halogeno-phenols increased in strength in the order: 2-fluorophenol < 2-chlorophenol < 2-bromophenol < 2-iodophenol has been based on changes in the OH stretching frequencies in the fundamental and overtone bands (Baker, 1958a; Mittke and Hecke, 1950; Zumwalt and Badger, 1940). However, Baker (1958a) showed that the ratio of intensities I_{trans}/I_{cis}, for the two hydroxyl stretching frequencies corresponding to structures I and II



trans

I



cis

II

increased in the same order implying increased stability of the trans structure compared to the cis. Baker and Kaeding (1959)

showed that when two halogens competed for the hydrogen bond in 2,6-di-halogeno-phenols, the relative strengths appeared to be: iodophenol < fluorophenol < bromophenol < chlorophenol. Allen and Reeves (1962) claim to confirm the order of hydrogen bond strengths: iodo < bromo < chloro in 2-halogeno-phenols by the chemical shift for the proton in the nuclear, magnetic resonance spectrum, but they did not obtain any evidence for hydrogen bonding in 2-fluorophenol.

Because of the ambiguous interpretation of the ortho-halo-phenol data in which the rigidly held aromatic system may prevent optimum interaction of the lower atomic weight halogen atoms with the hydroxyl group, Schleyer and West (1959) investigated the intermolecular hydrogen bonding of methanol and phenol to a series of alkyl halides. Their results for the frequency shift of the OH stretching vibration paralleled that found by Baker (1958a) for the ortho-halo-phenols and their own results for the β halo-ethanols. If an increasing shift in the OH stretching frequency can be reconciled with an increasing strength of hydrogen bond formation, then the relative ability of a covalently bound halogen atom to act as an acceptor for a hydrogen bond will increase in the order fluorine < chlorine < bromine < iodine.

However as the hydrogen bond to a halogen is weak, it is of little practical consequence to establish a sequence of acceptor abilities for the halogens and it is probable that

other effects, apart from hydrogen bonding, would be more important in determining the physical and chemical properties of these compounds.

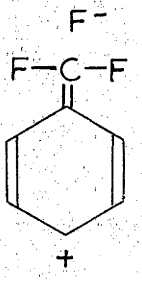
6.2 o-Halogeno-Anilines:

The values of the NH_2 stretching frequencies, ND_2 stretching frequencies and the first overtone NH_2 stretching frequencies for 22 halogeno-anilines are given in Tables 6.1 - 6.3 respectively.

ortho-Fluoro-aniline, together with 2,4- and 2,5-difluoro-aniline, gave no evidence of an intramolecular hydrogen bond being formed. The deviations of these compounds from the ν_{as}/ν_s relationship were -2.1, -0.1 and -1.7 respectively, which are not much greater than the standard deviation for the equation. With 4-fluoro-aniline the electron releasing, mesomeric effect more than counterbalances the electron attracting, inductive effect, so that the NH_2 stretching frequencies are lower than those of aniline. This net electron release from a para fluorine substituent has also been noted for the corresponding phenol (Baker, 1958b), though in this case the hydroxyl stretching frequency was increased. With ortho substitution by fluorine the NH_2 stretching frequencies are increased so that, at this close approach, the inductive effect dominates over the mesomeric effect. These relative effects of mesomerism and induction are consistent with the lowering of

the antisymmetric and symmetric stretching frequencies for 2,4-di-fluoro-aniline to values intermediate between those of 2-fluoro-aniline and 4-fluoro-aniline, while a second atom at position 5 can only exert an inductive effect so that the NH_2 stretching frequencies of 2,5-di-fluoro-aniline are at higher values than those of 2-fluoro-aniline. Deuteration of ortho-fluoro-aniline produced only a single NHD absorption for the mono-deuterated amine and the spectra in the first overtone region was of the type indicative of no hydrogen bonding.

As it had been argued that the small size of the fluorine atom prevented a bond from being formed, the spectrum of o-trifluoromethyl-aniline was also recorded. In this compound the fluorine atom would be: (a) in a sterically favoured position to form an H bond; (b) forming a six-membered ring on bonding; and (c) able to use an increased ability to accept a hydrogen bond if the hyperconjugation (III) suggested by Roberts et al. (1950) is real.



III

However in this compound there is evidence of a repulsive interaction similar to that observed in the ortho-

tert.-butyl-anilines. The calculated value of $\nu_s NH_2$ from equation 2.4 is 3.7 cm^{-1} less than the observed value; there is a separation of 18 cm^{-1} between the two NHD frequencies of the partially deuterated amine and the overtone symmetric NH_2 stretching vibration absorption has a pronounced high frequency shoulder. Both of these $\nu_s(0-2)$ absorptions have positive deviations from equation 2.5.

Hambly (1961) has pointed out that the electronegativity of an atom is not a measure of its ability to participate as an acceptor in hydrogen bond formation. A limited ability to donate electrons toward the protons is required and the ability of a covalently bound fluorine atom to act as an acceptor depends on the extent to which it has acquired excess negative charge from the rest of the molecule to which it is attached.

The deviation of the symmetrical stretching frequency of the NH_2 group from the predictions of equation 3.4 increases in the order: 2-fluoro-aniline < 2-chloro-aniline < 2-bromo-aniline < 2-iodo-aniline, which is in the order of decreasing electronegativity.

The NH and ND stretching vibrations of Nd_1,2-chloro-aniline and Nd_1,2-chloro,4-nitro-aniline show a slight assymmetry and there is definite evidence of doubling of these frequencies for mono-deuterated 2-bromo- and 2-iodo-aniline,

with the frequency separation increasing in the order: 2-chloro-aniline < 2-bromo-aniline < 2-iodo-aniline.

In the overtone region, the absorption band of the symmetric NH_2 stretching frequency has a shoulder on the high frequency side and when the halogen atom is varied, the increasing separation of the two bands parallels the separation observed for the NH bands in the mono-deutero-halogeno-anilines. The low frequency absorption shows increasing negative departure from equation 2.5 whereas the high frequency absorption gives an approximately constant positive deviation of 35 ± 2 cm^{-1}. A recent X-ray investigation of the crystal structure of 2,5-di-chloro-aniline, showed no evidence of a hydrogen bond (Sakurai et al., 1963).

Krueger (1962), on the basis of Linnett's equation (Linnett, 1945), has calculated that the H-N-H angle increases with the size of the halogen atom. However as Linnett's equation is not applicable where the NH bonds are not equivalent, his conclusion that the opening of bond angle parallels the increase in hydrogen bond strength is not valid. When Linnett's equation is applied to the 2,4,6-trihalogeno anilines, where we have shown that the NH bonds are equivalent, the H-N-H bond angle is found to be approximately constant.

In the symmetrically substituted 2,6-halogeno-anilines the deviations from equation 2.4 are greater than in the

corresponding ortho compounds. This result is in agreement with that already obtained for the 2,6-dialkyl-anilines and a further contradiction to the assumption (Bellamy and Williams, 1957; Richards and Walker, 1961) that if the amine has equivalent N-H bonds, it will be in agreement with equation 2.4.

The assumption that the N-H bonds are equivalent has been justified by the spectra of Nd_1, tri-chloro-, tri-bromo- and tri-iodo-aniline. In all cases there has only been one NH.D and one ND.H absorption observed. It would appear therefore that in 2,6-disubstituted aniline both the halogens are weakly hydrogen bonded to the amino group.

The failure to observe two NH absorptions in partially deuterated 2,4-di-bromo,6-chloro-aniline is probably due to the difficulty in resolving two absorptions of equal intensity and small frequency separation. The 2,6-di-halogeno,4-nitro-anilines show a different behaviour. The fundamental stretching frequencies are all doubled, although the members of the band are not fully resolved (Figure 6.1). When 2,6-di-bromo,4-nitro-aniline was partially deuterated the NH band had a similar shoulder. This doubling of absorption bands is probably due to rotational isomerism. The normal effect of substitution by a 4-nitro group is to raise both ν_{as} and ν_{s}, corresponding to a shortening of the NH bonds. The two members of each of the stretching bands of the 2,6-di-halogeno-anilines are respectively higher and lower than those of the 2,4,6-tri-halogeno-anilines.

This would be the result if the NH_2 group were rotated so that conjugation with the benzene ring and the p-nitro group was reduced, because the repulsive terms have reached such a value that they are comparable with the conjugation energy between the amine group and the rest of the molecule. It is consistent with this interpretation of the spectra in dilute solutions in carbon tetrachloride that the spectra of the solid in a potassium bromide disc gave only two very sharp absorption bands, indicating that only one isomer is present (Figure 6.1).

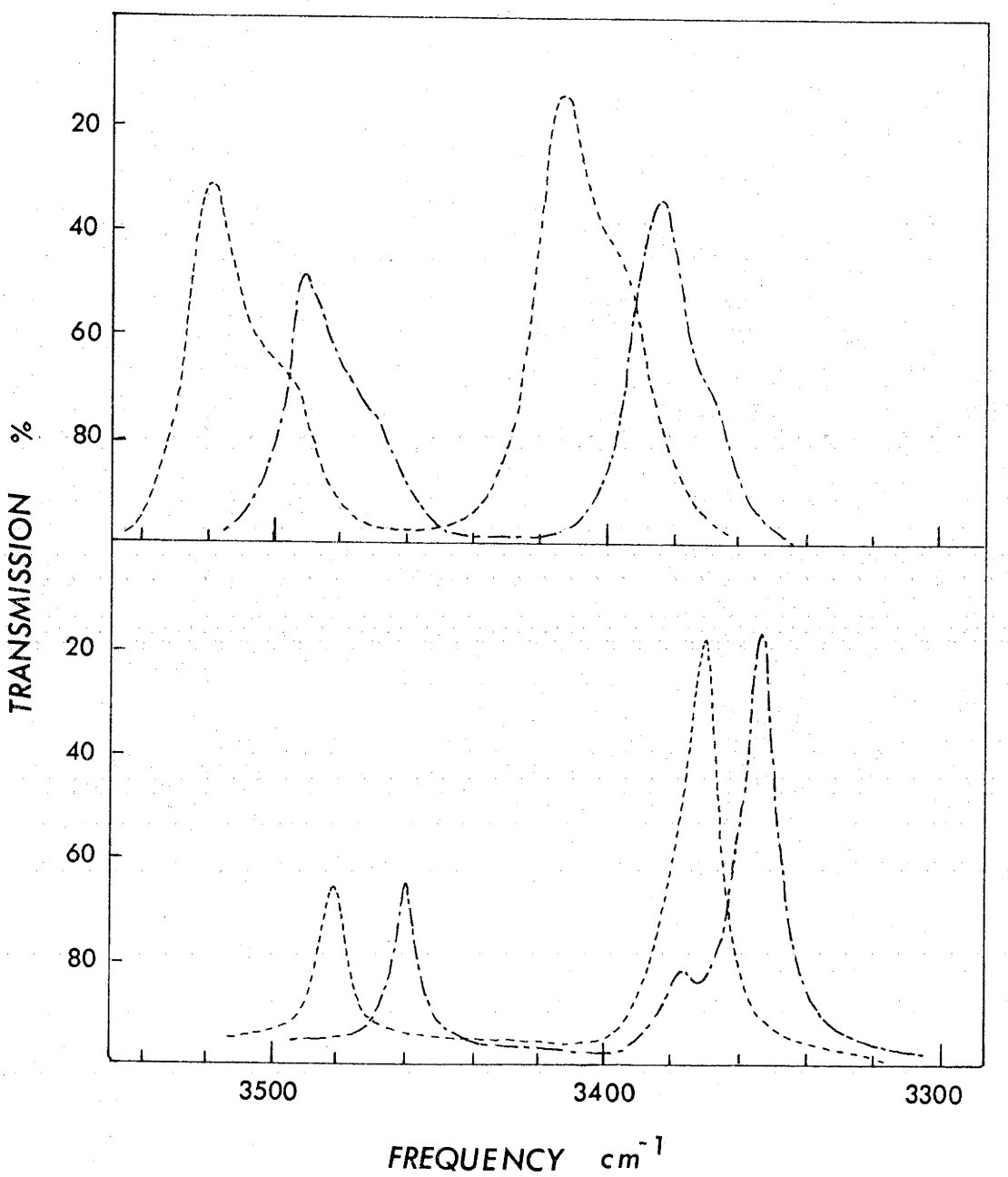


Fig. 6.1 - NH stretching frequencies of 2,6-dihalogeno-4-nitro-anilines.

a, dilute solution in CCl_4

b, solid in KBr disc.

----- 2,6-dichloro-4-nitro-aniline

- — - 2,6-di-iodo-4-nitro-aniline

TABLE 6.1

Fundamental Stretching Frequencies of NH_2 Groups in Halogeno-Anilines (cm^{-1})

Compound Number	Substituents	$\nu_{as}NH_2$	$\nu_{s}NH_2$	Deviation from Equation 2.4
37	2-F	3492	3402	-2.1
38	2-Cl	3495	3400	-6.2
39	2-Br	3491	3395	-8.4
40	2-I	3484	3387	-11.9
41	2,4-di-F	3482	3397	-0.1
42	2,5-di-F	3500	3408	-1.7
43	2,4-di-Cl	3494	3400	-5.5
44	2,5-di-Cl	3499	3403	-6.0
45	2,6-di-Br	3489	3392	-10.0
46	2,6-di-I,4-CH_3	3468	3374	-13.6
47	2-Cl,4-NO_2	3515	3413	-7.3
48	2,4,6-tri-Cl	3501	3402	-8.5
49	2,4,6-tri-Br	3492	3393	-11.1
50	2,4,6-tri-I	3473	3376	-14.8
51	2,6-di-Cl,4-NO_2	(3510 (3499 sh.	(3412 (3397 sh.	(-11.1 (-12.0
52	2,6-di-Br,4-NO_2	(3509 (3487 sh.	(3401 (3386 sh.	(-15.1 (-14.6

cont'd.

TABLE 6.1 cont'd

Compound Number	Substituents	$\nu_{as}NH_2$	$\nu_{s}NH_2$	Deviation from Equation 2.4
53	2,6-di-I,4-NO_2	(3400 (3467 sh.	(3384 (3369 sh.	(-18.7 (-17.5
54	2-CF_3	3515	3424	+3.7
55	3-CF_3	3493	3405	-0.5
56	4-CF_3	3499	3409	0.0
57	4-F	3474	3392	+0.5
58	2,4-di-Br,6-Cl	3497	3398	-0.6

sh. denotes shoulder

TABLE 6.2

Fundamental Stretching Frequencies of N-H and N-D Bonds in Deuterated and Partially Deuterated Halogeno-Anilines (cm^{-1})

Compound Number	Substituents	ν(NH,D)	$\nu_{as}(ND_2)$	ν(ND,H)	$\nu_{s}(ND_2)$
37	2-F	3437	2610	2541	(2493 (2459
38	2-Cl	(3455 sh. (3444	(2613 (2606	2549	(2499 (2464
39	2-Br	(3451 (3436	2611	(2548 (2536	(2496 (2461
40	2-I	(3450 (3421	(2607 (2588 sh.	(2548 (2526	(2491 (2458
46	2,6-di-I,4-CH_3	3423	2598	2528	(2477 (2442
47	2-Cl,4-NO_2	3464	2631	2559	(2514 (3475
49	2,4,6-tri-Br	3443	2614	2550	2486
52	2,6-di-Br,4-NO_2	(3457 (3435	-	-	-
54	2-CF_3	(3480 (3462	(2630 (2609 sh.	(2572 (2557	(2502 (2470
58	2,4-di-Br,6-Cl	3449	2617	2550	2490

sh. denotes shoulder

TABLE 6.3

First Overtones of Stretching Vibrations of NH_2 Groups in Halogeno-Anilines (cm^{-1})

Compound Number	Substituents	$\nu_{as}(2-0)$	$\nu_{s}(2-0)$	Deviation from Equation 2.5
37	2-F	6919	6715	+4
38	2-Cl	6935	(6759 sh. (6715	(+36 (-8
39	2-Br	6922	(6736 sh. (6697	(+33 (-16
40	2-I	6905	(6737 (6673	(+37
46	2,6-di-I,4-CH_3	6873	6650	-24
50	2,4,6-tri-I	6881	6651	-30
54	2-CF_3	6972	(6809 sh. (6763	(+57 (+11

sh. denotes shoulder

7 - AMINES WITH AN ortho-CARBONYL GROUP

7.1 NH_2 Stretching Frequencies:

The fundamental NH_2, NHD and ND_2 stretching frequencies are recorded in Tables 7.1 and 7.2. The first overtone NH_2 stretching frequencies of those compounds sufficiently soluble in carbon tetrachloride to give a reasonable absorption are given in Table 7.3. As the carbonyl frequency is susceptible to the effects of hydrogen bonding, the spectra of several of the compounds were recorded in the region 1700 cm^{-1} - 1400 cm^{-1} and the effects of deuteration on the carbonyl frequency and the NH_2 deformation frequency examined. These results are given in Table 7.4.

Hambly and Bonnyman (1958), from a comparison of the NH_2 and C=O stretching frequencies in ortho- and para-amino aceto-phenone and ortho- and para-carbomethoxy-aniline, concluded that there existed a weak bond between an amino hydrogen and the carbonyl group in the ortho compounds. They also concluded that as the negative charge on the oxygen atom increases, so will the strength of the hydrogen bond to it.

Moritz (1960) reported the existence of two N-H stretching frequencies in partially deuterated methyl anthranilate and 1-amino-anthraquinone. From the separation of these two frequencies he concluded that strength of the hydrogen bond present in the latter compound was twice of that in the former. Further, he found that there was only a limited correlation

between the departure from the equation of Bellamy and Williams (1957) and the difference between the cis and trans NH frequencies.

As unilateral hydrogen bonding will cause a marked lowering of the frequency of the symmetric vibration, while that of the antisymmetric vibration will decrease by a lesser amount, there will be an increase in the separation of the two frequencies as ν_s decreases, a trend which is opposite to that predicted by equation 2.4, which can be arranged to the form:

$$\nu_{as} - \nu_s = 0.4219\,\nu_s - 1348.2 \qquad (7.1)$$

Eleven of amines were found to give stretching frequencies which lie approximately on the line (Figure 7.1)

$$\nu_{as} - \nu_s = -0.8451\,\nu_s + 2984.8, \quad s = \pm 3.55. \qquad (7.2)$$

The main contributions to the standard deviation came from 1-amino,2-methyl-anthraquinone, in which there is a methyl group which is exerting a repulsive force on the amine group forcing it closer to the carbonyl and 1,4-diamino-anthraquinone, in which there are two hydrogen bonds present in the one molecule. The compound omitted from the correlation, 3-carbomethoxy-2-naphthylamine showed quite a considerable departure from the line. However, as will be shown later, it is thought that the weakest hydrogen bond in the carbonyl compounds examined exists in this amine, and that this approximate correlation will only apply where the hydrogen bonds present are of a similar magnitude.

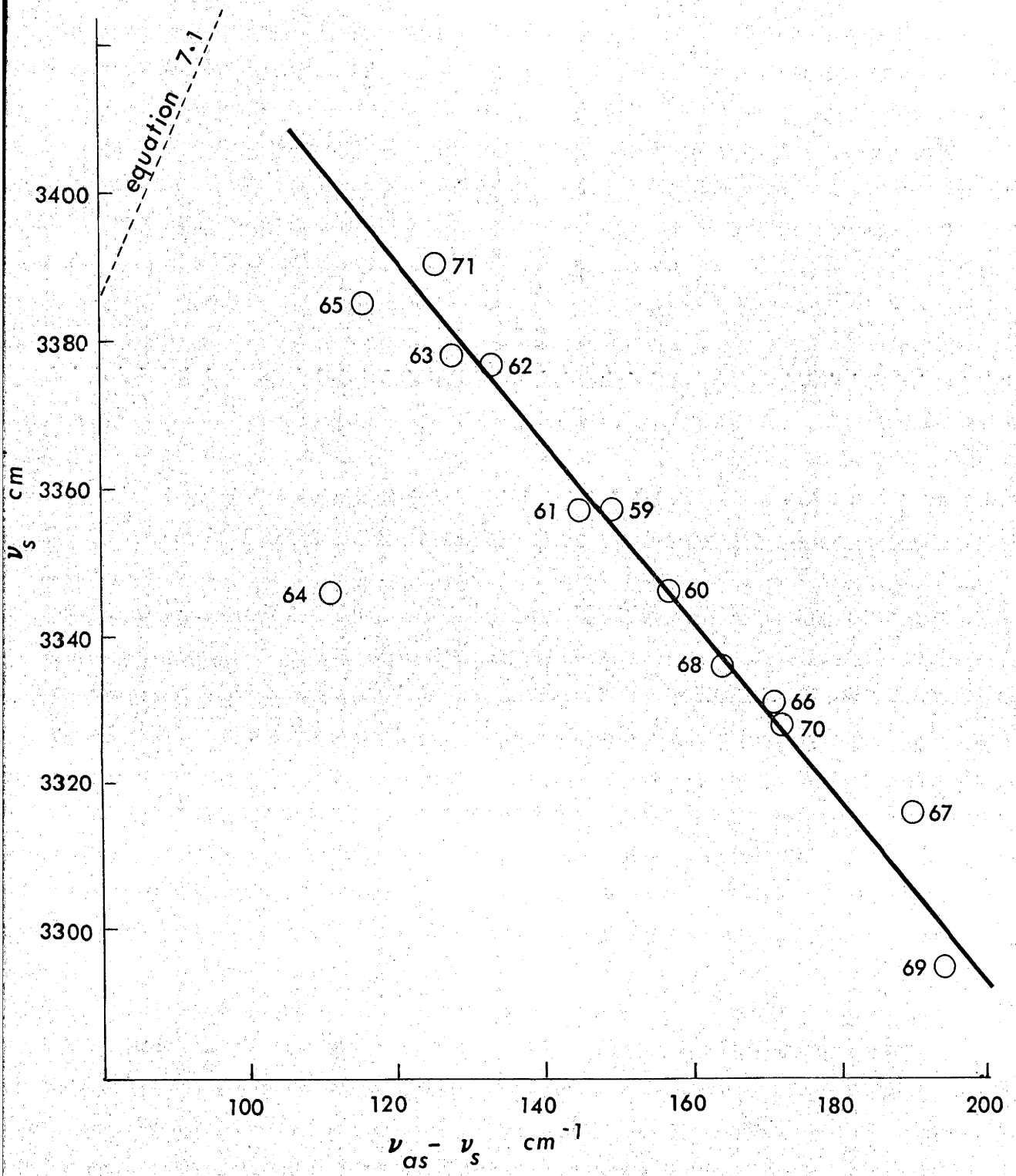


Fig. 7.1 - Correlation between the difference of anti-symmetric and symmetric stretching frequencies of NH_2 and symmetric frequency. The numbers correspond to compounds in table 7.1.

