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SPECTROSCOPIC STUDIES OF SOME IMIDATE SYSTEMS

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A THESIS SUBMITTED TO THE CITY UNIVERSITY

BY

JOHN CHARLES HUGHES B.Sc.

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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SUMMARY

In order to investigate the bonding of the imino hydrogen, a number of imidates were prepared and the infra-red spectra of the vapour, liquid and solution phases recorded, the N.M.R. spectra were studied and dipole moments measured. Results were interpreted in terms of the imino hydrogen being intermolecularly bonded in the aliphatic imidates, sterically hindered in the benzimidates and intramolecularly bonded in the trichloroacetimidates. The shoulder on the νNH mode in the infra-red spectra of benzimidates and phenylacetimidates is believed to be a νC=N overtone and not due to the presence of intermolecularly bonded species. Complete assignments of the infra-red spectra were also attempted.

Multiple regression analyses have been performed to relate the infra-red solvent effect shifts with the physical parameters of the solvents used for the νC=O vibration of a wide variety of carbonyl solutes. Relationships have been empirically deduced which have been shown to be statistically more favourable than the Buckingham or KBM relationships for carbonyl solutes. The order of the solvent molecules, as described by the standard entropy S^0, or E_T value of the solvent, and the distance of approach of the solvent molecule appear more important than solvent-solute interaction effects.

From a study of the infra-red spectra of phthalic anhydride in solution at various temperatures the bands associated with the νC=O modes have been identified.

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CHAPTER 1

The Structure and Spectra of Imidates

A. IMPORTANCE AND USES

Despite the great biological importance of the C=N group, the azomethine group, as a structural unit, the physico-chemical data available for this system is considerably less than for the analogous carbonyl and ethylenic groupings. It was this lack of physico-chemical data, spectral data in particular, that prompted this present study of a group of azomethine compounds, namely the imidates.

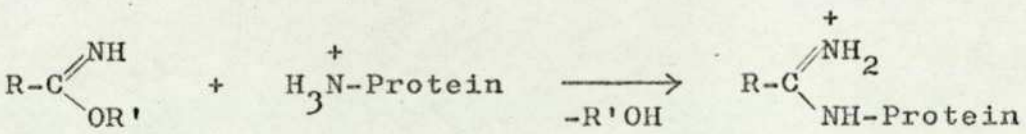
As a group, the imidates, imino esters, imino ethers or imidic acid esters as they have variously been called, have been known for nearly a century.[1] They remain, however, a group of compounds which have received relatively little attention, and whose spectra (1.E), have not been fully explored.

While studies have been made on the effect of acid-base catalysts on the yields of hydrolysis products of the imidates,[2] much of the present interest would seem to be centered on the uses of imidates as intermediates in organic syntheses and polymerisation processes.

Synthetically, interest has been stimulated by the relatively easy conversion of imidates into substituted triazines.[3,4,5] The triazines themselves, are potentially useful in that they offer preparative routes to dyestuffs, whitening agents, resins, pesticides, surface active agents and medicines.[6] Similar syntheses of triazoles,[7] also offer preparative routes

to thermally stable polymers.[8]

Biochemically, the use of imino esters as starting materials for peptide synthesis[9] and modification of proteins by reaction with imino esters under relatively mild conditions[10-17] may prove important.



Condensation of imidoesters of higher fatty acids with diamino compounds produces products whose salts are soluble in water and are of reported therapeutic value,[18] while, more recently, it was noted that imidic esters react with bovine kallikrein inactivator to give crosslinked protein blood coagulents.[19]

Cordes and Neubauer[20,21] studied the condensation of imino ethers with aldehydes in the presence of substances, such as ureas, which may condense with aldehydes. Products obtained included a yellow resin which could be moulded at 100°C under pressure, a glue for wood and paper, and resins suitable for use as adhesives, or additives for adhesives. Imidatosilanes are used as room temperature vulcanisers.[22]

Of greatest potential, however, may be the preparation of perfluoroacyl imidates[23,24] and their subsequent polymerisation.[25,26] If one considers the properties of nylon and P.T.F.E., a crosslinked polymer containing fluoro groupings,

which would result from perfluoroimidate polymerisation, could have very desirable properties.

B. SYNTHETIC PREPARATION OF IMIDATES

The majority of preparations of imidates have been based on the Pinner synthesis.[27] This synthesis is performed in two stages, firstly the condensation of an alcohol and a nitrile under anhydrous conditions in the presence of hydrogen chloride or hydrogen bromide gas to give the imidate hydrohalide:-

$$RCN + R'OH + HCl \longrightarrow R\text{-}C(NH.HCl)OR'$$

In the second stage, to be discussed later, the imidate is released from the hydrohalide.