On partial deuteration all the compounds with a single carbonyl ortho to the amino group gave two NH and two ND stretching frequencies, characteristic of the rotational isomers which are hydrogen and deuterium bonded. For the carbonyl compounds studied, the separation of the bonded and unbonded frequencies of NH and ND bears an approximately linear relationship to the difference between the experimental value of ν_s and that predicted by equation 2.4 (Figure 7.2). Values for a typical 2-amino-aromatic sulphone, a 2-amino sulphide, 2-iodo-aniline, 2-cyano-aniline, 2-amino-1,4-naphthoquinone also fit this relationship. Because of the variety of forces other than hydrogen bonding that can operate between ortho substituents, this degree of correlation is surprising. Amongst the carbonyl compounds, 2-aminobenzophenone and 1-amino,2-methyl-anthraquinone show significant deviations from the correlation lines. The 2-halogeno-anilines lie to the right-hand side and it is probable that in these cases other ortho effects are more important than the weak hydrogen bond formed. The values for 2-nitro-aniline also lie to the right of the lines suggesting that there is some other effect involved in this case.

Dearden and Forbes (1960) have suggested that the amino group in 2-aminobenzaldehyde may be rotated so that a

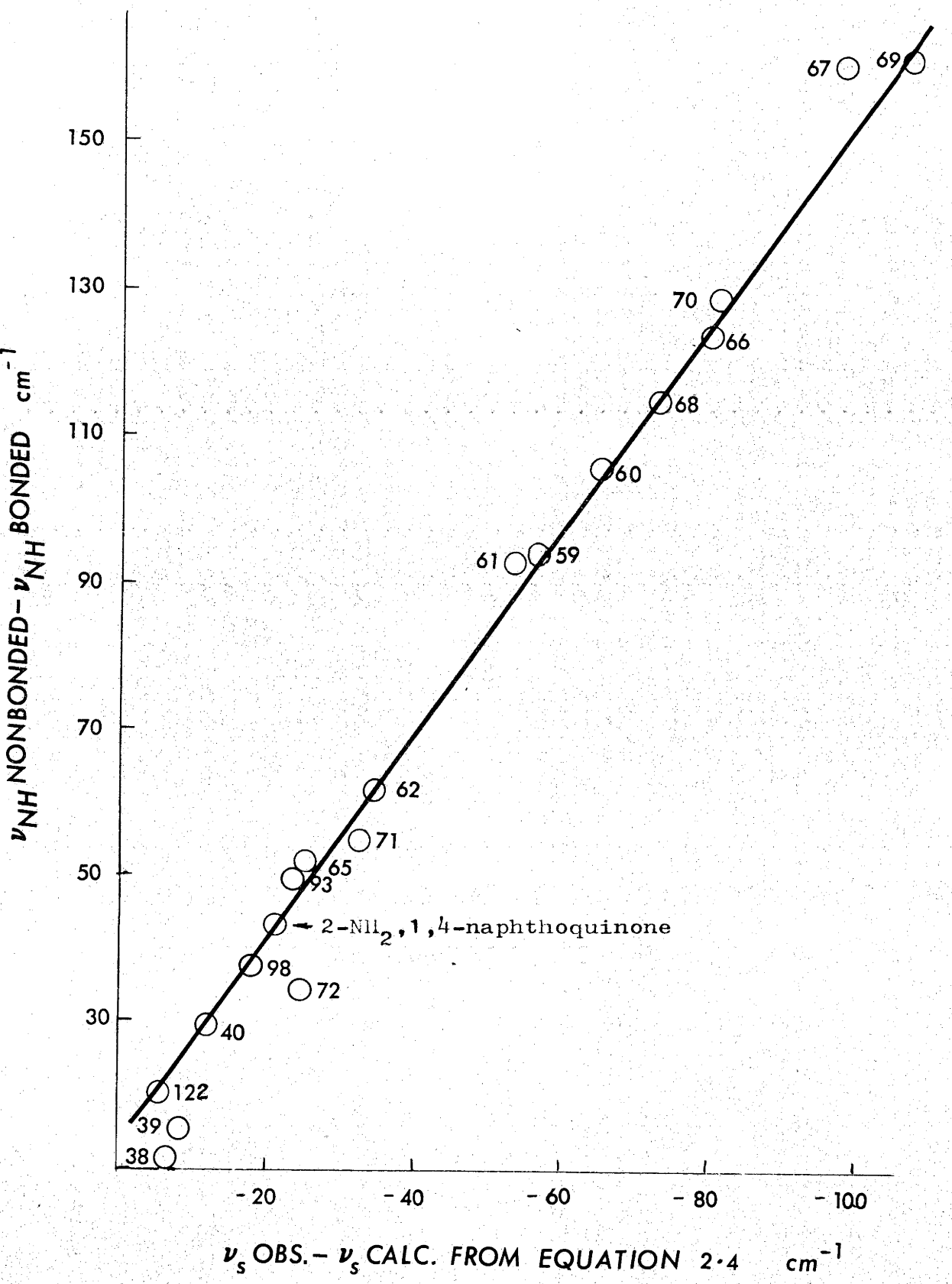
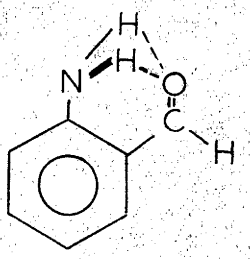


Fig. 7.2 - Correlation between separation of NH stretching frequencies for monodeuterated anilines, and departure from predictions of equation 2.4

bifurcated bonding (I) of both hydrogens can occur.

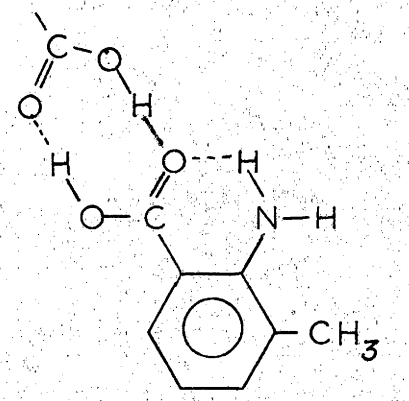


I

However mono-deuteration shows that only one hydrogen is involved in hydrogen bonding. Furthermore it would be expected that the two lone pairs of electrons on the oxygen atom would be sp^2 hybridized and so would be in the plane of the aromatic ring with one directed towards, and one away from, the amino group, a situation which would be unfavourable to hydrogen bonding of this nature. When 2,6-dicarbomethoxy-aniline is mono-deuterated, only a single NH and ND absorption are observed. This indicates that the hydrogen atoms are symmetrically situated. This would require the amine group to be bilaterally hydrogen bonded or to be rotated so as to form a bifurcated bond to one carbonyl group. As there is only a single carbonyl absorption observed, both carbonyl groups must be equally involved in hydrogen bonding. As has been common with other 2,6-disubstituted anilines, 2,6-dicarbomethoxy-aniline has a significant departure from equation 2.4.

Recently Brown and Marsh (1963) showed that in

crystalline 2-amino,3-methylbenzoic acid (II) both intermolecular and intramolecular hydrogen bonding to the carbonyl

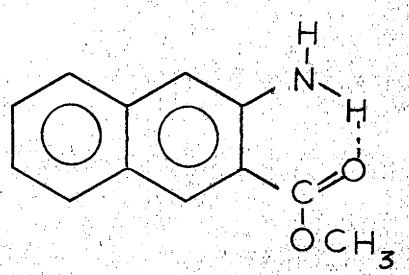


II

group occurred simultaneously and that the resulting bonded dimer was planar. The spectra of anthranilic acid and Nd_1-anthranilic acid are in accord with this result. The NH_2 stretching frequencies are sharp and on mono-deuteration two NH absorptions are observed. The broad, bonded OH absorption at about 3000 cm^{-1} decreases in intensity and shifts to ca. 2300 cm^{-1}. As is common with carboxylic acids, the dimer exists even in dilute solution in carbon tetrachloride and there is no "free" OH absorption.

If the major determinant of the departure of the NH_2 stretching frequencies from equation 2.4 and the separation of the stretching frequencies of the bonded and non-bonded hydrogen atoms is the strength of the unilateral hydrogen bond that is formed, then that in 2-amino,3-carbomethoxy-

naphthalene (III) is the weakest for the thirteen carbonyl



III

compounds studied. This is probably related to the extra length (Cruickshank, 1962) of the bond between carbon atoms 2 and 3 of the naphthalene ring. Bryson and Werner (1960) concluded that the hydrogen bond in 2-amino,3-nitro-naphthalene was the weakest amongst those in the nitro-naphthylamines with the substituents on the adjacent atoms.

The separation produced by hydrogen bonding on the symmetric NH_2 stretching frequency in the overtone region is at a maximum for the carbonyl compounds. Along the series of carbonyl compounds studied, the low frequency member became broader and decreased in peak intensity as the strength of the bond increased (Figure 7.3). The separation of the bonded and non-bonded NH frequencies for the mono-deuterated compounds shows a curvilinear correlation (Figure 7.4) with the separation of $\nu_s(0\text{-}2)$, for those cases which also showed good correlations in Figure 7.2. The splitting of this overtone band is thus related to the strength of the hydrogen bonds that have been formed.

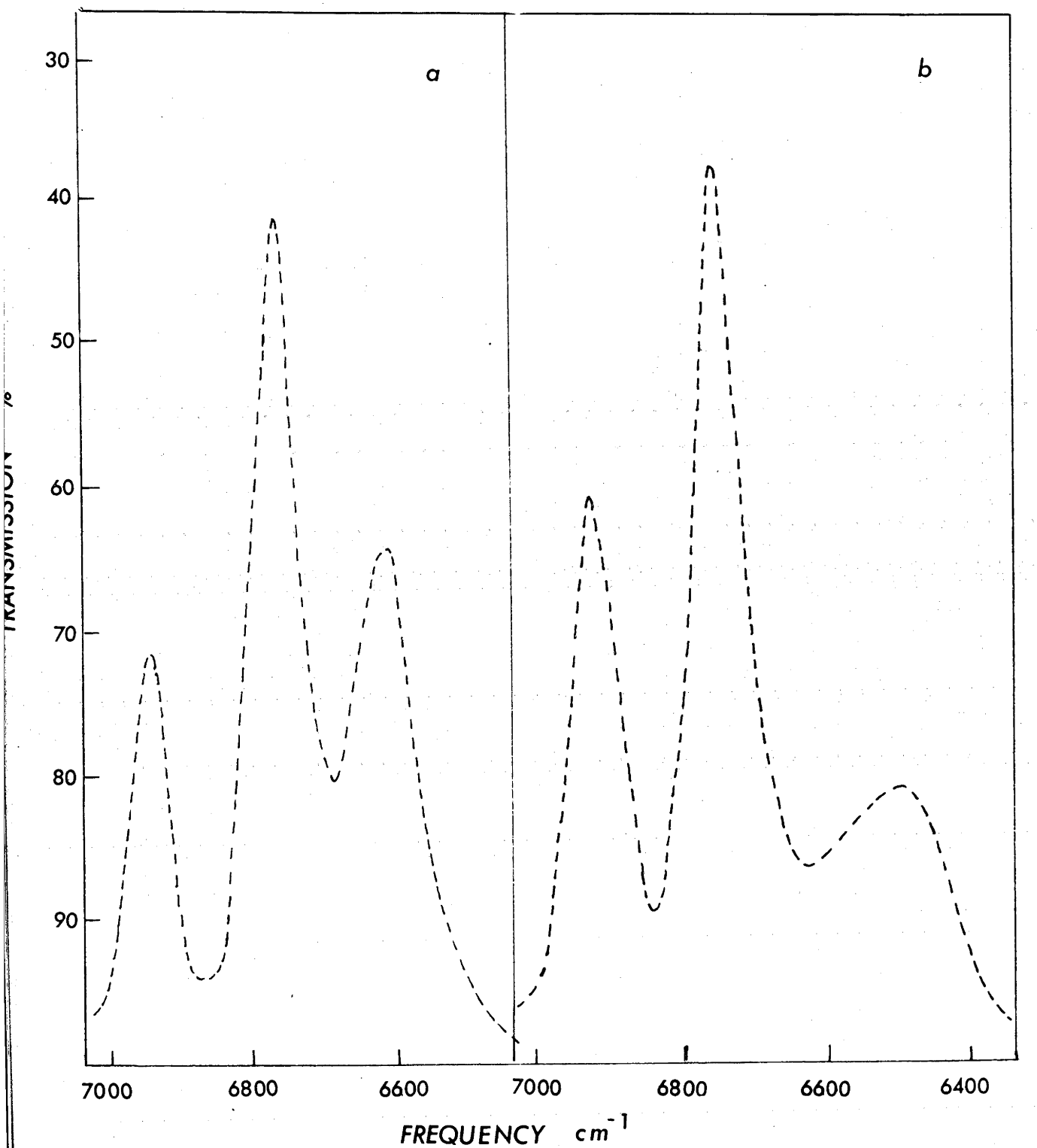


Fig. 7.3 - First overtone absorption bands of NH_2 stretching vibrations.

a, methyl anthranilate.

b, 2-amino-acetophenone.

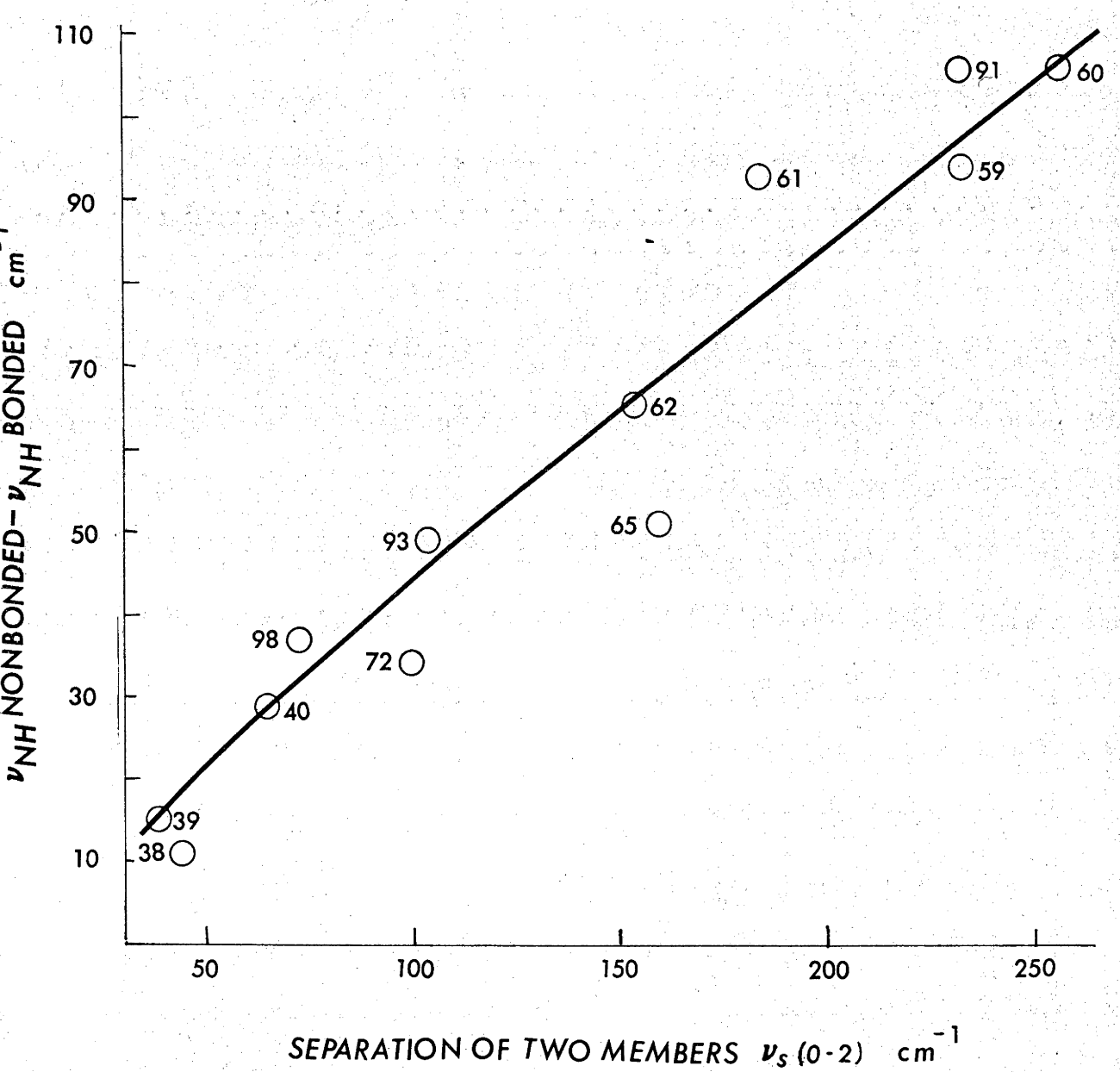


Fig. 7.4 - Correlation between separation of NH stretching frequencies for monodeuterated anilines and separation of two members of $\nu_s(0-2)$ overtone band.

Krueger's suggestion (1963) that the low frequency absorption is a combination band would seem to be incorrect. The spectrum of NNd_2-methyl anthranilate in the overtone region had three absorption bands, corresponding to the first overtone ND_2 stretching frequencies, at 5187, 5007 and 4873 cm^{-1}. The relative intensities of these three absorptions were similar to those found for the first overtone NH_2 stretching frequencies of methyl anthranilate. It is unlikely that a combination band, which involves other than NH_2 vibrations, would reappear after deuteration at a lower frequency.

The behaviour of 2-amino-benzophenone is anomalous. Although the correlations shown in Figures 7.1 and 7.2 indicate that the hydrogen bond in this compound has a similar strength to that in 2-amino-benzaldehyde, the second member of $\nu_s(0\text{–}2)$ is so broad that it is not possible to obtain an accurate value or its absorption maximum. This may account for the deviation from Figure 7.4.

Solubility limits the absorptions that can be observed in the overtone region for the anthraquinones. 1-Amino,2-methyl-anthraquinone, which from other correlations has the strongest hydrogen bond amongst those in the present study, has sufficient solubility to enable $\nu_{as}(0\text{–}2)$ and the high frequency member of $\nu_s(0\text{–}2)$ to be measured, but it has not been possible to determine the frequency of the second, extremely broad member expected for $\nu_s(0\text{–}2)$.

7.2 Carbonyl Frequencies:

The ability of a carbonyl group to accept a hydrogen bond is related to the base strength of its oxygen atom. Its basicity will be stronger when the carbonyl group is polarised by the transfer of electronic charge to the oxygen atom, with a consequent lowering of bond order and a reduction of the vibration frequency of the C=O bond. An inverse relationship is therefore to be expected between a measure of the strength of the hydrogen bond, and the vibration frequency of the carbonyl group in the absence of the amino substituent. Figure 7.5 shows the correlation between the separation of the NH frequencies of the rotational isomers of the mono-deutero compound and the carbonyl frequency in the absence of an amino group. There is general agreement with the expectation that the strongest hydrogen bonds are formed to those oxygen atoms which have acquired the largest excess of negative charge, and so reduced their electronegativity. This correlation is much less exact than the others. The modification of the electron distribution in the carbonyl group produced by an ortho-amino substituent will affect the strength of the hydrogen bond that is formed. Since the lowest carbonyl frequency is that of benzophenone (1666 cm^{-1}), it would be predicted to have the most basic carbonyl oxygen atom and to form the strongest hydrogen bond. The evidence generally is not in agreement with this. It is probable that, in forming

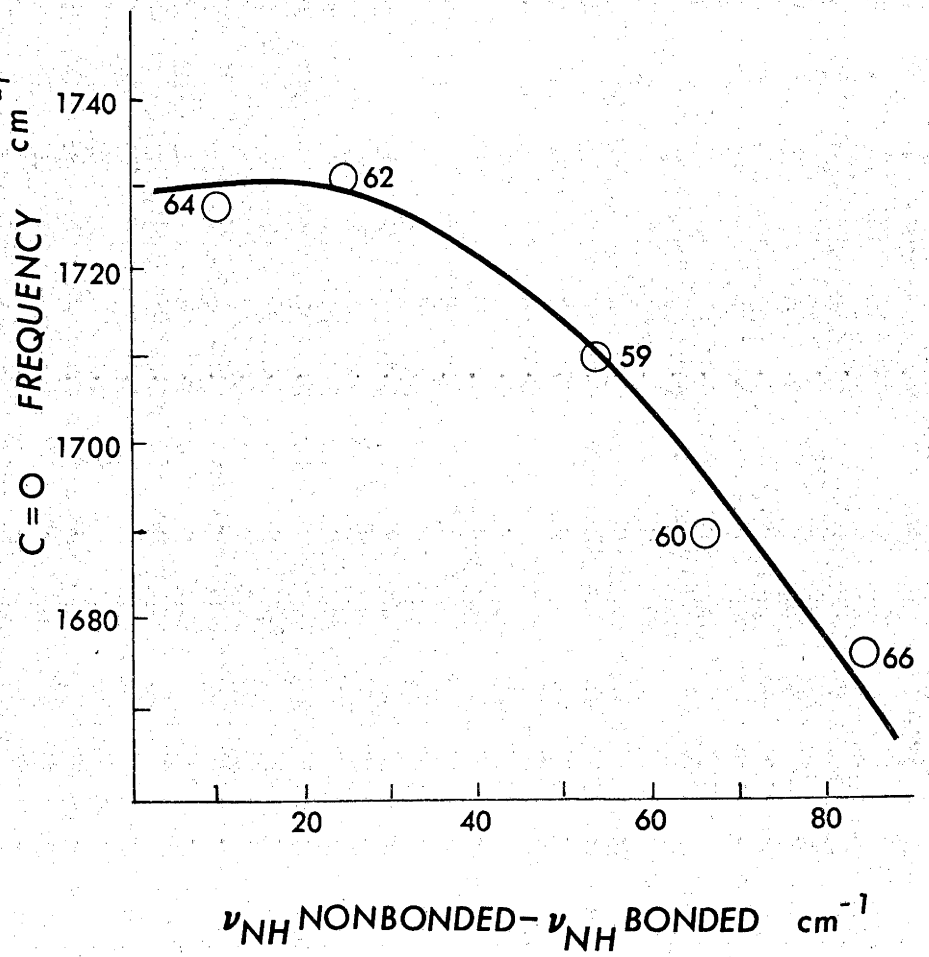
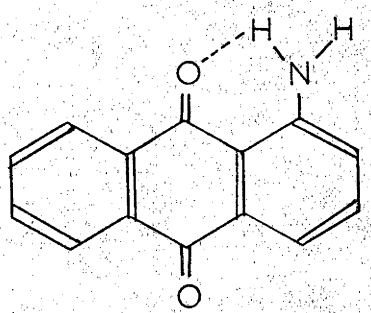


Fig. 7.5 - Dependence of strength of hydrogen bond on unbonded carbonyl frequency. The numbers refer to compounds in table 7.1.

a hydrogen bond, the carbonyl group changes its orientation with respect to the two aromatic rings and so loses some of its conjugation with them and becomes less basic.

Gramstad (1963) showed that in the system phenol, carbon tetrachloride, carbonyl compound, the ability to accept a proton from phenol to form a hydrogen bond increases in the order: aromatic esters, aromatic aldehydes, aromatic ketones. He also found that, although the carbonyl frequency in benzophenone is lowered by conjugation with the benzene rings, there is not a simultaneous enhancement of hydrogen bonding ability. This apparent anomoly is described as being due to a steric or conjugative effect, or both.

In the 2-amino-carbonyl compounds the complete deuteration of the amine group causes a slight increase in the intensity of the carbonyl absorption and a shift of approximately 3 cm^{-1} to lower frequency. In 1-amino-anthraquinone (IV), according to Hambly and Bonnyman (1958),



IV

the absorption band at 1673 cm^{-1} is due to the carbonyl group at

position 10 and the absorption at 1644 cm^{-1} to the hydrogen bonded carbonyl at position 9. In agreement with this the band at 1673 cm^{-1} remains unchanged when the molecule is deuterated but that at 1644 cm^{-1} intensifies slightly and moves to 1641 cm^{-1} in the ND_2 compound. In the compounds 1,4-diamino- and 1,5-diamino-anthraquinone where both carbonyl groups are equally involved in the acceptance of hydrogen bonds, the carbonyl absorption at 1673 cm^{-1} is not observed but that at approximately 1650 cm^{-1} (nujol) which has been assigned to hydrogen bonded carbonyl is still present.

7.3 NH_2 Deformation Vibrations:

It has been usual to consider that the adsorption which occurs about 1620 cm^{-1} in aromatic primary amines is due to the "scissor" deformation of the NH_2 group (Bellamy, 1960). Califano and Moccia (1957) and Evans (1960), who have studied aniline and some of its derivatives before and after deuteration, have pointed out that there appears to be a considerable interaction between this NH_2 deformation mode and the substituent-sensitive, aromatic vibration at 1280 cm^{-1} which involves stretching of the C-N bond. After deuteration, the two modes still interact so that absorptions, predominantly aromatic substituent-sensitive at approximately 1300 cm^{-1} and predominantly ND_2 deformation at 1150 cm^{-1}, are found.

The situation in the case of the ortho-carbonyl

derivatives of aniline is more complex. On deuteration almost all the aromatic vibrations in the region 1400–1610 cm^{-1} change in frequency and intensity. A difference spectrum, with the NH_2 compound in one beam and the ND_2 compound at the same concentration in the other beam, swings sharply from one side of the zero line to the other on going through most of the absorption bands in this region. There is no pure NH_2 deformation mode. In all cases two absorption bands, one above and one below 1600 cm^{-1}, disappear on complete deuteration (Figure 7.6), and a new sharper but weaker absorption appears between their former positions. This new absorption is probably the CH, in plane, deformation mode which normally occurs at about 1600 cm^{-1} but which has been interacting with the NH_2 deformation mode (Table 7.4).

Flett (1948) attributed the strong band at 1604 cm^{-1} to a vibrational mode of the hydrogen bonded carbonyl group in 1-amino-anthraquinone. Hambly and Donnyman (1958) attributed this absorption to the NH_2 scissor deformation. When this compound is deuterated the strong bands at 1604 cm^{-1} and 1545 cm^{-1} vanish and a strong, sharp band appears at 1597 cm^{-1}. This is contrary to the expectation for a carbonyl group. Confirmatory evidence for the interpretation of Hambly and Donnyman is derived from the similar behaviour of 1-amino,2-methyl-anthraquinone and 1-amino,5-chloro-anthraquinone on deuteration.

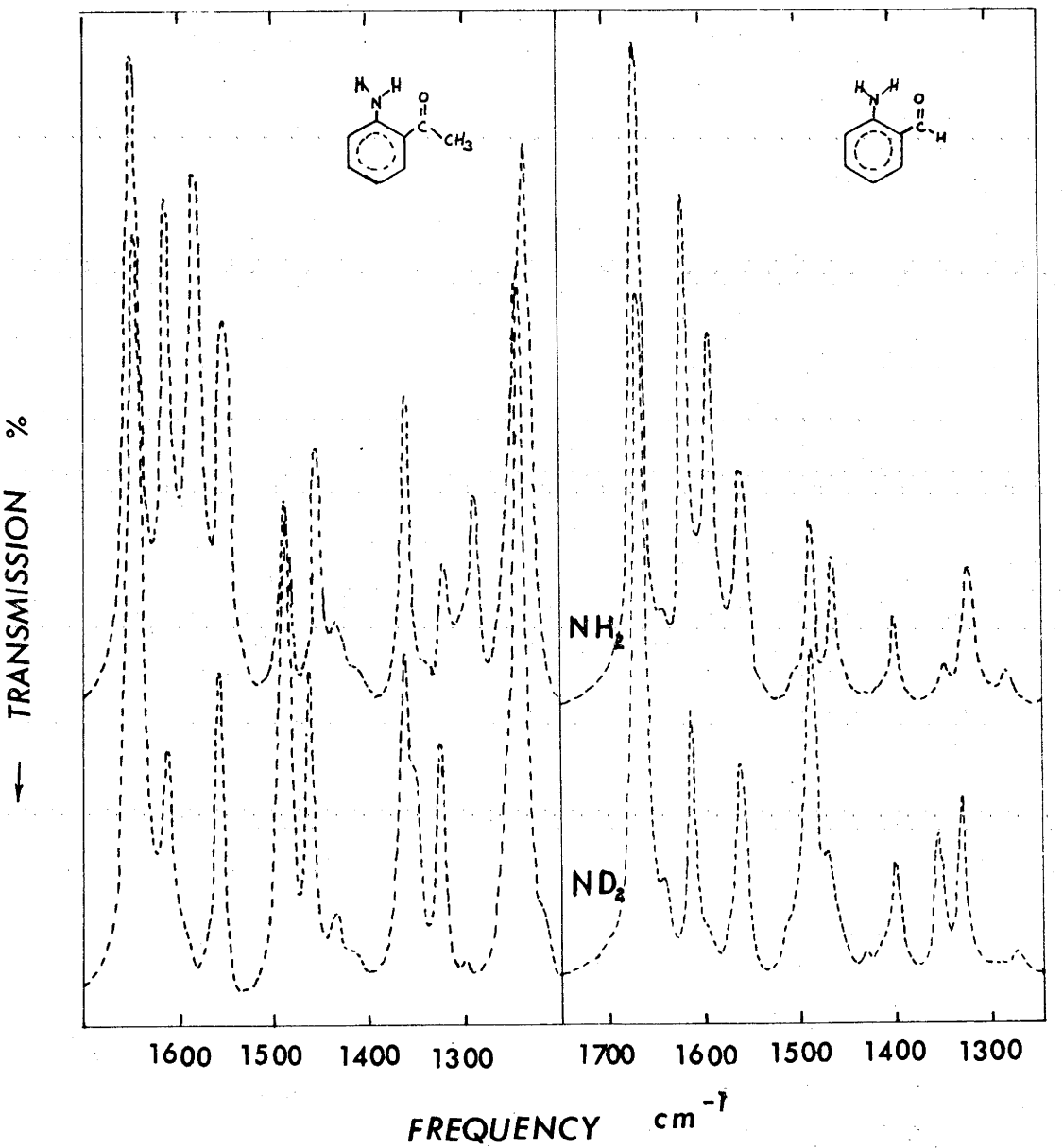


Fig. 7.6 - Spectra of carbonyl compounds in the 1700-1200 cm^{-1} region before and after deuteration.

TABLE 7.1

Fundamental NH_2 Stretching Frequencies of Anilines with an ortho-Carbonyl Group (cm^{-1})

Compound Number	Compound	$\nu_{as}NH_2$	$\nu_{s}NH_2$	Deviation from Equation 2.4
59	2-Amino-benzaldehyde	3506	3357	-56.9
60	2-Amino-acetophenone	3503	3346	-65.8
61	2-Amino-benzophenone	3502	3357	-54.1
62	Methyl Anthranilate	3507	3377	-37.6
63	Ethyl Anthranilate	3506	3378	-36.6
64	2,6-Dicarbomethoxy-aniline	3457	3346	-33.5
65	3-Carbomethoxy,2-naphthylamine	3501	3385	-25.4
66	1-Amino-anthraquinone	3502	3331	-80.1
67	1-Amino,2-methyl-anthraquinone	3506	3316	-97.9
68	1-Amino,5-chloro-anthraquinone	3502	3338	-73.1
69	1,4-Diamino-anthraquinone	3489	3295	-107.0
70	1,5-Diamino-anthraquinone	3500	3328	-81.7
71	Anthranilic Acid	3511	3385	-32.4

TABLE 7.2

Fundamental Stretching Frequencies of NH and ND Bonds in Deuterated and Partially Deuterated Anilines with an ortho-Carbonyl Group (cm^{-1})

Compound Number	Compound	ν_{NH}	ν_{ND}	$\nu_{as}ND_2$	$\nu_{s}ND_2$
59	2-Amino-benzaldehyde	(3463 (3389	(2568 (2509	2622	(2471 (2454 (2440
60	2-Amino-acetophenone	(3482 (3376	(2566 (2503	2620	(2468 (2450
61	2-Amino-benzophenone	(3477 (3384	(2563 (2510	2619	2451
62	Methyl Anthranilate	(3478 (3411	(2565 (2523	2624	(2463 (2452
64	2,6-Dicarbomethoxy-aniline	3405	2517	2603	2441
65	3-Carbomethoxy,2-naphthyl-amine	(3472 (3421	(2561 (2529	2621	(2478 (2467
66	1-Amino-anthraquinone	(3483 (3359	(2566 (2491	2619	2446
67	1-Amino,2-methyl-anthraquinone	(3495 (3334	(2579 (2474	2620	2438
68	1-Amino,5-chloro-anthraquinone	(3481 (3360	(2566 (2496	2619	2447
69	1,4-Diamino-anthraquinone	(3480 (3318	-	-	-
70	1,5-Diamino-anthraquinone	(3482 (3353	-	-	-
71	Anthranilic Acid	(3478 (3423	-	-	-

TABLE 7.3

Overtone NH_2 Stretching Frequencies of Anilines with an ortho-Carbonyl Group (cm^{-1})

Compound Number	Compound	$\nu_{as}(0-2)$	$\nu_{s}(0-2)$
59	2-Amino-benzaldehyde	6929	(6764 (6532
60	2-Amino-acetophenone	6924	(6755 (6498
61	2-Amino-benzophenone	6921	(6752 (6568
62	Methyl Anthranilate	6940	(6760 (6612
63	Ethyl Anthranilate	6928	(6758 (6598
64	2,6-Dicarbomethoxy-aniline	6862	(6615 sh. (6563
65	3-Carbomethoxy,2-naphthylamine	6941	(6760 (6624
67	1-Amino,2-methyl-anthraquinone	6918	6762 ?

sh. denotes shoulder

TABLE 7.4

Effects of Deuteration on Carbonyl, NH_2 Deformation, and Associated Vibration Bands (cm^{-1})

Vibration	1-amino-anthraquinone		1-amino-2-methyl-anthraquinone		1-amino-5-chloro-anthraquinone	
	NH_2	ND_2	NH_2	ND_2	NH_2	ND_2
C=O, free	1673	1673	1671	1671	(1686 sh. (1677	(1687 sh. (1677
C=O, H-bonded	1644	1641	(1641 (1633 sh.	(1638 (1632 sh.	1642	1640
" δNH_2"	1603	-	1604	-	1607	-
	1594	1597	1598	1597	-	1597
	1582	1582	1580	1580	(1581 (1567 sh.	1580
				1563		1556
	1544	-	1553	-	1547	-
				1485		1486

Vibration	2-amino-benzaldehyde		2-amino-acetophenone		2-amino-benzophenone	
	NH_2	ND_2	NH_2	ND_2	NH_2	ND_2
C=O	1674	1671	1653	1650	1638	1634
" δNH_2 "	1619	-	1616	-	1617	-
		1615		1612		1610
	1592		(1580 (1578 sh.		1601	1601
	1557	1560	1552	1555	1550	

sh. denotes shoulder

TABLE 7.4 cont'd

Vibration	Methyl anthranilate		Methyl 4-amino-benzoate	
	NH_2	ND_2	NH_2	ND_2
C=O	1699	1696	1719	1719
" δNH_2"	1617	-	1620	-
	1589	1612	1605	1610
		1578	1580	
	1560	1567		
		1503	1518	1519

8 - NITRO-ANILINES AND NITRO-NAPHTHYLAMINES

8.1 Introduction:

The existence of a strong intramolecular hydrogen bond in ortho-nitro-phenol is well known and its presence has been confirmed by a number of physical and chemical tests. It had been assumed that as ortho-nitro-aniline shows similar behaviour in its simple physical properties, viz. steam volatility, solubility in non-polar solvents, depression of "wet" m.p., in comparison to its para isomer, it would by analogy also possess a strong intramolecular hydrogen bond. However this is not the situation and numerous attempts have been made to determine the existence of an intramolecular bond in ortho-nitro-aniline. Lutskii and Kondratenko (1959) and Richards and Walker (1961), from the dipole moments on the nitroanilines in benzene and dioxane, concluded that the results could be explained by postulating an intramolecular hydrogen bond in ortho-nitro-aniline. Dyall and Hambly (1958) interpret the fundamental infra-red NH stretching frequencies as indicating the existence of a hydrogen bond in the 2,6-dinitro- and 2,4,6-trinitro-aniline but that in ortho-nitro-aniline no hydrogen bond of significant strength exists. From a study of the nitro group frequencies Urbanski and Dabrowska (1958) reached a similar conclusion. Whetsel, Roberson and Krell (1958), however, in an investigation of the first overtone NH_2 stretching frequencies conclude that

there is strong intramolecular bonding. Moritz (1960), from the existence of *cis* and *trans* isomers of the NHD group, also demonstrated the presence of an intramolecular hydrogen bond in *ortho*-nitro-aniline.

8.2 NH_2 Stretching Frequencies:

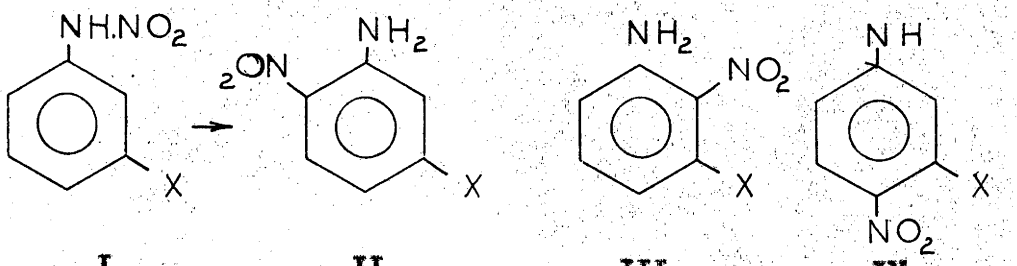
The fundamental NH_2 stretching frequencies of fifteen substituted *ortho*-nitro-anilines and two nitro-naphthylamines are recorded in Table 8.1, together with their deviations from the modified Bellamy and Williams equation. Also included are two 3-substituted and two 6-substituted *ortho*-nitro-anilines from the work of Dyall and Hambly (1958). The spectra of these four compounds were recorded as dilute solutions in tetrachloroethylene.

The deviation of ν_s from the predicted value for the compounds listed (with the exception of the nitro-naphthylamines and the 3-substituted nitro-anilines) lie in the range 26.9 ± 6.7 cm^{-1}. Substitution in the 6-position increases the deviation to above that in *ortho*-nitro-aniline as does the presence of electron-withdrawing substituents in the 4-position. In 6-methyl-2-nitro-aniline the increase is probably brought about by a direct steric interaction between the methyl and the amino group, forcing the latter closer to the nitro group, giving the so-called "steric facilitation of the hydrogen bond". The effect of di-*ortho*-nitro-substitution would be to bring the

amino group even more into co-planarity with the benzene ring and increasing the interaction between the nitro group and the hydrogens of the amino group. This is in accord with the results of Dyall and Hambly (1958) and Dyall (1961) that 2,6-dinitro-anilines form stronger intramolecular hydrogen bonds than does ortho-nitro-aniline.

The effect of an additional substituent in the 3-position of a 2-nitro-aniline is to weaken the hydrogen bond markedly. This must be related to a rotation of the nitro group out of the plane of the benzene ring, which reduces its conjugation with the aromatic nucleus and makes it a poorer acceptor of the hydrogen bond. As a direct result of this lowering of conjugation, the C_{ar}–N bond to the amino group will lose some of its sp^2 character and tend to that found in aniline, with a resultant lowering of the stretching frequency of the NH_2 vibrations and an increase in the hydrogen bonding distance. The overall effect therefore will be to weaken the hydrogen bond.