Pinner's work,[1,27] which follows chronologically an unsuccesful attempt by Beckurts and Otto[28] to prepare imidates by this method, was important in establishing not only the major method of preparation, but also in elucidating the properties and reactivity of the compounds.

The reaction is normally carried out at, or below, 273K in the presence of a diluent. This diluent is usually an inert solvent, but in certain cases an excess of the alcohol has been used as a diluent,[29-31] but this is likely to be conducive to ortho ester formation (see 1C) and may be difficult to remove in the case of the higher boiling aliphatic alcohols. Although the use of anhydrous chloroform,[29] dioxan[32] and benzene[27,29,33] have been reported, diethyl ether[27,34-37] would appear to be the most succesful diluent.

Ethanol and methanol generally give good yields in the Pinner synthesis, while satisfactory yields involving n-propyl,[38] iso-propyl,[39] butyl,[38] isobutyl,[1] and benzyl[40] alcohols have been reported. Extensions of the method to glycols[41,42] and mercaptans[43-45] have also been made, while phenyl chloroacetimidate hydrochloride has been prepared using chloroacetonitrile and phenol as the starting materials,[46] although it is not indicated whether the free imidate can be obtained.

The conversion of the hydrochloride into the free imidate was originally performed by treating the imidate hydrochloride, suspended in ether, with a concentrated aqueous solution of potassium carbonate.[27] As mentioned later (see 1C) the imidate hydrochlorides are relatively easily hydrolysed to the corresponding normal esters, and hence the use of an aqueous medium for the release of the imidate from its salt is likely to result in the presence of impurities. The hydrolysis is relatively quick in the case of the lower aliphatic members, which tend to be hygroscopic[27,47] but the use of aromatic nitriles confers greater stability to hydrolysis.[48] Despite the hygroscopic nature of the lower aliphatic imidate hydrochlorides, the free imidates have still been prepared in a highly pure state using the original method, by concentrating the potassium carbonate solution until it had the consistency of a paste and performing the reaction at lower temperatures.[49]

In 1960, Reynaud and Moreau[36] reinvestigated the reaction, in an ethereal medium, between ammonia and imidate hydro-

chlorides. This reaction has been extensively used as a method of preparing amidines.[50] Reynaud and Moreau noticed that mechanistically the preparation of amidine hydrochlorides from imidate hydrochlorides had been shown to occur in two stages:-[51]

A) $R\text{-}C(=NH.HCl)(OC_2H_5) + NH_3 \longrightarrow R\text{-}C(=NH)(OC_2H_5) + NH_4Cl$

B) $R\text{-}C(=NH)(OC_2H_5) + NH_4Cl \longrightarrow R\text{-}C(=NH.HCl)(NH_2) + C_2H_5OH$

Reynaud and Moreau showed that, if the temperature was maintained at 258K and the ammonium chloride formed filtered off at this temperature, the reaction could be halted at the end of the first stage, i.e. with the preparation of the pure imidate. Using this method, Reynaud and Moreau,[36,37] successfully prepared a variety of imidates in good yield. The obvious advantage of the method is that the reaction is performed in a non-aqueous medium, thereby reducing the probability of hydrolysing the imidate hydrochloride. This method has been adopted for the majority of the preparations described in Chapter 2B.

The hydrochlorides derived from trichloroacetonitrile, i.e. $Cl_3C.C(=NH,HCl).OR$, are instantaneously unstable at room temperature,[52] undergoing the Pinner rearrangment (see 1C).

Generally the stability of the hydrochloride is decreased by an electron acceptor grouping on the acid part of the hydorhalide and increased by electron acceptor substituents on the alcoholic part. Preparatively, the instability of the hydrochloride is of academic interest only, as trichloroacetonitrile reacts directly on refluxing with methanol[53,54] to give the imidate:-

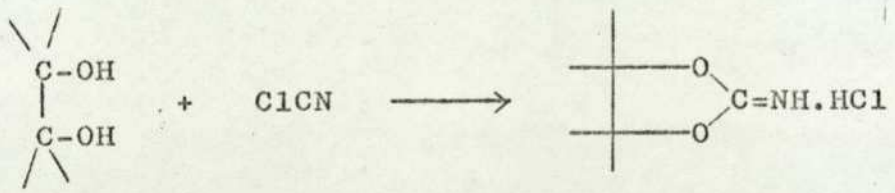
$$Cl_3C.CN + CH_3OH \longrightarrow Cl_3C.C(=NH).O.CH_3$$