Hunter (1954) reports indications of a similar effect in the products of the rearrangement of meta-substituted phenylnitramines I. Chromatographic separation of the products gives an order of adsorption on the column of IV > III > II



I II III IV

X = NO , F, Cl, Br, I

It had been established by Moyer (1950) that among isomeric compounds, the isomer which is capable of a chelate hydrogen bond structure is the most weakly adsorbed on a chromatogram. He infers that the formation of hydrogen bonds between adsorbent and adsorbate is a major cause of chemisorption, and that intramolecular satisfaction of these bonds will give a resultant weakening of forces retaining the compound in the column. The above order can therefore be interpreted as meaning that II and IV are chelated and non-chelated respectively whereas III occupies an intermediate position, resulting from interference between the nitro group and the group in the 8-position. However evidence of this nature is suspect as the extent of adsorption is also concerned with the base dissociation constant. In later work, Moyer (1953) found the order of increasing adsorption for a series of nitro-naphthylamines to be: 8-nitro,1-naphthylamine < 5-nitro,1-naphthylamine < 2-nitro,1-naphthylamine = 1-nitro,2-naphthyl-amine < 4-nitro,1-naphthylamine. This result cannot be interpreted in terms of intramolecular hydrogen bonding.

Dyall and Hambly (1958) found that 2,3-dinitro-aniline exhibits a doubling of both $\nu_s NO_2$ and $\nu_{as} NO_2$, the latter frequencies being similar to that obtained for ortho-dinitrobenzene and ortho-nitro-aniline. This would indicate that it is the NO_2 group in the 3-position which is being rotated out of the plane of the ring and that in this compound

the strength of the hydrogen bond would be only slightly less than that in ortho-nitro-aniline.

Most of thecompounds in Table 8.1 were subjected to deuteration and the results for the NH.D, ND.H and ND_2 stretching frequencies are shown in Table 8.2. Figure 8.1 shows the plot of the deviation from equation 2.4 versus the separation of the NH.D frequencies, and indicates that there is a rough correlation between the relative strengths of the hydrogen bonds predicted by both methods. However in only one ortho-nitro-aniline does the separation of the NHD frequencies approach that found in the carbonyl compounds. 6-Methyl-2-nitro-aniline has a separation of 57 cm^{-1} compared to 65 cm^{-1} for ethyl anthranilate and 51 cm^{-1} for 3-carbomethoxy, 2-napthylamine.

The appearance of multiple absorption for the NH_2 stretching frequencies of 2-nitro,4-amino-aniline and 2-nitro, 5-amino-aniline requires some explanation. The fundamental stretching frequencies of the phenylene-diamines in carbon tetrachloride solution appear as two sharp bands in the infra-red spectra. These lie at ca 3440 and 3350 cm^{-1} and are lowest of the aromatic NH_2 frequencies recorded. This would indicate that the two groups are not coupled and behave as independent vibrators. It would be expected that the amine groups in 2-nitro,4-amino-aniline (V) and 2-nitro,5-amino-

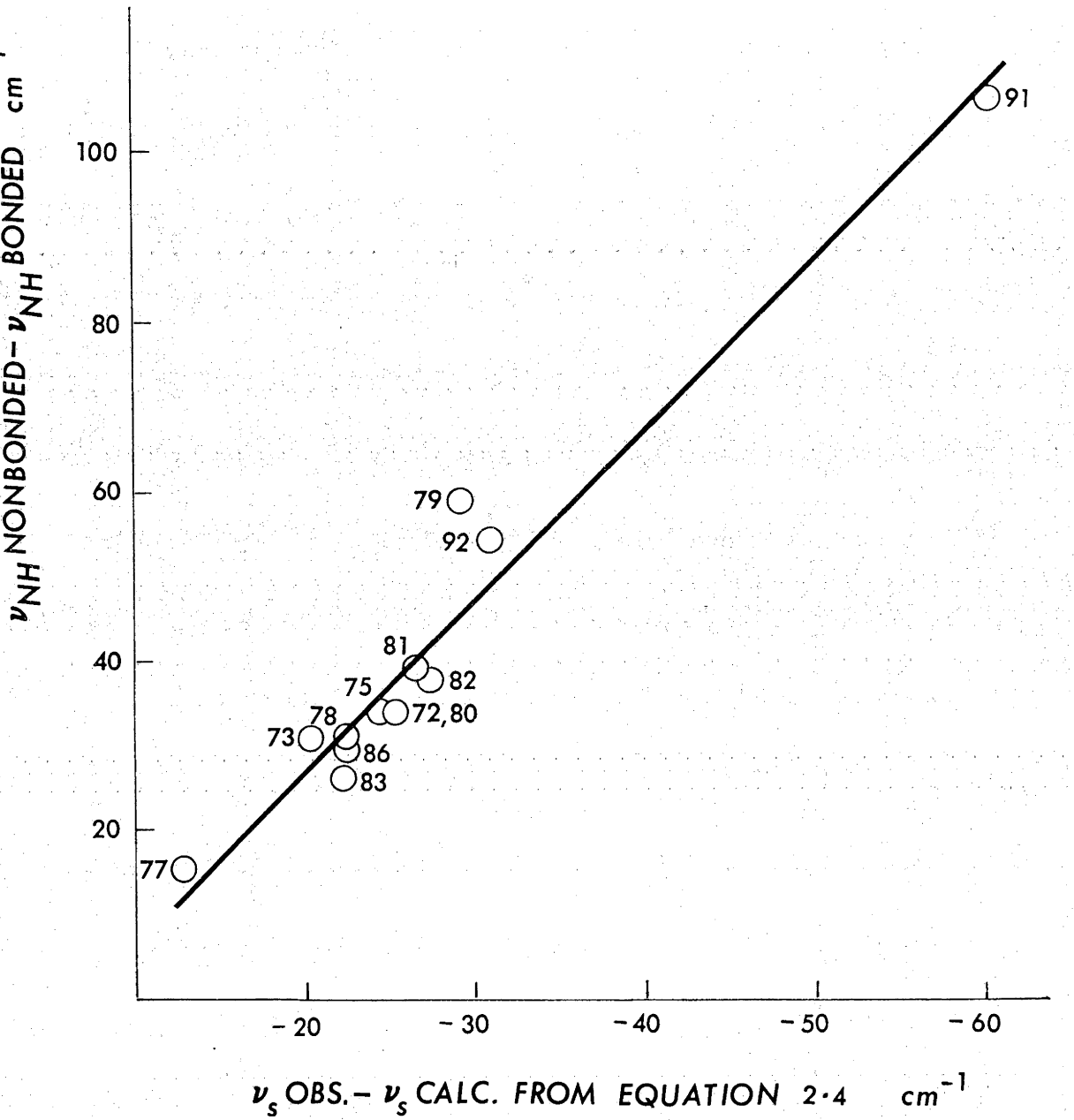
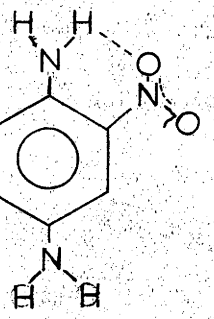
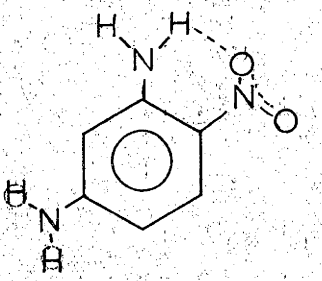


Fig. 8.1 - Correlation between separation of NH stretching frequencies for monodeuterated nitroanilines and the departure from the predictions of equation 2.4.

aniline (VI) would exhibit separate pairs of absorptions corresponding to the different environments of the amine groups in the molecule.



V



VI

However, the spectra observed (Figure 8.2) showed three absorptions. In (V) the antisymmetric stretching frequency was doubled, with the high frequency absorption of much greater intensity than the lower frequency band and in (VI) the symmetric band was doubled, both absorptions being of equal intensity. In 2-nitro,4-amino-aniline, the NH_2 groups should have frequencies similar to 2-nitro-aniline and 3-nitro-aniline respectively but modified by interaction with the para-amino-group. The 1-amino group, because of its conjugation to the nitro group becomes a weaker donor of electrons and a better acceptor so that there will be a net electron transfer from the 4-amino group to the 1-amino group. The 1-amino group will become less planar and lose some of its conjugation with the ortho-nitro group and thus weaken the hydrogen bond. The lowering of its conjugation with the nitro

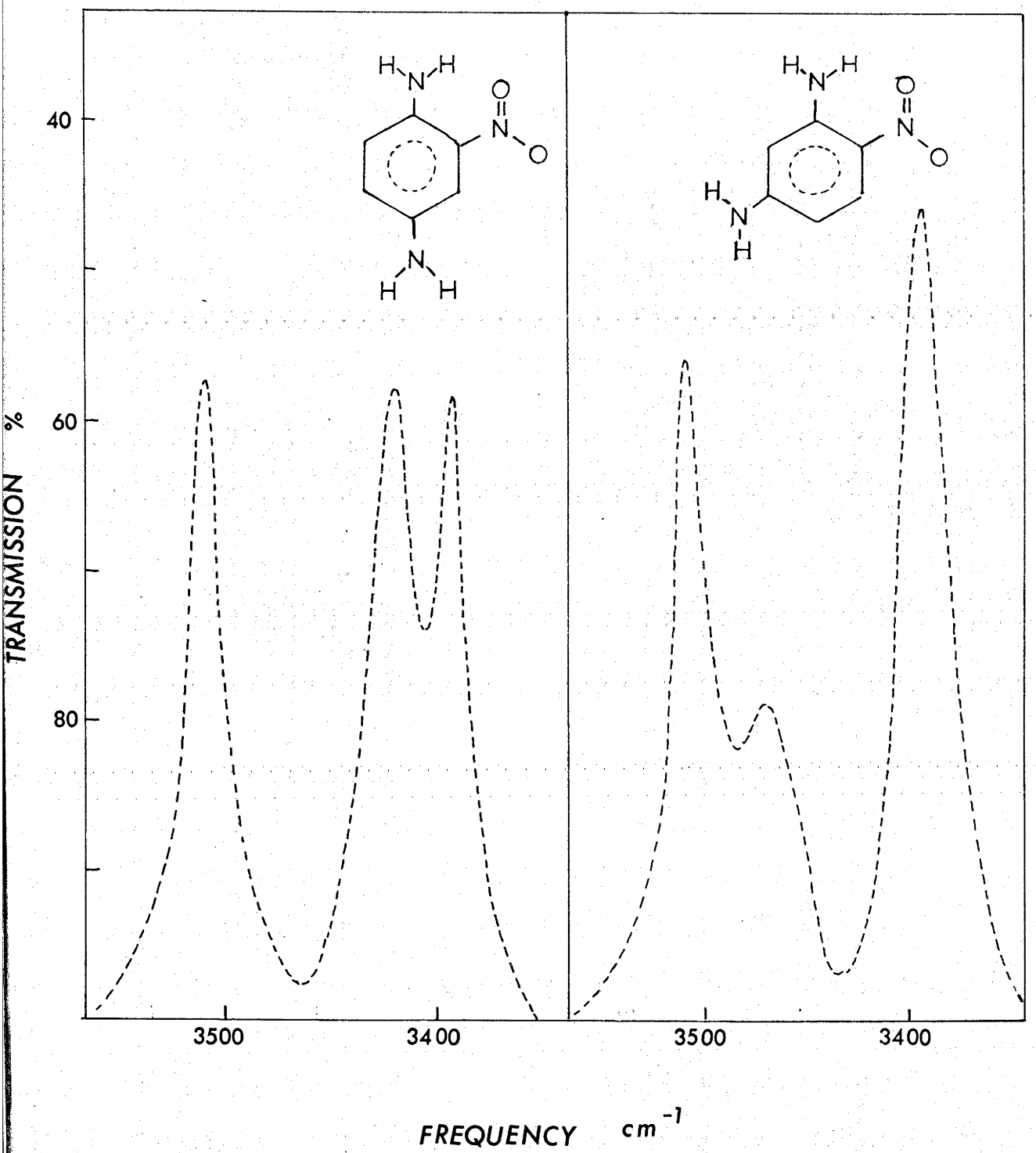
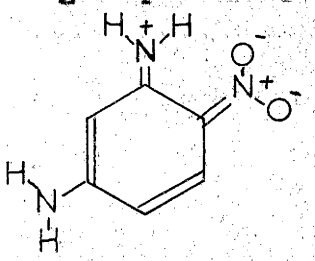


Fig. 8.2. - NH stretching frequencies of 2-nitro-phenylenediamines

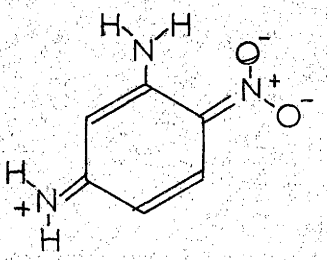
group and the increase in electron density on its nitrogen atom will weaken both the force constants of the free and bonded NH links of the 1-amino group. The decrease in hydrogen bonding will increase the force constant in the bonded N-H link so that the difference in force constants between the two N-H links will be less than in ortho-nitro-aniline. The decrease in frequencies from those in ortho-nitro-aniline will be larger for the antisymmetric than for the symmetric frequency. The electron attracting inductive effect of the nitro group on the 4-amino group will be lessened by the former group's conjugation and hydrogen bond formation with the 1-amino group. This will lower the frequencies to below that in meta-nitro-aniline. If the frequency of the lower member of ν_{as} is substituted in equation 2.4, a "hypothetical" value of 3390 cm^{-1} is obtained for ν_s for the 4-amino group. This is only 6 cm^{-1} lower than the single absorption observed for ν_s in 2-nitro,4-amino-aniline. As it is expected that the intensity of this absorption will be much less than that arising from ν_s for the 1-amino group, then it is probable that it cannot be resolved from ν_s for the amino group at position 1. For partially deuterated 2-nitro,4-amino-aniline there are three NH absorptions. The two at higher frequencies can be associated with the NHD group at position 1. They are of equal intensity and are separated by 26 cm^{-1} compared to 34 cm^{-1} for ortho-nitro-aniline, indicating that the idea of a weaker hydrogen bond between the 1-NH_2 and 2-NO_2 group than in

ortho-nitro-aniline is probably correct. The third absorption is much weaker than the other two and can be related to the NH stretching frequency of the NH_2 group at position 4.

The NH_2 stretching frequencies in 2-nitro,5-amino-aniline should be similar to those in ortho-nitro-aniline and para-nitro-aniline but altered by the effect of the meta-amino group. The nitro-group can conjugate with either amino substituent (VII and VIII) with the resonance form VIII being the more favoured because of increased stability due to increased positive charge separation.



VII



VIII

The decrease in conjugation of type VII will make the 1-amino group a poorer donor for a hydrogen bond compared to the amino group in ortho-nitro-aniline. However this will be offset by the increase in basicity of the oxygen atom on the nitro group by conjugation of type VIII. The overall effect will be an increase in hydrogen bond strength and a corresponding decrease in the NH_2 stretching frequencies. The amino group in the 5-position will be dominated by the effect of the nitro group in the 2-position and will have NH_2 stretching frequencies very

close to those observed for para-nitro-aniline. The separation between the $\nu_{as}NH_2$ for the two amine groups will be very small and the low intensity of ν_{as} for the amine in the 5-position would make it difficult for it to be resolved from ν_{as} for the amine group in the 1-position.

It should be emphasised that these effects are small and depend on a delicate balance between the inductive and mesomeric effects of the groups concerned.

Bryson and Werner (1960), from a study of the NH_2 stretching frequencies of fourteen isomeric mononitro-naphthylamines in carbon tetrachloride and pyridine deduced the presence of hydrogen bonding in 2-nitro,1-naphthylamine, 1-nitro,2-naphthylamine, 3-nitro,2-naphthylamine and 8-nitro,1-naphthylamine. The method used was that originally applied by Short (1952) to detect chelation in amino-quinolines and amino-acridines. In changing the solvent from carbon tetrachloride to pyridine, the NH_2 frequencies are lowered. However if one hydrogen is already involved in chelation, there would be less alteration of the frequency than when both amino hydrogens are free to form bonds. Bryson and Werner found that the decrease in frequency was uniform for all the compounds studied, except for those mentioned where the nitro and amino groups are adjacent. In these cases the decrease was about half that observed in other cases.

The results obtained in the present work confirm the presence of hydrogen bonding in 2-nitro,1-naphthylamine and 1-nitro,2-naphthylamine, with the former compound possessing the stronger bond. 2-Nitro,1-naphthylamine gives a deviation from equation 2.4 and a separation of the NH.D frequencies in the mono-deuterated compounds of over twice that found for 1-nitro,2-naphthylamine. It would appear that the steric effect of the peri hydrogen atom is considerable when it is acting as a "buttressing" group. The apparent large increase in hydrogen bond strength when there is either a peri hydrogen or a methyl group adjacent to the amino group on one side, and a nitro group on the other, may in part be more of the effect of increased difference in the environment of the two protons. The repulsion exerted by the peri hydrogen atom or 8-methyl group would tend to raise the frequency of the "free" N-H vibration, and thereby give an increase in the separation of cis and trans N-H stretching frequencies for the NH.D group. It would also have the effect of increasing the departure of the frequencies from equation 2.4.

The nitro-anilines, because of low solubility, are difficult to examine in the first overtone region. The results for the five compounds studied are given in Table 8.3.

The absorption outlines are of a type indicating medium to strong hydrogen bonding (Figures 8.3 c.f. figure 7.3), with the separation of the two members of $\nu_s(0\text{-}2)$ increasing

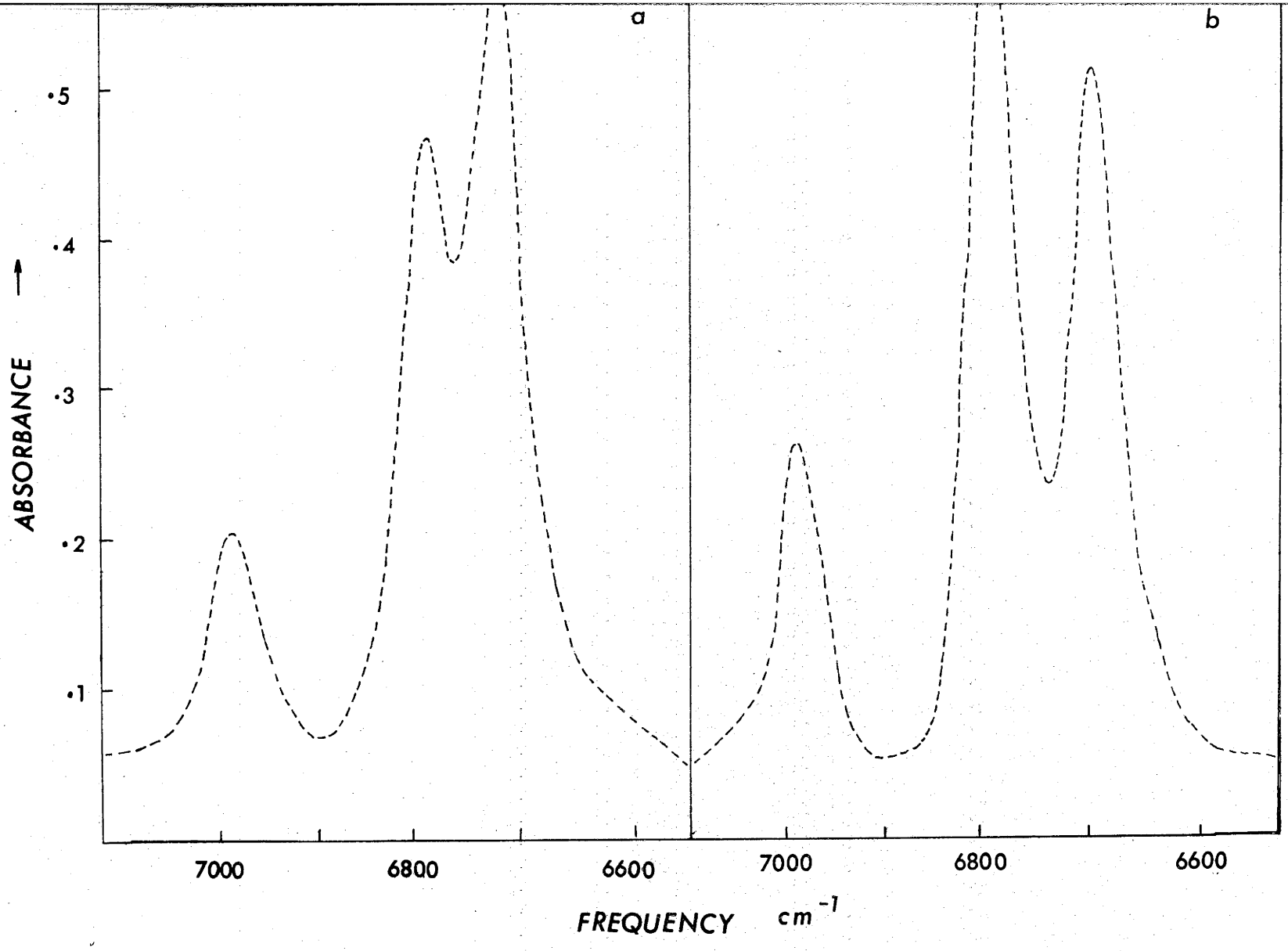


Fig. 8.3 - First overtone absorption bands for 2-nitro-anilines.
a, 3-methyl, 2-nitro-aniline; b, 2-nitro-aniline;

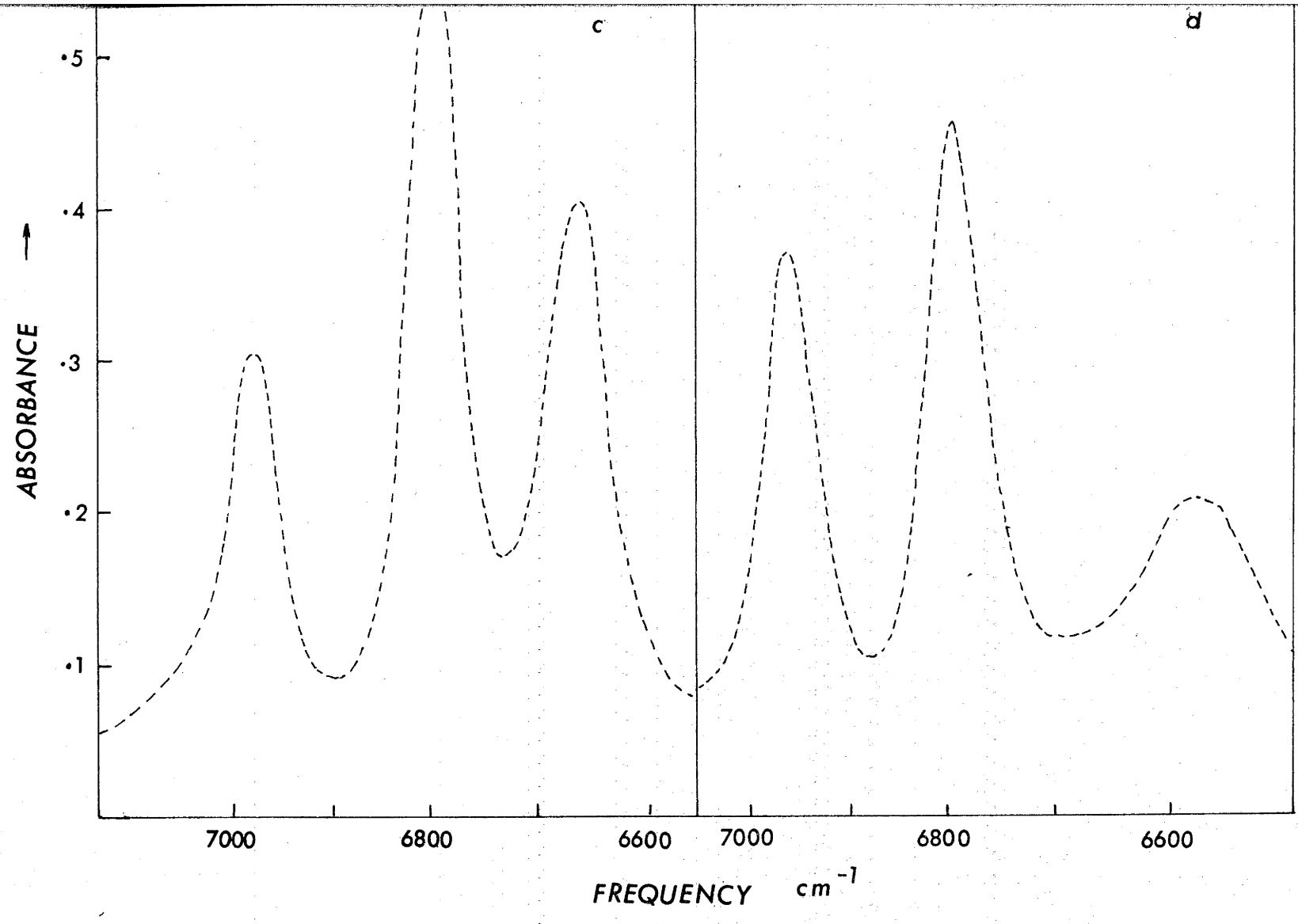


Fig. 8.3 - First overtone absorption bands for 2-nitro-anilines.

c, 6-methyl, 2-nitro-aniline; d, 2-nitro, 1-naphthylamine.

with increasing strength of the hydrogen bond.

8.3 NH_2 Deformation Frequencies:

The effect of hydrogen bonding on the NH_2 deformation frequency should be to raise it above its normal value of approximately 1620 cm^{-1} (Califano and Moccia, 1957). Dyall and Hambly (1958) have assigned a strong band at 1624 cm^{-1} in ortho-nitro-aniline to this mode and point out that with 2,6-dinitro-aniline the frequency and the intensity of this absorption are increased as would be expected with increased hydrogen bonding in this compound. Dyall (1961) found that although the NH_2 deformation mode at 1624 cm^{-1} in 4-nitro-aniline showed a frequency increase of 17 cm^{-1} when the solvent was changed from chloroform to pyridine, the corresponding band in 2-nitro-aniline was only slightly altered with a similar solvent change.

In view of the results obtained with the carbonyl compounds in this region, in which it was not possible to assign a single frequency to the deformation mode, ortho-nitro-aniline, 2,6-dinitro-aniline and 3-methyl,2-nitro-aniline and their N.N. di-deuterated derivatives were recorded in the region 1700 cm^{-1} - 1400 cm^{-1}. The results are given in Table 8.4.

The spectra in this region are confusing. Deuteration causes only minor changes in spectrum in all cases and there are no obvious frequency shifts observed (Figure 8.4).

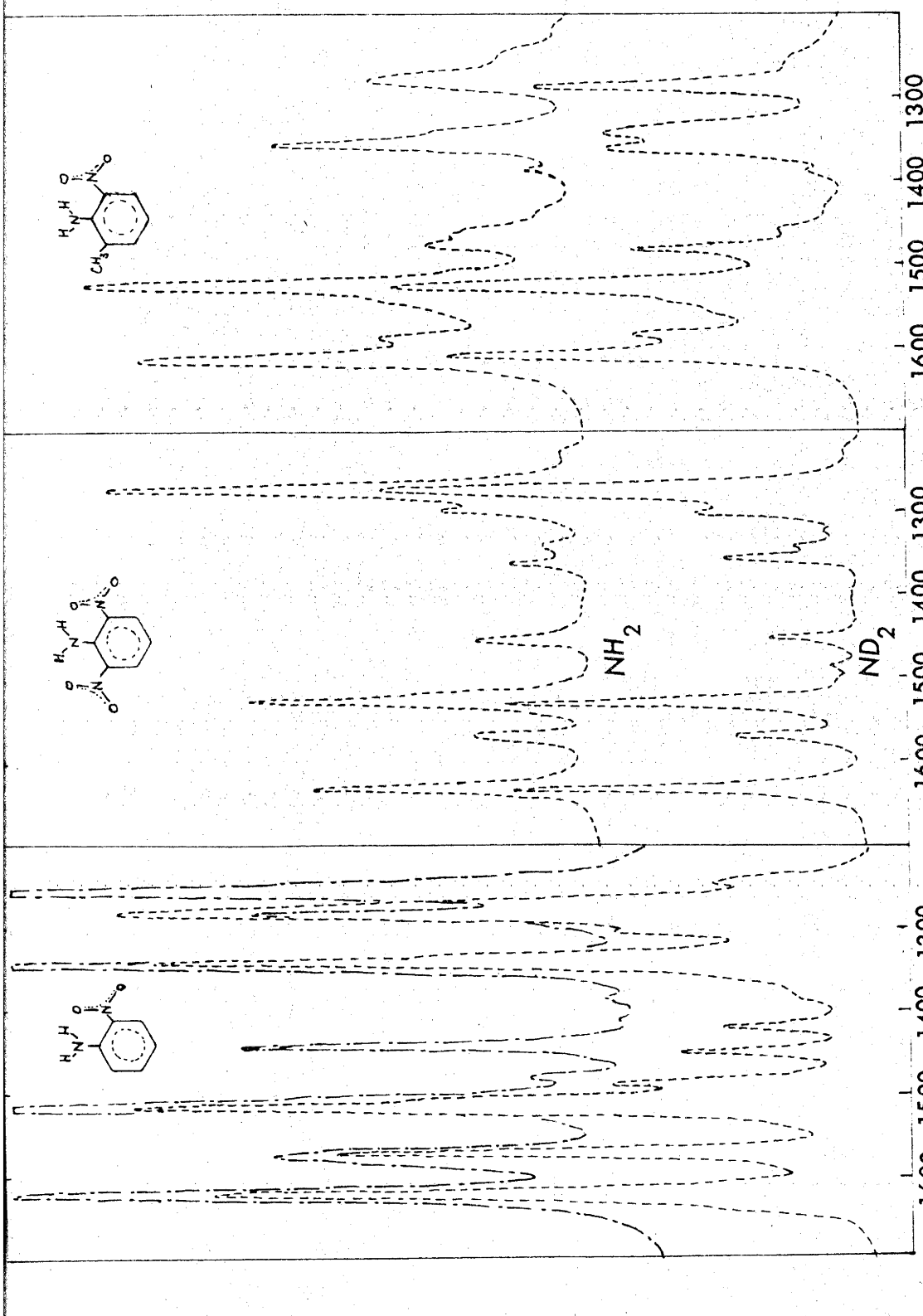


Fig. 8.4 - Spectra of 2-nitro-anilines in the 1700-1200 cm^{-1} region before and after deuteration.

The band at approximately 1620 cm^{-1}, which had been assigned to the NH_2 deformation mode (Dyall and Hambly), is affected only slightly in both position and intensity and therefore cannot result from an NH_2 vibration and is probably due to an aromatic in plane deformation mode. It is probable that in the ortho-nitro-anilines, the NH_2 group becomes strongly coupled to the NO_2 vibration. In the case of 2,6-dinitro-aniline, the effect of the two NO_2 groups bonding to the amino hydrogens could conceivably impose their antisymmetric stretching frequency upon the "scissor" motion of the NH_2. This would imply that the oxygens bonded to the hydrogens were vibrating "in phase". The overall effect would be to cause the NH_2 deformation vibration to occur at or about the same frequency as the NO_2 antisymmetric stretching vibration. The effect of deuteration on this absorption is in fact to remove a low frequency shoulder at 1513 cm^{-1}, which gives some support to this argument.

In the mono-nitro-anilines the hydrogen bond would in effect uncouple the NH_2 deformation vibration so that we will have two NH deformation modes, one resulting from the "free" N-H and one from the bonded NH. As is the case with secondary amines both of these absorptions would be expected to be weak. In ortho-nitro-aniline, a weak shoulder at 1583 cm^{-1} is removed by deuteration as is a weak broad absorption at approximately

1500 cm^{-1} in 3-methyl,2-nitro-aniline. It is possible that these are due to the NH deformation mode.

The assignment of any absorption as being due to an NH_2 "scissor" vibration in compounds possessing a moderately strong hydrogen bond appears to be of dubious validity. In the para and meta compounds, and in those compound in which the hydrogen bond is weak there is no coupling between this motion and the vibrations of the other substituent, and the deformation vibration occurs at its normal frequency, ca. 1610 cm^{-1}. However when moderate to strong intramolecular hydrogen bonds are present in the molecule, coupling undoubtedly occurs between the "scissor" motion and the aromatic ring vibrations and/or the stretching vibrations of the ortho substituent group which, in general, occur in this region. This has the effect of causing large shifts in the NH_2 deformation frequency and also changing the aromatic ring deformation vibrations in the same region.

TABLE 8.1

NH_2 Stretching Frequencies of 2-Nitro-Anilines (cm^{-1})

Compound Number	Substituents	ν_{as}	ν_s	Departure From Equation 2.4.
72	2-NO_2	3522	3400	-25.2
73	2,3-di-NO_2	3518	3402	-20.4
74	2,4-di-NO_2	3519	3394	-29.0
75	2,5-di-NO_2	3520	3399	-24.8
76	2,6-di-NO_2	3473	3364	-30.2
77	2-NO_2,3-CH_3	3510	3402	-12.7
78	2-NO_2,4-CH_3	3521	3402	-22.5
79	2-NO_2,6-CH_3	3522	3396	-29.2
80	2-NO_2,4-Cl	3522	3400	-25.2
81	2-NO_2,5-Cl	3517	3395	-26.7
82	2-NO_2,4-CF_3	3523	3398	-27.9
83	2-NO_2,4-NH_2	(3512 (3472	3396	(-22.1 (+6.0
84	2-NO_2,5-NH_2	3515	(3417 (3388	(-3.0 (-32.0
85	2,4,6-tri-NO_2	3460	3348	-33.6
86	2-NO_2,4-OCH_3	3515	3398	-22.2
87	2-NO_2,3-OCH_3*	3507	3402	-12.6
88	2-NO_2,3-Cl*	3505	3403	-10.2
89	2-NO_2,6-OCH_3*	3523	3399	-26.9
90	2-NO_2,6-Cl*	3508	3392	-23.3
91	2-NO_2,1-naphthylamine	3521	3364	-60.5
92	1-NO_2,2-naphthylamine	3516	3388	-31.0

* Dyall and Hambly (1958) dilute solution in C_2Cl_4.

TABLE 8.2

Fundamental ND_2, NH.D and ND.H Stretching Frequencies of Deuterated and Partially Deuterated ortho-Nitro-Anilines

Compound Number	Substituents	$\nu_{as}ND_2$	$\nu_{s}ND_2$	NDH	NHD
72	2-NO_2	(2639 (2628 sh.	(2490 (2473	(2565 (2549	(3481 (3447
73	2,3-di-NO_2	2634	2484	(2566 (2548	(3478 (3447
74	2,4-di-NO_2	2639	(2494 sh. (2469 sh.	(2570 (2543	
75	2,5-di-NO_2	2637	2480	(2567 (2547	(3480 (3448
76	2,6-di-NO_2	(2619 (2609 sh.	2465	2536	3427
77	2-NO_2,3-CH_3	2629	(2516 (2481	(2559 (2554	(3467 (3452
78	2-NO_2,4-CH_3	2634	2467	(2562 (2549	(3478 (3447
79	2-NO_2,6-CH_3	(2646 sh. (2633	2469	(2574 (2540	(3493 (3434
80	2-NO_2,4-Cl	(2640 (2631 sh.	(2497 sh. (2487 (2460 sh.	(2567 (2547	(3483 (3449
81	2-NO_2,5-Cl	(2641 (2628 sh.	(2486 (2473 sh.	(2565 (2543	(3480 (3441
82	2-NO_2,4-CF_3	2638	(2495 sh. (2480 (2468 sh.	(2567 (2547	(3484 (3446

cont'd.

sh. denotes shoulder

TABLE 8.2 cont'd

Compound Number	Substituents	$\nu_{as}ND_2$	$\nu_{s}ND_2$	NDH	NHD
83	2-NO_2,4-NH_2	(2639 sh. (2631 (2594 sh.	(2486 (2450	(2558 (2546 (2534 sh.	(3470 (3444 (3427 sh.
85	2,4,6-tri-NO_2	2603	(2459 (2443	2525	3407
86	2-NO_2,4-CCH_3	2633	(2488 (2476 sh.	(2560 (2547	(3474 (3444
91	2-NO_2,1-naphthylamine	2635	(2488 (2472	(2584 (2518	(3500 (3394
92	1-NO_2,2-naphthylamine	2630	(2482 (2462	(2566 (2534	(3481 (3434

sh. denotes shoulder

TABLE 8.3

First Overtones of Stretching Vibrations of NH_2 Groups in ortho-Nitro-Anilines (cm^{-1})

Compound Number	Substituents	ν_{as}(0-2)	ν_{as}(0-2)	
72	2-NO_2	6986	6791	6691
77	2-NO_2,3-CH_3	6978	6784	6729
79	2-NO_2,6-CH_3	6978	6802	6662
91	2-NO_2,1-naphthylamine	6963	6802	6570
92	1-NO_2,2-naphthylamine	6964	6773	6697

TABLE 8.4.

Effect of Deuteration on Absorption Bands of 2-Nitro-Anilines between 1700 and 1250 cm^{-1}

2-Nitro-Aniline		2,6-Di-Nitro-Aniline		2-Nitro,3-Methy-Aniline	
NH_2	ND_2	NH_2	ND_2	NH_2	ND_2
1624	1622	1635	1633	1611	1608
1583 sh.	-	1614 sh.	1614 sh.	1585 w	1580 w
1575	1570	1566	1564	1541 sh.	1541 sh.
1515	1516	1523	1523	1520	1520
1503 sh.	1500 sh.	1512 sh.	1512 sh.	1500	-
1480 w	1480 w	1455	-	1476	1480
1445	1453	1450	1452	-	-
-	1423	-	-	1383 w	-
1344	1345	1358 w	1350	1358	1360
-	1305 sh.	1337 w	1338 w	1340 sh.	1340
1288	1285	1300 w	1298	-	-
1260	1270 sh.	1276	1270	1278	1278
-	1250 w	-	-	1250 sh.	1250 sh.

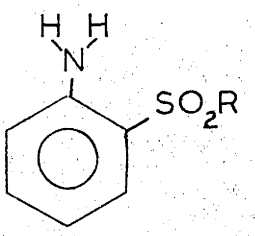
sh. denotes shoulder
w. weak

O - AMINO SULPHONES AND SULPHIDES

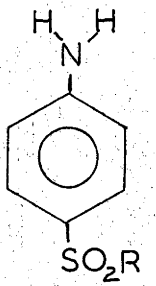
In ortho-nitro-aniline it is believed that the two groups are held approximately coplanar with the benzene ring, by conjugation with the benzene ring and each other, and are therefore in a position favourable to hydrogen bonding. The sulphone group has a different geometry from the nitro group and in addition it has been claimed (Koch and Moffitt, 1951; Freeman and Hambly, 1957) that the sulphone group does not show appreciable conjugation with the benzene ring when the molecule is in its electronic ground state, but conjugation frequently occurs in excited states. There is, however, evidence of conjugation in the ground state of diphenyl sulphones and other molecules in which two unsaturated centres are attached to the SO_2 group (Koch and Moffitt, 1951; Sime and Abrahams, 1960). The electron-attracting inductive effect of the sulphonyl group is very powerful and there is ample evidence of changes in the bond order of the S=O linkages when the sulphone group is attached to electron yielding groups. A reduction in bond order will transfer negative charge to the oxygen atom and make it a better acceptor of a hydrogen bond.

The deviation for an ortho-sulphonyl group from equation 2.4 is of the same order as an ortho-nitro group. The four compounds with formula I (R = $-CH_3$, $-C_2H_5$, -iso-C_3H_7,

$-C_6H_5$)



I



II

show deviations of -23 ± 4 cm^{-1}, whereas the two para-compounds of formula II (R = $-CH_3$, $-C_6H_5$) conform to the relationship.

Partial deuteration of 2-methylsulphonyl- and 2-phenylsulphonyl-aniline gave further evidence of interaction between the amino group and the oxygen in the ortho-sulphones. The separation of the bonded and non-bonded NH frequencies (ca. 49 cm^{-1}) would indicate a hydrogen bond strength intermediate to that found in ortho-nitro-aniline and methyl anthranilate.

The spectra in the 1st overtone region confirm the observations of Wheteel et al. (1958).

The finding that the hydrogen bond from the amino group to the sulphone group is stronger than to the nitro group contrasts with the behaviour of phenols where the 2-nitro-phenols show considerably lower OH stretching frequencies than those found for 2-sulphonyl-phenols (Table 9.2).

Hambly (1961) has pointed out that the absence of an intermolecular hydrogen bond in hydrogen sulphide, which would require sulphur to act both as a donor and acceptor, has led to the misconception that sulphur does not take part in the formation of hydrogen bonds. There is, however, considerable evidence to the contrary. Hopkins and Hunter (1942) have shown that when the sulphur atom is in a thio-carbonyl group, it can readily act as an acceptor for a hydrogen bond. Recently Schleyer and West (1959) found that phenol and methanol formed intermolecular hydrogen bonds to di-n-butyl-sulphide. Despite the larger covalent radii of the sulphur atom, this bond was of comparable strength to that formed to di-n-butyl-ether.

Whetsel et al. (1958) have noted a splitting of the $\nu_s(C-2)NH_2$ stretching frequency in 2-amino-phenyl-methyl-sulphide and have attributed this to hydrogen bond formation. The present work has confirmed this result (Table 9.2)

Four 2-amino-sulphides and two 4-amino-sulphides have been recorded in the region of the fundamental NH_2 stretching vibration and the frequencies are recorded in Table 9.1. The 2-amino-sulphides were partially deuterated and their NH stretching frequencies measured.

In common with other para-substituted anilines, the 4-amino-sulphides conformed to equation 2.4. However the

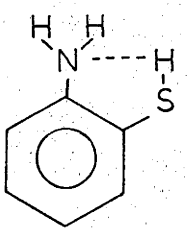
2-amino-sulphides showed negative departures from this relationship, indicating that there was a hydrogen bond of similar strength to that in ortho-nitro-aniline. The existence of a hydrogen bond was confirmed by the presence of two N-H absorptions in the partially deuterated compounds. The absence of a similar interaction in the 2-alkoxy-aniline is probably related to the smaller size of the oxygen atom which keeps its lone pair orbitals further from the hydrogen atoms of the amino group.

The evidence for a moderately strong hydrogen bond in the 2-amino-sulphides is not necessarily a measure of the intrinsic power of a divalent sulphur atom to accept a hydrogen bond, but rather an adjustment of the system to a condition of minimal energy when a lone pair orbital of the sulphur atom is held firmly in the neighbourhood of the amino group.

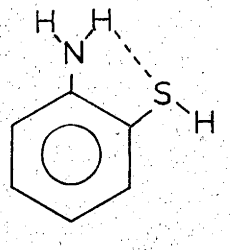
The results obtained for 2-amino-thio-phenol are of some interest. Baker and Shulgen (1958) have shown that in 2-amino-phenol there is no evidence of a O-H···N or N-H···O hydrogen bond whereas in 2-dimethylamino-phenol there is a strong intramolecular hydrogen bond between the hydroxyl group and the nitrogen atom. The spectrum of 2-amino-thio-phenol, however, gives strong evidence of both N-H···S and S-H··N hydrogen bonds. The NH_2 stretching frequencies show a considerable departure from equation 2.4 and there are two SH

frequencies of markedly different intensities [illegible] indicative of "free" and "bonded" vibrations.

The NH_2 group will, because of its resonance interaction with the aromatic nucleus, tend to align itself with both hydrogens in the plane of the ring. The presence of an S-H (or O-H) in the ortho position will cause steric interaction between one of the protons of the amino group and the proton of the substituent group. This interaction will cause rotation of the amino group. Because of the smaller covalent radius of the oxygen atom, the hydroxyl group will not cause the NH_2 group to rotate sufficiently to allow the nitrogen lone pair to come close enough for hydrogen bond formation. The SH group, however, will cause appreciable rotation of the amino group so that the geometry of the system permits the formation of a weak intramolecular hydrogen bond. As the amino hydrogen can also form a hydrogen bond to the sulphur atom there exists an equilibrium between the cis (III) and trans (IV) conformation of the S-H group relative to the amino group.



III



IV

This would account for the observation of two S–H stretching frequencies in 2-amino-thio-phenol and two NH stretching frequencies in the partially deuterated compound.

TABLE 9.1

Fundamental NH_2 Stretching Frequencies of Amino-Sulphides and Sulphones (cm^{-1})

Compound Number	Substituents	ν_{as}	ν_s	NHD
93	2-SO_2CH_3	3473	3367	(3445 (3396
94	2-$SO_2C_2H_5$	3478	3368	
95	2-SO_2-*iso*-C_3H_7	3475	3367	
96	2-SO_2Ph	3485	3380	(3457 (3413
97	2-SCH_3	3472	3368	(3454 (3423
98	2-SPh	3486	3382	(3453 (3416
99	4-SO_2CH_3	3500	3408	
100	4-SO_2Ph	3500	3409	
101	4-SCH_3	3481	3394	
102	4-SPh	3492	3401	
103	2-S-S-PhNH_2	3490	3388	(3454 (3423
104	2-SH	3474	3377	(3444 (3410

SH Stretching Frequencies (cm^{-1})

2-Amino-Thio-Phenol	2613	2543

TABLE 9.2

First Overtone NH_2 Stretching Frequencies

Compound Number	Substituents	ν_{as}(0–2)	ν_{s}(0–2)	
93	2–SO_2CH_3	6683	6733	6628
94	2–$SO_2C_2H_5$	6684	6731	6627
95	2–SO_2·iso–C_3H_7	6698	6744	6636
97	2–SCH_3*	6673	6716	6609
98	2–SPh	6907	6731	6658
99	4–SO_2CH_3	6954	6739	
102	4–SPh	6920	6702	

* Whetsel et al. (1958)

TABLE 9.3

Fundamental OH Stretching Frequencies of

Nitro- and Sulphonyl-Phenols

Compound Number	Substituents	ν_{O-H}
105	None	3611
106	2-NO_2	3243
107	4-NO_2	3597
108	2-$MeSO_2$	3324
109	2-$PhSO_2$	3317

10 - INTRAMOLECULAR HYDROGEN BONDING TO NITROGEN

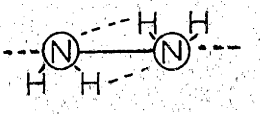
The spectra of several amines in which an intramolecular hydrogen bond between the amino group and a neighbouring nitrogen atom would be thought possible, and their N-deuterated derivatives, were recorded in the region of the fundamental NH_2 stretching frequencies and the results are listed in Table 10.1.

10.1 Di-amines:

The absence of a hydrogen bond between the hydroxyl and amino groups in ortho-amino-phenol has been said to be due to the unfavourable orientation of the amino group in the plane of the benzene ring, preventing the hydroxyl hydrogen from approaching to within bonding distance of the lone pair of electrons on the nitrogen (Baker and Shulgin, 1958). However in N,N-dimethyl,ortho-amino-phenol, the N-methyl group has sufficient steric interaction with the hydroxyl proton to rotate the dimethyl group out of the plane of the ring so that the free electron pair on the nitrogen is directed towards the hydroxyl group and thus provides conditions favourable for hydrogen bond formation.

It would be expected that a similar situation would exist with ortho-phenylenediamine and its N,N-dimethyl derivative. Although the results show that the latter compound possesses a hydrogen bond, which is comparable in

strength to that in ortho-nitro-aniline, the diamine also exhibits some degree of bonding. The low NH_2 stretching frequencies of the diamines indicate that the amino groups must exist in an almost pyrimidal configuration. In the ortho-diamines it would be expected that the two amino groups would orient themselves so that the hydrogens of one group would be directed above and those of the other group below the plane of the aromatic ring (I).

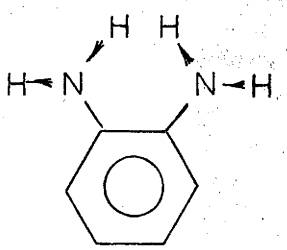


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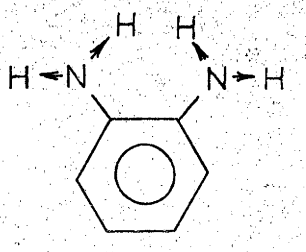
This type of conformation would reduce hydrogen/hydrogen interactions to a minimum and also permit the hydrogen atom on one amino group to form a hydrogen bond with the lone pair of electrons on the other.

Models of the two diamino-naphthalenes studied indicate that there would be considerable interaction between the two amino groups in 1,8-diamino-naphthalene. However the spectra of the partially deuterated compounds would point to 1,2-diamino-naphthalene having the stronger hydrogen bond (separation of NH.D frequencies 41 cm^{-1} to 27 cm^{-1}).

The existence of a hydrogen bond between the two amino groups should produce some mechanical coupling of the NH_2 stretching frequencies. If such a coupling did take place, it would be expected that there would be four NH_2 stretching frequencies corresponding to "in phase" and "out of phase" motions of the amino group (II, III).

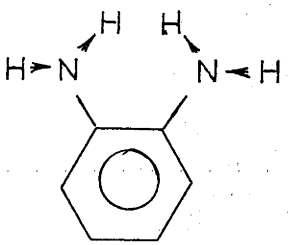


"in phase" antisymmetric

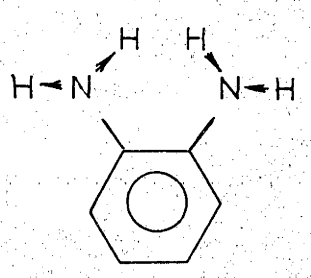


"in phase" symmetric

II



"out of phase" antisymmetric



"out of phase" symmetric

III

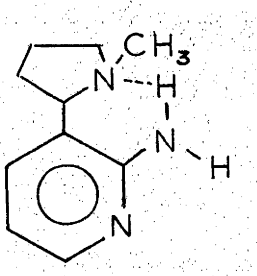
However in all cases only two sharp absorption bands are observed, indicating that the coupling is insufficient to

produce appreciable differences in the vibration frequencies.

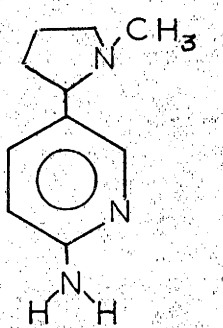
Krueger (1962) has reported that N,N-dimethyl-*ortho*-phenylenediamine reacts rapidly with carbon tetrachloride. This reaction was not found in the present work even after several days, so long as the solutions were handled in subdued light. Exposure to bright sunlight, however, causes a rapid darkening of the solution.

10.2 α-Amino-Nicotine and α'-Amino-Nicotine.

The existence of an intramolecular hydrogen bond in α-amino-nicotine has been postulated by Gol'dfarb and Kondakova (1959). They based this conclusion on the different products obtained from the reaction of an alkyl iodide with α-amino-nicotine (IV) and α'-amino-nicotine (V). Whereas V gave the expected alkiodide, IV was substituted on nitrogen in the pyridine ring.



IV



V

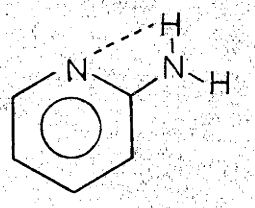
Models of these two compounds show that in IV the amine group is forced into close proximity with the pyrollidine

nitrogen so that it would be expected that the hydrogen bond formed would be of reasonable strength.

The deviation of the symmetric frequency from the predictions of equation 2.4 is -85.6 cm^{-1}, which is of the same order of magnitude as that found for 2-methyl,1-amino-anthraquinone, which possesses the strongest hydrogen bond of any of the compounds studied. Further, the shapes of the absorption bands are of interest as, whereas the two NH_2 absorptions have generally been sharp and of approximately equal intensity, in this case the symmetric stretching vibration has a half band width of four times that of the antisymmetric, giving the appearance of typical bonded and non-bonded vibrations. The appearance of the NH absorptions in the partially deuterated compounds lends support to this idea as they are of the same relative intensities and are separated by 140 cm^{-1} compared to 177 cm^{-1} for the NH_2 stretching frequencies. The possibility that the bond is almost strong enough to uncouple the NH_2 vibration cannot be overlooked.

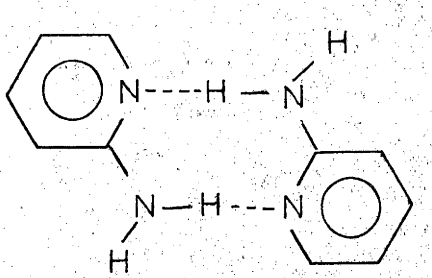
α'-amino-nicotine gave a slight positive deviation from the ν_{as}/ν_s relationship, with the frequencies slightly lower, ca. 20 cm^{-1}, than 2-amino-pyridine, which is probably due to the electron donating N-methyl pyrrolidyl group in the 3-position. Partial deuteration of this compound produced a slight doubling of the NH absorption with a separation of 14 cm^{-1}. This would imply hydrogen bond formation between the amino-group

and the pyridine nitrogen, giving a four-membered ring structure VI.



VI

As Morita (1961) had reported that 2-amino-pyridine gave only a single absorption on deuteration, the spectrum of this compound and 6-methyl,2-amino-pyridine were recorded before and after partial deuteration. The separation of the NH(D) frequencies in these compounds were 15 cm^{-1} and 14 cm^{-1} respectively, and furthermore both compounds gave negative deviations from the modified Bellamy and Williams equation of ca. 10 cm^{-1}. A possible cause of this evidence for a hydrogen bond would be the existence of dimers VII.



VII

As the doubling of the NH.D band is still present at concentrations of 0.01M, it would require an intermolecular bond of reasonable magnitude to maintain the bond at this dilution. However the separation of the NH.D absorption indicates that the bond concerned is relatively weak so that it is unlikely that intermolecular association is the cause.

Confirmation of this view is had in the results obtained for 4-amino-pyridine and 2-amino-pyrimidine. Both compounds would be capable of forming intermolecular bonds but both compounds exhibit a single NH frequency on mono-deuteration indicating that the NH_2 group is symmetrically situated. Like the para-substituted anilines, 4-amino-pyridine agreed with equation 2.4 whereas 2-amino-pyrimidine gave a deviation of the same magnitude as 2-amino-pyridine. It would appear therefore that Mason's suggestion (1958,) [illegible] of an intramolecular hydrogen bonding in 2-amino-pyridine is correct.

10.3 2-Amino-thiazole:

This compound also gave evidence of hydrogen bonding, but only to one of the hetero-atoms. If bonding had been to both atoms, the NH stretching frequency separation in the partially deuterated compound would not have been as large as that observed (23 cm^{-1}), because both NH links would have been involved in weak hydrogen bonds of equivalent magnitude. The bonding in all these compounds, although unexpected, is probably

related to the ring C–N distance in N-heterocyclic compounds being shorter than the ring C–C distance in aromatic compounds.

10.4 6-Methoxy,8-amino-quinoline:

In 8-amino-quinoline the intramolecular N–H···N hydrogen bond has only a small effect on the NH_2 stretching frequencies (Short, 1952). In contrast the O–H···N hydrogen bond in 8-hydroxy-quinoline causes a considerable lowering of the O–H stretching frequency. Short, however, showed the existence of a definite bond by the reduced NH_2 frequency shift for the 6-amino- as compared to the 5-amino-quinoline on changing the solvent from carbon tetrachloride to pyridine. Morita (1960) reported the effect of deuteration on 2-methyl,8-amino-quinoline. The results indicated the presence of a hydrogen bond comparable to that in ortho-nitro-aniline. In the present work 6-methoxy,8-amino-quinoline has been examined and the results are in agreement with the conclusions of previous workers.

10.5 2-Amino-benzonitrile:

There has been some difference of opinion regarding the existence of an intramolecular hydrogen bond in 2-cyano-phenol. Hunter (1954) deduced the absence of such a bond because Auwers (1897) found that 2-cyano-phenol was associated in solution. He attributed its absence to the distance between the proton and the electrons of the triple bond.

Lüttke and Mecke (1950) and Krueger and Thompson (1959) found spectroscopic evidence for an extremely low concentration of a cis-, together with the trans-, form of the compound since the hydroxyl stretching vibrations gave rise to two absorption bands of very unequal intensity both in the fundamental and overtone regions of the spectrum. The values of the observed frequencies were said to indicate an extremely weak bond, weaker than that in 2-ethoxy-phenol or 2-bromo-phenol (cf. Flett, 1957). The NH stretching frequencies of 2-cyano-aniline show only a small negative departure from equation 2.4 but the separation of the two NH.D frequencies was greater than that found for 2-bromo-aniline. Models show that the amino group is unable to rotate in the presence of an ortho-cyano-group so that close approach to the electrons of the triple bond is possible.

TABLE 10.1

NH_2 Stretching Frequencies (cm^{-1})

Compound Number	Compound	ν_{as}	ν_{s}	ν NHD
110	ortho-phenylenediamine	3436	3350	(3413 (3370
111	N,N-dimethyl-ortho-diamine	3448	(3386 (3349	(3428 (3384
112	1,2-diamino-naphthalene	3437	3340	(3414 (3473
113	1,8-diamino-naphthalene	3439	3353	(3408 (3381
114	α -amino-nicotine	3470	3293	(3454 (3314
115	α' -amino-nicotine	3491	3405	(3465 (3451
116	2-amino-pyridine	3510	3407	(3469 (3454
117	6-methyl,2-amino-pyridine	3509	3407	(3466 (3452
118	4-amino-pyridine	3507	3413	3460
119	2-amino-pyrimidine	3543	3429	3487
120	2-amino-thiazole	3492	3394	(3460 (3497
121	8-amino,6-methoxy-quinoline	3501	3389	(3468 (3436
122	2-amino-benzonitrile	3505	3408	(3467 (3447

11 - GENERAL OBSERVATIONS

11.1 2,6-Disubstituted Anilines:

The empirical equation relating the antisymmetric and symmetric NH_2 stretching frequencies

$$\nu_s = 0.7033\,\nu_{as} + 948.2 \qquad (2.4)$$

for meta- and para-substituted anilines has been assumed to hold for any amine where the two NH bonds are equivalent (Bellamy and Williams, 1957; Richards and Walker, 1961). However, during the present investigation it has become increasingly obvious that equivalence of the bonds is not the only factor involved and the deviation has at times been greater than in the corresponding mono-substituted ortho compound. There are also some para-substituted compounds which do not conform to the equation.

Linnett (1945) derived two equations relating the symmetric and antisymmetric stretching frequencies of an isolated NH_2 group to the stretching force constant k and the apparent HNH angle θ. The two equations can be written as

$$4\pi^2 \nu_s^2 = k\left[1/M_H + (1 + \cos\theta)/M_N\right] \qquad (11.1)$$

$$4\pi^2 \nu_{as}^2 = k\left[1/M_H + (1 - \cos\theta)/M_N\right] \qquad (11.2)$$

where M_H and M_N are the masses of the hydrogen and nitrogen atoms respectively. This treatment assumes that the nitrogen

and hydrogen atoms move along the NH bond direction and that the stretching force constant is much larger than the deformation and interaction force constants. McKean and Schatz (1956) have shown that this is a valid assumption in the ammonia molecule. By eliminating k from the two equations we can readily obtain a simple relationship between ν_{as}, ν_s and cos ϕ.

$$\nu_s = \nu_{as} \left[\frac{2C}{(C - M_H \cos\phi} - 1 \right]^{\frac{1}{2}} \qquad (11.3)$$

where $C = M_H + M_N$.

It has been shown (Krueger, 1962) that both the apparent bond angle and the NH stretching force constant increase in an approximately linear manner, depending on the Hammett values of the meta- and para-substituents. It is not surprising therefore that it is possible to obtain an empirical relationship between ν_s and ν_{as} for these compounds. The result is more a reflection of a linear variation of stretching force constant with bond angle for anilines in which only the inductive and mesomeric effects of the substituent will affect k and ϕ (Figure 11.1).

It has been shown that in symmetrically substituted di-ortho anilines the two NH bonds are equivalent. Now, if we have 2,6-disubstitution by hydrogen bond acceptors, we have an opening out of the bond angle, but instead of the corresponding

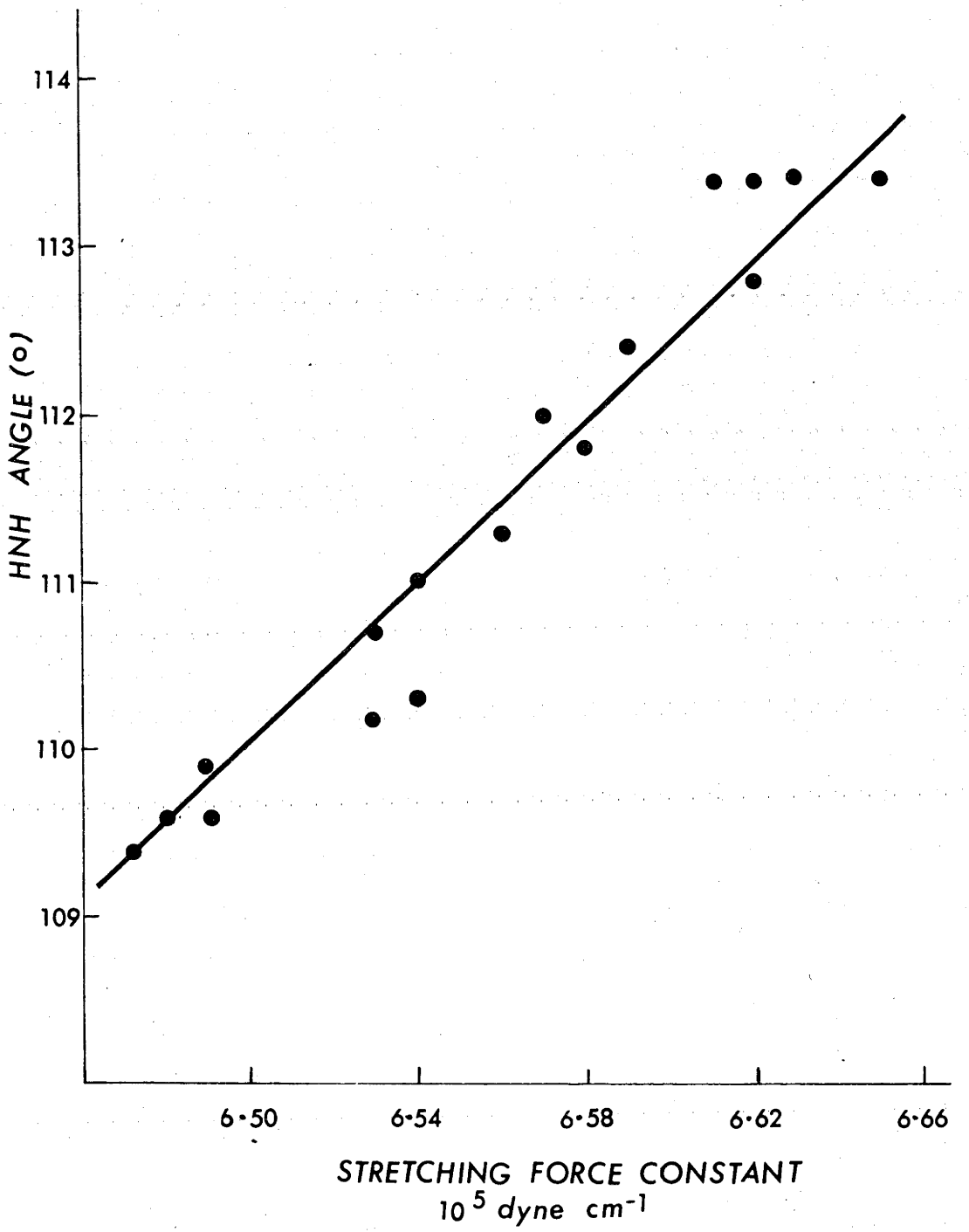
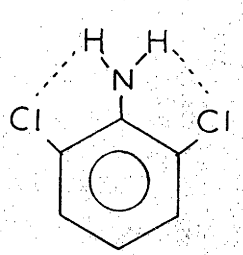
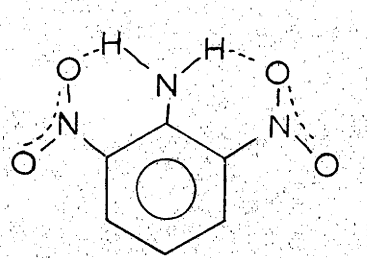


Fig. 11.1 - Correlation between NH stretching force constant k and HNH bond angle θ for para-substituted anilines.

increase in the stretching force constant, we have a decrease. This trend is shown in Figure 11.2. For any given di-ortho substituents the effect of changing the group in the para position should roughly parallel the effect observed in the series of para compounds, viz. increasing k with increasing θ, and this is in fact observed (Figure 11.2). Now, assuming, we have a para-substituted and a 2,6-disubstituted aniline both with the same NH stretching force constant, then the 2,6-disubstituted aniline will, by virtue of its greater bond angle, have a negative departure from equation 2.4. The calculated bond angle has increased with the increasing strength of the hydrogen bond and the stretching force constant has remained practically unchanged in the 2,6-dihalogeno-anilines and decreased in the 2,6-dinitro-anilines. Because of the geometry of the system, it is probable that, in the former case (I), the non-linearity of the hydrogen bond is more effective in opening the HNH bond angle than in lowering the stretching force constant by lengthening the bond. For the latter compounds (II), the bond angle is more likely to be governed by the mesomeric effects of the nitro group and the bond weakening by the hydrogen bond is the main effect.



I



II

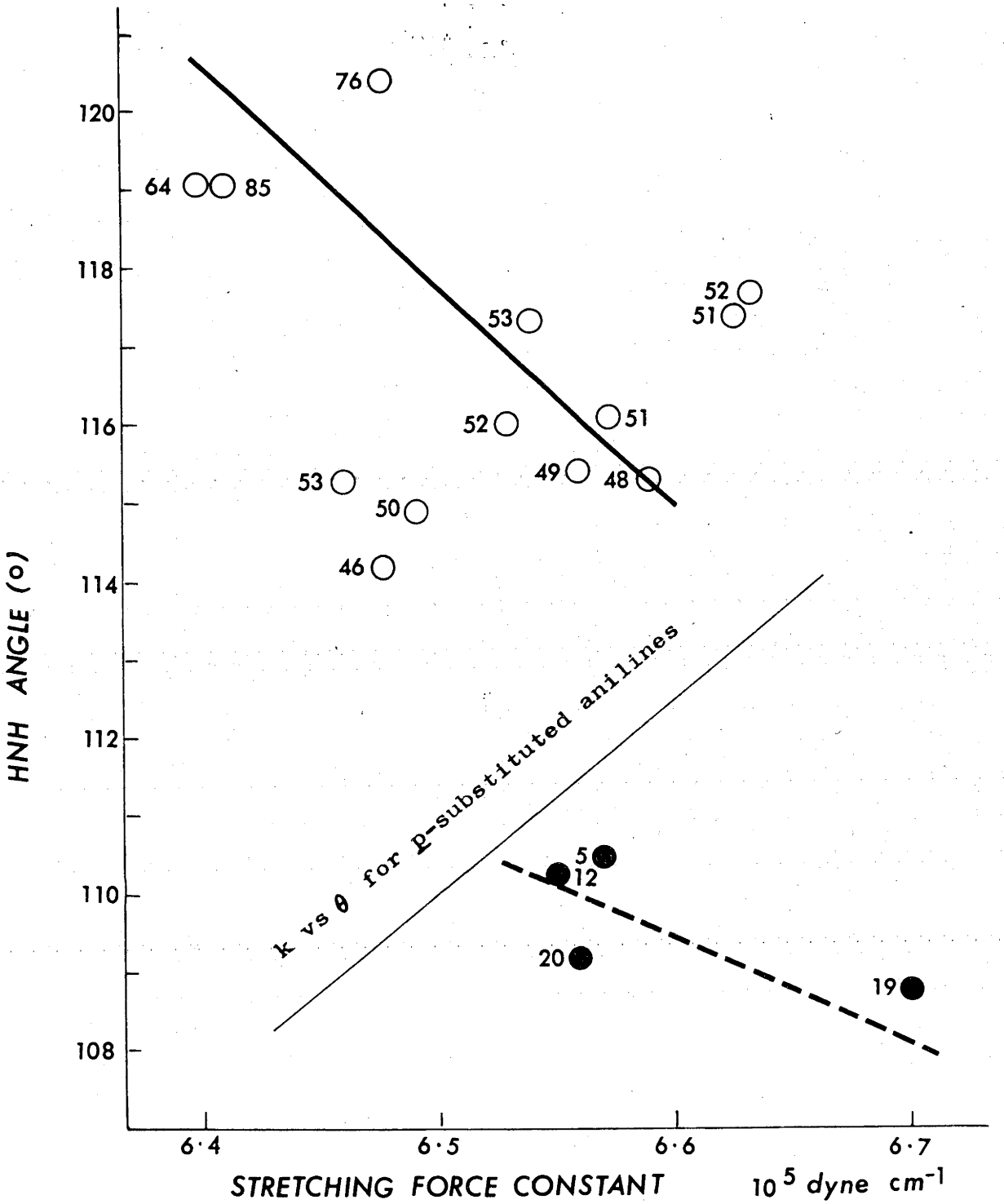


Fig. 11.2 - Correlation between NH stretching force constant k and HNH bond angle for 2,6-disubstituted aniline. Numbers refer to compound in table 11.1.

● Substituents having a repulsive effect

○ Substituents forming a hydrogen bond

In 2,4,6-tri-tert.-butyl-aniline, there would be steric compression of the NH bond and a decrease in the bond angle. This will give an increase in stretching force constant with a decrease in bond angle, a trend exactly opposite to the 2,6-disubstitution already discussed. It would be expected that compounds of this type, in which there is a repulsive interaction between the groups in the 2- and 6-positions and the amine group, will give a positive departure from equation 2.4.

11.2 Overtone Frequencies:

Although the appearance of two absorptions for the asymmetric NH_2 stretching vibration in the overtone region can be correlated with an interaction between the ortho-substituent and the amine group, the reason for the splitting is still uncertain.

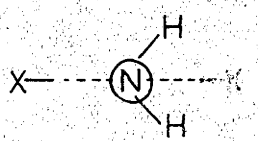
Hambly (1961) has suggested that a double potential minimum, in which the intramolecularly bound proton can exist in two positions, one closer to the nitrogen atom and one closer to the acceptor atom, may be responsible for the observations. Whereas this explanation would explain the situation which exists for unilateral hydrogen bonding, it does not account for the doubling produced by repulsive interaction. It also does not satisfactorily explain the decreased splitting observed for bilateral bonding in 2,6-disubstituted anilines.

Krueger (1963) has argued on the basis of anharmonicity

constants that the low frequency member is the non-bonded vibration. The converse can also be reasoned. The deuteration studied in the fundamental region have given definite evidence of a hydrogen bond being formed and that the symmetric and antisymmetric frequencies reflect the formation of such a bond. Any calculation of anharmonicity constants, involving these frequencies will have no meaning unless we use the corresponding "bonded" frequencies in the overtone region. Further, it could be expected that as the hydrogen bonds formed are weak, the anharmonicity constant would have a "normal" value. The low frequency absorption on this analysis would correspond to the bonded vibration and the high frequency absorption, which has either a negative or low value for the anharmonicity constant, to the non-bonded vibration.

However, under either analysis it is necessary to postulate two conformations corresponding to the bonded and non-bonded forms of the NH_2 group. Krueger's idea appears to be that the NH_2 group retains its relative orientation to the acceptor group but that there is an energy barrier between bonded and non-bonded forms. An alternative way the existence of bonded and non-bonded forms can be achieved is to have rotation of the amine groups so that it is orientated with a hydrogen atom above and below the plane of the aromatic ring. The existence of rotational isomers of this type has been

postulated for the 2,6-dihalogeno,4-nitro-anilines in which both the fundamental symmetric and antisymmetric frequencies are doubled. If, because of the increased vibrational amplitude of the NH_2 stretching vibration in the overtone, the repulsive force between the amino hydrogen and the ortho substituent becomes more important than the weak hydrogen bond between the atoms, then the energy barrier resisting rotation by the amino group could be overcome, giving rise to a second conformation (III).



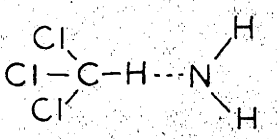
III

This type of explanation would account for many of the observed facts, including the decreased splitting in 2,6-disubstituted compounds and ortho-tert.-butyl-aniline. However, as the period of vibration of the N-H bond is short, it is doubtful if the lifetime of the second conformation be sufficient to give the results observed.

Another explanation which could be invoked is that this is a case of "inversion doubling" similar to that observed in ammonia, in which the splitting for $\nu_s(0-1)$ is small

but for ν_s(0-2) is appreciable (Herzberg, 1947). However, it could be argued that, if this was the explanation then a similar doubling should be observed in the meta-and para-substituted anilines. The formation of a strong intramolecular hydrogen bond by the amine group would bring that group more into coplanarity with the benzene ring and thus making it easier for the inversion of the amino group to take place.

The effect of different solvents on the NH_2 stretching frequencies are interesting and lend some support to the "inversion hypothesis". Whetsel (1961) has observed that in ortho-nitro-aniline and ortho-methylsulphonyl-aniline, the high frequency component of ν_s(0-2) falls at very nearly the same position in both carbon tetrachloride and chloroform, but that the low frequency component shifts towards higher frequencies. Whetsel has interpreted the hydrogen bonding to be of the type (IV) which is



IV

in agreement with earlier spectroscopic evidence by Krueger and Thompson (1957).

Krueger (1963) also observed a shift (ca. 100 cm^{-1}) to higher frequencies of the low frequency absorption in ethyl

anthranilate. The decrease in the frequency separation of the ν_s(0-2) absorptions could then be due to the steric hindrance to inversion produced by the presence of the chloroform molecule bonded to the nitrogen lone pair. This intermolecular hydrogen bond would also reduce the conjugation of the NH_2 group with the ring and weaken the original intramolecular hydrogen bond. It must be admitted, however, that the effects observed could also be explained in terms of "free" and "bonded" NH vibrations and that it will be the bonded vibration that is affected by the hydrogen bonding of the chloroform to the nitrogen atom.

The effect of several solvents, which can act as hydrogen bond acceptors, on the $\nu_{as}(0\text{-}2)NH_2$ and $\nu_s(0\text{-}2)NH_2$ frequencies of 2-nitro,6-methyl-aniline and methyl anthranilate are given in Table 11.2. The shapes of the absorption curves are shown in Figure 11.3. With increasing basicity of the solvent, the intensity of ν_{as}(0-2) and the high frequency member of ν_s(0-2) decreases and they both shift to lower frequencies. The low frequency member of ν_s(0-2) is relatively unaffected in intensity but moves to higher frequencies.

As was the case with chloroform, we have a decreased frequency separation of ν_s(0-2) which is dependant on the strength of the intermolecular hydrogen bond to the solvent.

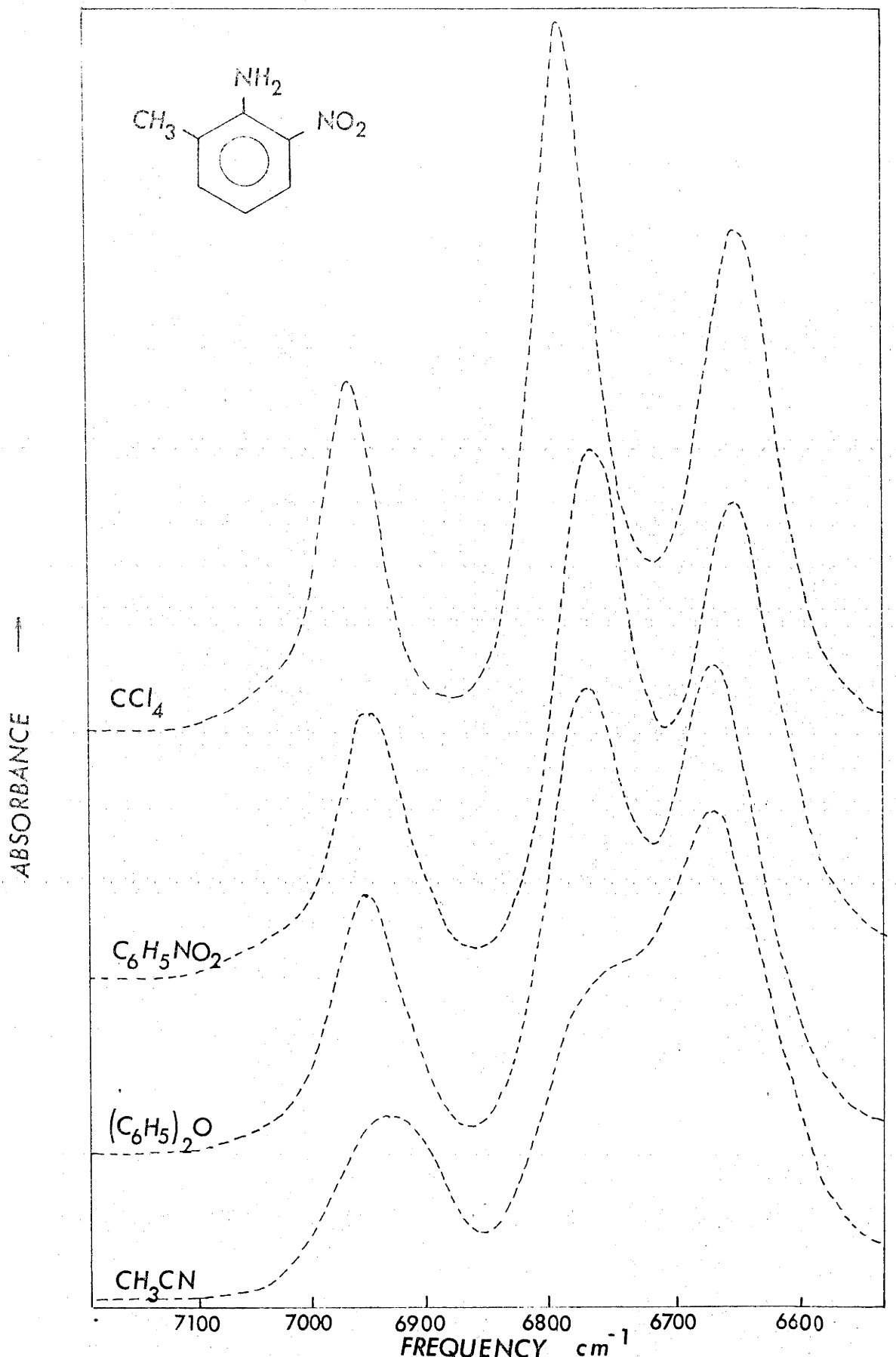
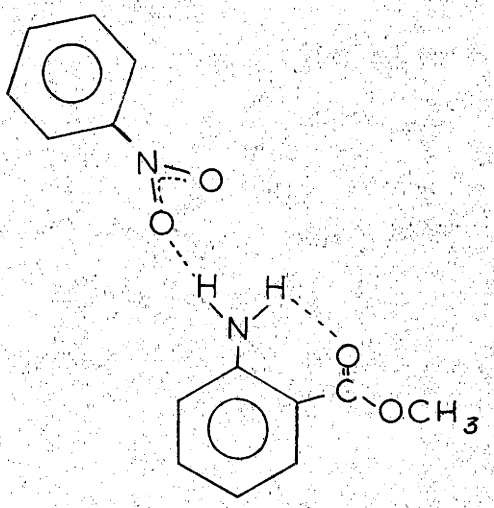


Fig. 11.3 - Solvent effects on ν(0-2) NH_2.

the intermolecular bond is probably formed by the free N-H link (V).



V.

The effect of the solvent molecule attached to this bond would be to decrease the possibility of "inversion" and thereby decreasing the frequency separation between the two ν_s(O-2) absorptions.

None of the explanations invoked seem to fit all the facts and it appears that some alternative explanation will have to be found. However the empirical fact remains that in anilines in which there is an <u>ortho</u> substituent capable of interacting with the amino group, a splitting of $\nu_s(O\text{-}2)NH_2$ will be observed. The magnitude of the separation and the shape of the absorption curve is indicative of the relative strength and type of interaction.

TABLE 11.1

Calculated Stretching Force Constants and Bond Angles for the NH_2 Group in 2,6-Disubstituted Anilines

Compound Number	Substituents	K x 10^{-5} dynes/cm	α°
5	2,6-di-CH_3	6.57	110.5
12	2,4,6-tri-CH_3	6.55	110.3
19	2,4,6-tri-$C(CH_3)_3$*	6.70	108.7
20	2,4,6-tri-$CH(CH_3)_2$*	6.56	109.2
46	2,6-di-I,4-CH_3	6.47	114.2
48	2,4,6-tri-Cl	6.59	115.3
49	2,4,6-tri-Br	6.56	115.4
50	2,4,6-tri-I	6.49	114.9
51	2,6-di-Cl,4-NO_2	(6.64 (6.57	(117.4 (116.1
52	2,6-di-Br,4-NO_2	(6.60 (6.53	(117.7 (116.0
53	2,6-di-I,4-NO_2	(6.54 (6.46	(117.3 (115.3
64	2,6-di-CO_2CH_3	6.40	119.1
78	2,6-di-NO_2	6.47	120.4
85	2,4,6-tri-NO_2	6.41	119.1

* Whetsel et al. (1958)

TABLE 11.2

Solvent Effects on 1st Overtone NH_2 Stretching Frequencies (cm^{-1})

6-Methyl,2-Nitro-Aniline

Solvent	ν_{as}(0–2)	ν_{s}(0–2)	
CCl_4	6978	6802	6662
$C_6H_5NO_2$	6964	6784	6684
$(C_6H_5)_2O$	6963	6775	6666
CH_3CN	6945	6770	6667

Methyl Anthranilate

Solvent	ν_{as}(0–2)	ν_{s}(0–2)	
CCl_4	6944	6770	6609
$C_6H_5NO_2$	6935	6743	6640
$(C_6H_5)_2O$	6925	6738	6623
CH_3CN	6930	6716	6653

12 - APPENDIX

This section is divided into two parts. The first is a comprehensive table of all the compounds reported in this thesis, with a brief indication of their source, method of purification and the criteria used to identify these compounds as pure specimens. The second part is devoted to a description of the methods used to prepare the amines which were not obtainable commercially.

12.1 Purification of Primary Amines:

All liquid amines were distilled under reduced pressure before use and a middle fraction of constant boiling point collected. The purity of each sample was checked on an F & M temperature programmed vapour phase chromatograph using a silicone grease column.

The solid amines were recrystallised from a suitable solvent until a constant melting point was obtained. All melting points are in degrees centigrade and are uncorrected.

The analyses reported were carried out by the C.S.I.R.O. Microanalytical Service, Melbourne.

The following abbreviations have been used in Table 12.1:

aq. - aqueous

C/HCl - commercial product supplied as the amine hydrochloride

dist. red. press – distilled under reduced pressure, ca. 10 mm.

pet. ether – petroleum ether, b.p. 60–80°C

prep. – prepared during the present work

recryst. – recrystallised

V.P.C. – Vapour Phase Chromatography

* – results of Krueger (1962,1963)

≠ – results of Dyall and Hambly (1958)

TABLE 12.1

Purification and Identification of Primary Aromatic Amines

No.	Substituent	Source	Purification	Purity Check
1	2-CH_3	C	dist. red. press	V.P.C., N-acetyl 109° (110°)
2	2,3-di-CH_3	C	dist. red. press	V.P.C., N-acetyl 134° (135°)
3	2,4-di-CH_3	C	dist. red. press	V.P.C.
4	2,5-di-CH_3	C	dist. red. press	V.P.C.
5	2,6-di-CH_3	C	dist. red. press	V.P.C., N-acetyl 177° (177°)
6	2-CH_3,5-iC_3H_7	C	dist. red. press	V.P.C.
7	2-CH_3,4-NO_2	C	recryst. ethanol	m.p. 128° (129°)
8	2-CH_3,5-NO_2	C	recryst. aq. ethanol	m.p. 107° (107°)
9	2-CH_3,4-NH_2	C/HCl	recryst. benzene	m.p. 63° (64°)
10	2-CH_3,5-NH_2	C	recryst. water	m.p. 100° (99°)
11	2-CH_3,5-N(C_2H_5)$_2$	C/HCl	+ NaOH aq. extracted into CCl_4	
12	2,4,6-tri-CH_3	C	dist. red. press	V.P.C.
13	2,6-di-CH_3,3,5-di-NO_2	prep.	Recryst. ethanol	m.p. 176° (177°)
14	2,6-di-CH_3,4-NO_2	prep.	recryst. ethanol	m.p. 163-164° (163.5 - 164.5°)
15	2-C_2H_3	C	dist. red. press.	V.P.C.
16	2-C(CH_3)$_3$	prep.	dist. red. press.	V.P.C., N-acetyl 165° (165-166°) analysis

TABLE 12.1 cont'd

No.	Substituent	Source	Purification	Purity Check
17	2-$C(CH_3)_3$,5-Cl	prep.	dist. red. press.	V.P.C. analysis
18	2-$CH(CH_3)_2$*	—	——	——
19	2,4,6-tri-$C(CH_3)_3$*	—	——	——
20	2,4,6-tri-$CH(CH_3)_3$*	—	——	——
21	2,5-di-$C(CH_3)_3$*	—	——	——
22	1-naphthylamine	C	recryst. aq.ethanol	m.p. 50° (50°)
23	2-naphthylamine	C	recryst. water	m.p. 113° (113°)
24	1-amino-anthracene	C	recryst. ethanol	m.p. 129° (130°)
25	2-amino-anthracene	C	recryst. ethanol	m.p. 238° (238°)
26	Di-amino-durene	prep.	recryst. water	m.p. 148° (149°)
26a	2,6-di-CH_3,4-NH_2	prep.	recryst. benzene/ ligroin	m.p. 101° (101°)
27	2-C_6H_5	C	recryst. aq.ethanol	m.p. 49° (49-50°)
28	2-OCH_3	C	dist. red. press.	V.P.C.
29	2-OC_2H_5	C	dist. red. press.	V.P.C.
30	2,5-di-OCH_3	C	recryst. ethanol	m.p. 81° (81°)
31	2,5-di-OC_2H_5	C	recryst. ethanol	m.p. 86° (86-87°)
32	2-OCH_3,4-NO_2	C	recryst. ethanol	m.p. 138° (138-140°)
33	2-OCH_3,5-NO_2	C	recryst. ethanol	(m.p. 118° (118°)
34	2-OCH_3,3-Cl,5-NO_2	prep.	recryst. ethanol	m.p. 110°
35	2-OCH_3,1-naphthylamine	C	recryst. water	m.p. 54° (54°)
36	dianisidine	C	recryst. ethanol	m.p. 110°

No.	Substituent	Source	Purification	Purity Check
37	2-F	C	dist. red. press.	V.P.C.
38	2-Cl	C	dist. red. press.	V.P.C., N-acetyl, m.p. 87° (87-88°)
39	2-Br	C	dist. red. press.	V.P.C., N-acetyl, m.p. 99° (99°)
40	2-I	prep.	recryst. aq.ethanol	m.p. 56° (56.5°), N-acetyl m.p. 109° (109-110°)
41	2,4-di-F	C	dist. red. press.	V.P.C.
42	2,5-di-F	C	dist. red. press.	V.P.C.
43	2,4-di-Cl	C	recryst. aq. methanol	m.p. 62° (62°)
44	2,5-di-Cl	C	recryst. ligroin	m.p. 50° (50°)
45	2,6-di-Br	C	recryst. ethanol	m.p. 83° (83-84°)
46	2,6-di-I,4-CH_3	prep.	recryst. ethanol	m.p. 125° (125°)
47	2-Cl,4-NO_2	C	recryst. ethanol	m.p. 104-105° (105°)
48	2,4,6-tri-Cl	C	recryst. ligroin	m.p. 78.5° (78.5°)
49	2,4,6-tri-Br	prep.	recryst. ethanol	m.p. 120° (122°), N-acetyl, m.p. 232° (232°)
50	2,4,6-tri-I	prep.	recryst. ethanol	m.p. 185° (185.5°)
51	2,6-di-Cl,4-NO_2	C	recryst. ethanol	m.p. 189° (189-190°)
52	2,6-di-Br,4-NO_2	prep.	recryst. ethanol	m.p. 202° (206°) N-acetyl 234° (234°)

No.	Substituent	Source	Purification	Purity Check
53	2,6-di-I,4-NO_2	prep.	recryst. ethanol	m.p. 249-250° (248°)
54	2-CF_3	C	dist. red. press.	V.P.C.
55	3-CF_3	C	dist. red. press.	V.P.C.
56	4-CF_3	C	dist. red. press.	V.P.C.
57	4-F	C	dist. red. press.	V.P.C.
58	2,4-di-Br,6-Cl	prep.	recryst. aq.ethanol	m.p. 103-104° (103°)
59	2-CHO	prep.	steam.dist.	m.p. 37,5° (38-39°)
60	2-CH_3CO	C	dist. red. press.	V.P.C.
61	2-C_6H_5CO	C	recryst. ethanol	m.p. 106-107° (105-106°)
62	2-CO_2CH_3	C	dist. red. press.	V.P.C.
63	2-$CO_2C_2H_5$	C	dist. red. press.	V.P.C. ca 1% methyl anthranilate
64	2,6-di-CO_2CH_3	prep.	recryst. ethanol	m.p. 103-104° (103-104°)
65	3-CO_2CH_3,2-naphthyl-amine	prep.	recryst. ethanol	m.p. 104° (104-105°)
66	1-NH_2-anthraquinone	C	recryst. ethanol	m.p. 251° (252°)
67	1-NH_2,2-CH_3-anthra-quinone	C	recryst. $C_6H_5NO_2$	m.p. 204-205° (205°)
68	1-NH_2,5-Cl-anthra-quinone	C	recryst. ethanol	m.p. 218-219° (219°)
69	1,4-di-NH_2-anthra-quinone	C	recryst. ethanol	m.p. 266-267° (268°)

No.	Substituent	Source	Purification	Purity Check
70	1,5-di-NH_2-anthra-quinone	C	recryst. ethanol	—— (319°)
71	2-CO_2H	C	recryst. ethanol	m.p. 144° (144-146°)
72	2-NO_2	C	recryst. water	m.p. 71-71.5° (71.5°)
73	2,3-di-NO_2	C	recryst. benzene	m.p. 129° (128.5-129°)
74	2,4-di-NO_2	C	recryst. aq. acetone	m.p. 180-181° (180°)
75	2,5-di-NO_2	C	recryst. ethanol	m.p. 139° (138°)
76	2,6-di-NO_2	prep.	recryst. ethanol	m.p. 137.5-138.5° (138°)
77	2-NO_2,3-CH_3	C	recryst. benzene/ pet. ether	m.p. 107° (107-107.5°)
78	2-NO_2,4-CH_3	C	recryst. aq. ethanol	m.p. 116.5° (117°)
79	2-NO_2,5-CH_3	C	recryst. aq. ethanol	m.p. 96.5° (97°)
80	2-NO_2,4-Cl	C	recryst. water	m.p. 117° (116.5°)
81	2-NO_2,5-Cl	C	recryst. benzene	m.p. 126° (126.5°)
82	2-NO_2,4-CF_3	C	recryst. water	m.p. 106-107°
83	2-NO_2-4-NH_2	C	recryst. water	m.p. 137-138° (137°)
84	2-NO_2,5-NH_2	C	recryst. water	m.p. 160-161° (161°)
85	2,4,6-tri-NO_2	prep.	recryst. acetic acid	m.p. 188° (188°)

No.	Substituent	Source	Purification	Purity Check
86	2-NO_2,4-OCH_3	C	recryst. ethanol	m.p. 124-125°
87	2-NO_2,3-OCH_3 ♯	—	———	———
88	2-NO_2,3-Cl ♯	—	———	———
89	2-NO_2,6-OCH_3 ♯	—	———	———
90	2-NO_2,6-Cl ♯	—	———	———
91	2-NO_2,1-naphthylamine	C	recryst. aq.ethanol	m.p. 143° (144°)
92	1-NO_2,2-naphthylamine	C	recryst. ethanol	m.p. 127-127.5° (127.5°)
93	2-SO_2CH_3	prep.	recryst. benzene/ pet. ether	m.p. 65° Analysed
94	2-$SO_2C_2H_5$	prep.	recryst. benzene/ pet. ether	m.p. 72° Analysed
95	2-SO_2.<u>iso</u>-C_3H_7	prep.	recryst. benzene/ pet. ether	m.p. 83° Analysed
96	2-SO_2Ph	prep.	recryst. benzene/ pet. ether	m.p. 122°
97	2-SCH_3	C	dist. red. press	V.P.C. m.p. 35.5°
98	2-SPh	prep.	dist. red. press	V.P.C.
99	4-SO_2CH_3	prep.	recryst. benzene/ pet. ether	m.p. 133°
100	4-SO_2Ph	prep.	recryst. benzene/ pet. ether	m.p. 176°
101	4-SCH_3	prep.	dist. red. press.	V.P.C.
102	4-SPh	prep.	recryst. benzene/ pet. ether	m.p. 95.8°
103	2-S-S-$PhNH_2$	C	recryst. aq.ethanol	m.p. 92° (93°)
104	2-SH	C	dist. red. press.	V.P.C.

No.	Substituent	Source	Purification	Purity Check
105	Phenol	C	——	m.p. 40° (41°)
106	2-NO_2-Phenol	C	recryst. ethanol	m.p. 44° (44.9°)
107	4-NO_2-Phenol	C	sublimed	m.p. 114° (114°)
108	2-SO_2CH_3-Phenol	prep.	recryst. ethanol	——
109	2-SO_2PH-phenol	prep.	recryst. ethanol	m.p. 96° (96-98°)
110	2-NH_2	C	recryst. water	m.p. 102° (102-103°)
111	2-$N(CH_3)_2$	prep.	dist. red. press.	V.P.C.
112	1,2-di-NH_2-naphthalene	C	recryst. water	m.p. 97° (98°)
113	1,8-di-NH_2-naphthalene	C	recryst. aq. ethanol	m.p. 66° (66.5°)
114	α-amino-nicotine	prep.	recryst. ligroin	m.p. 125° (125°)
115	α'-amino-nicotine	prep.	recryst. as hydrochloride	m.p. 60° (60°)
116	2-NH_2-pyridine	C	recryst. ligroin	m.p. 57° (57.5°)
117	6-CH_3,2-NH_2-pyridine	C	dist. red. press.	V.P.C., m.p. 41°
118	4-NH_2-pyridine	C	recryst. benzene	m.p. 158° (158°)
119	2-NH_2-pyrimidine	C	sublimed	m.p. 127° (127-128°)
120	2-NH_2-thiazole	C	recryst. ethanol	m.p. 89° (90°)
121	8-NH_2,6-OCH_3-quinoline	C	recryst. water	m.p. 41°
122	2-CN	C	recryst. CS_2	m.p. 51° (51°)

12.2 Preparation of Primary Aromatic Amines:

Acetyl Derivatives:

The acetyl derivatives listed in Table 12.1, were prepared by dissolving the amine in acetic acid and adding a slight excess of acetic anhydride. The mixture was heated on a water bath for five minutes and diluted with water. The precipitated acetanilide was recrystallised from ethanol or light petroleum.

13: 2,6-Dimethyl,3,5-dinitro-aniline

The acetyl derivative of 2,6-dimethyl-aniline was nitrated and the resulting product hydrolysed by the method of Noelting and Stocklin (1891)

14: 2,6-Dimethyl,4-nitro-aniline

This compound was made by the nitration of the p-toluene sulphonyl derivative of 2,6-dimethyl-aniline according to the directions of Wepster (1954). The resulting sulphonanilide was hydrolysed by refluxing with dilute sulphuric acid to give the desired amine.

15: 2-tert.-Butyl-aniline:

Tert.-butyl benzene was nitrated by the method of Craig (1935) and the nitration product separated into fractions by distillation and chromatography. The separated fractions were reduced with hydrogen in the presence of Raney

nickel by the method of Bickart et al. (1952) and the reduced product again fractionated.

The N-acetyl derivative was prepared and analysed. (Found: C, 75.4; H, 8.8; N, 7.7; O, 8.5%. Calc.: C, 75.4; H, 9.0; N, 7.3; O, 8.4%)

2-tert.-Butylanilinium-2-naphthalene sulphonate prepared by the method of Wepster (1957) had an m.p. 190°C, lit. 190°C.

17: 2-tert.-Butyl,5-chloro-aniline

4-tert.-Butyl-aniline, isolated from the preparation of 2-tert.-butyl-aniline was nitrated by the method of Bickart (1952) to give 2-tert.-butyl-5-amino-nitrobenzene. The product (20 g.) was diazotised with hydrochloric acid and sodium nitrite and the resulting mixture added to cuprous chloride (11 g.) in concentrated hydrochloric acid (60 ml.) at 20-25°C. The mixture was heated on a water bath for thirty minutes and steam distilled. The pale yellow oil was taken up in benzene, dried, and distilled under reduced pressure. The product (13 g.) had b.p. 141-142°C/18 mm and gave on analysis (Found: C, 56.7; H, 5.7; N, 6.2; O, 15.4; Cl, 16.2. Calc. for: $C_{10}H_{12}O_2NCl$: C, 56.2; H, 5.7; N, 6.6; O, 15.0; Cl, 16.6%)

The nitro-compound (10 g.) was dissolved in 95% ethanol (30 ml) and reduced with hydrogen in the presence of Raney nickel at 25°C. Fractional distillation gave 8 g. of an almost colourless product,

b.p. 131-133°C/8mm. (Found: C, 65.6; H, 7.6; N, 8.0; Cl. 19.5%.

Calc. for $C_{10}H_{14}NCl$: C, 65.4; H, 7.7; N, 7.6; Cl. 19.3%).

26: Diamino-durene

Dinitrodurene, prepared by the method of Smith (1944) from durene, was reduced with hydrogen in the presence of Raney nickel to give the desired product.

26a: 2,6-Dimethyl, 4-amino-aniline

2,6-Dimethyl, 4-nitro-aniline was reduced with hydrogen in the presence of Raney nickel.

34: 2-Methoxy, 3-Chloro, 5-nitro-aniline

2-Hydroxy, 3-chloro, 5-nitro-aniline was dissolved in sodium hydroxide and the theoretical quantity of dimethyl sulphate added. The precipitated product was recrystallised from ethanol.

40: 2-Iodo-aniline

2-Nitro-aniline was diazotised by the method of Baeyer (1905) and treated with excess potassium iodide to yield 2-iodo-nitrobenzene which was reduced with stannous chloride to yield the desired amine.

46: 2,6-Di-iodo, 4-methyl-aniline

p-Toluidine was dissolved in a water/ether mixture and treated with iodine in the presence of a suspension of calcium carbonate.

49: 2,4,6 - Tribromo-aniline

Bromine was reacted with aniline hydrochloride by the method of Vogel (1961b).

50: 2:4:6 - Tri-iodo-aniline

Aniline hydrochloride was reacted with iodine monochloride by a method similar to that used for the preparation of tri-bromo-aniline.

52: 2,6-Di-bromo, 4-nitro-aniline, and

53: 2,6-di-iodo, 4-nitro-aniline

These compounds were prepared by the action of bromine and iodine monochloride on 4-nitro-aniline under the conditions described by Sandin et al (1944).

58: 2-Chloro, 4,6-dibromo-aniline

An aqueous solution of 2-chloro-aniline was reacted with two moles of bromine to give the desired product.

59: 2-Amino-benzaldehyde

2-Nitro-benzaldehyde was reduced with ferrous sulphate by the method of Smith and Opie (1955) and the product isolated by steam distillation.

64: 2,6-Dicarbomethoxy-aniline

2,6-Dimethyl-aniline was acetylated and then oxidised with potassium permanganate. The product was deacetylated by boiling with acid and methylated to the di-ester with diazomethane.

65: 3-Carbomethoxy, 2-naphthylamine

2-Amino, 3-naphthoic acid was methylated with diazomethane to give the required ester.

66: 2,6-Di-nitro-aniline

This compound was prepared from chlorobenzene by the method of Hegedus (1950).

85: 2,4,6-Tri-nitro-aniline

Picric acid was heated with urea and mixture extracted with water. The residue remaining after extraction was extracted with acetone and the acetone extract concentrated to yield picramide in good yield (Spenser and Wright, 1946).

93, 94, 95: 2-Methyl-sulphonyl-, 2-ethyl-sulphonyl and 2-iso-propyl-sulphonyl-aniline

2-Nitro-thiophenol, prepared from 2,2'-nitro diphenyl-disulphide by the method of Foster and Reid (1924) was dissolved in sodium hydroxide and the theoretical amount of the respective alkyl sulphate (methyl, ethyl) or bromide (iso-propyl) added. The alkyl sulphide prepared in this manner was oxidised to the sulphone. The 2-alkyl-sulphonyl-nitrobenzene was then reduced with tin and hydrochloric acid to the desired amine.

Analysis: 93, Found: C, 49.2; H, 5.2; N, 8.0; O, 18.9; S, 18.8%
Calc.: C, 49.1; H, 5.3; N, 8.2; O, 18.7; S, 18.7%

94, Found: C, 51.8; H, 6.0; N, 7.7; O, 17.3; S, 17.2%
Calc.: C, 51.9; H, 6.0; N, 7.6; O, 17.3; S, 17.3%

95, Found: C, 54.3; H, 6.5; N, 7.0; O, 16.1; S, 16.0%
Calc.: C, 54.3; H, 6.6; N, 7.0; O, 16.1; S, 16.1%

96, 97: 2-Phenyl-sulphonyl- and 2-phenyl-thio-aniline

2-Chloro-nitrobenzene was heated with thiophenol and potassium hydroxide in the presence of a copper catalyst. The cooled product was extracted with carbon tetrachloride and distilled under reduced pressure. Part of the 2-nitro-diphenyl sulphide prepared in this manner was oxidised to the sulphone and reduced with tin and hydrochloric acid to 2-Phenyl-sulphonyl-aniline (96). The remainder of the 2-nitro-diphenyl-sulphide was reduced with tin and hydrochloric acid to 2-Phenyl-thio-aniline (97).

99: 4-Methyl-sulphonyl-aniline

This compound was prepared from 4,4'-dinitro-phenyl-disulphide by a similar method to that used for 2-methyl-sulphonyl aniline.

100, 102: 4-Phenyl-sulphonyl-aniline and 4-Phenyl-thio-aniline

4-Chloro-nitro-benzene and thio-phenol were heated together in the presence of potassium hydroxide and copper powder. The product was isolated from the reaction mixture by extraction with carbon tetrachloride. The 4-nitro-diphenylsulphide was then converted into the named products by a procedure analogous to that used for 2-phenyl-sulphonyl- and 2-phenyl-thio-aniline.

101: 4-Methyl-thio-aniline

4-Methyl-thio-nitrobenzene obtained during the preparation of 4-methyl-sulphonyl-aniline was reduced with tin and hydrochloric acid to yield 4-methyl-thio-aniline.

108: 2-Methyl-sulphonyl-phenol

2-Methyl-sulphonyl-anisole was prepared from 2-bromo-anisole and methane sulphonyl fluoride by a Grignard reaction. This compound was then demethylated by heating with 48% hydrobromic acid to give 2-methyl-sulphonyl-phenol.

109: 2-Phenyl-sulphonyl-phenol

2-phenyl-sulphonyl-anisole was prepared from 2-bromo-anisole and benzene sulphonyl fluoride by a Grignard reaction. Prolonged heating with 48% hydrobromic acid gave the desired phenol.

111: N,N-Dimethyl-o-phenylene-diamine

2-Nitro-aniline was methylated with methyl iodide and the resultant product reduced by hydrogen in the presence of Raney nickel.

114, 115: α-and α'-Amino Nicotine

The two isomes were obtained by the reaction of sodamide with nicotine dissolved in xylene (Tschitschibabin and Kirssanow, 1924). The α-amino nicotine was recrystallised several times from water (to remove α'-amino nicotine) and from ligroin. The α'-amino nicotine was purified by repeated recrystallisation of the hydrochloride from alcohol.

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