This reaction would appear to be a particularly favourable example of the normal base catalysed, reaction of nitriles with alcohols which has been investigated by Marshall and Acree[55] and Schaefer and Peters.[56] Schaefer and Peters confirmed, using a Taft factor/equilibrium constant correlation, that the yield of imidate was dependent on the electronegativity of the nitrile substituent. The reaction was found to give inadequate conversion with benzonitrile and simple aliphatic nitriles. Low yields were also obtained when the presence of large groupings on the nitrile hindered the reaction.[56]

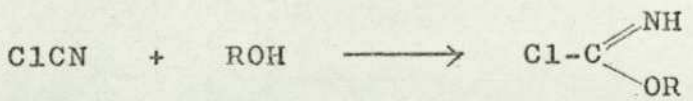
The yield is also affected by the choice of catalyst. The reaction between trichloroacetonitrile and methanol, which is particularly favourable due to the electronegativity of the CCl_3 grouping, may be catalysed by basic impurities in the reactants or reaction vessel. This would appear to be confirmed

by the work of Cramer et al[57] who prepared a series of trichloroacetimidates by refluxing trichloroacetonitrile with a variety of aliphatic alcohols in the presence of basic catalysts. In the preparation of eighteen such compounds, five catalysts, potassium carbonate, potassium tetrabenzylaluminate, sodium n-butylate, sodium n-octylate and lithium iso-propylate, were used. An attempt to prepare ethyl trichloroacetimidate without the use of a catalyst, during the present work, was unsuccessful, confirming the necessity of a basic catalyst.

For the purposes of the present work, interest was mainly centered on the preparation of simple molecules and on systems in which conjugation and intra- or intermolecular bonding could be studied. In this respect, the formation of a cyclic iminocarbonate by the addition of cyanogen chloride to vicinal diols:-[58]



Suggested the following interesting preparation:-



Unfortunately it would appear that the reaction will

proceed further to give the N-cyano imidate[59] or iminocarbonate.[60] Shaefer and Huffman[59] found that N-cyano imidates were the products when imidates or imidate hydrochlorides were treated with cyanogen chloride at 273K in anhydrous ether:-

$$RC(=NH.HCl)OR' + ClCN \longrightarrow RC(=NCN)OR' + 2HCl$$

$$RC(=NH)OR' + ClCN \longrightarrow HCl + RC(=NCN)OR'$$

Hedayatullah and Denivelle,[60] however, found that cyanogen halides reacted with phenols to give iminocarbonates:-

$$ArOH, ArONa + XCN \longrightarrow (ArO)_2C=NH$$

Analogous behaviour might be expected if the phenol was replaced by an alcohol.

Preparatively, the use of the base catalysed method for the formation of perfluoroacyl imidates[23,24] may prove important due to the previously discussed use of these as polymer intermediates (see 1A).

Finally, in this section, a mention is made of a recent new method of preparation.[61,62] The original paper[61] described the preparation of ethyl formimidate hydrochloride, ethyl acetimidate hydrochloride and ethyl caprolactimidate hydro-

chloride by the reaction of ethyl chloroformate with formamide. Suydam et al[62] extended this method to cover the reaction between ethyl chloroformate and aliphatic amides:-

$$RCONH_2 + EtOCOCl \longrightarrow RC(=NH.HCl)OEt + CO_2\uparrow$$

This method was not pursued, due to the general suitability of the Pinner method, and its inapplicability to benzimidates and phenylacetimidates. The method may, however, prove to be as good as the Pinner method for simple aliphatic imidates, although the greatest potential is in the preparation of N-substituted derivatives.

C. PROPERTIES OF IMIDATES AND IMIDATE HYDROCHLORIDES

The chemical properties presented in this section are not intended to be exhaustive (for a wider investigation of the reactions of imidates, the work of Baccar[63] should be consulted). An attempt has been made to collect together those properties which have a direct bearing on the stability of imidates or are associated with the preparation of derivatives, from imidates, which might be interesting from a spectroscopic standpoint.

1) The imidate hydrochlorides have limited stability.[27,64] Decomposition back to the original nitrile and alcohol (A), conversion into esters by hydrolysis (B) and formation of ortho esters by warming the hydrochloride with excess alcohol(C) have all been reported.

$$R\text{-}\underset{\underset{OR'}{|}}{C}\text{=}NH.HCl \xrightarrow{\Delta} RCN + R'OH + HCl \qquad .....(A)$$

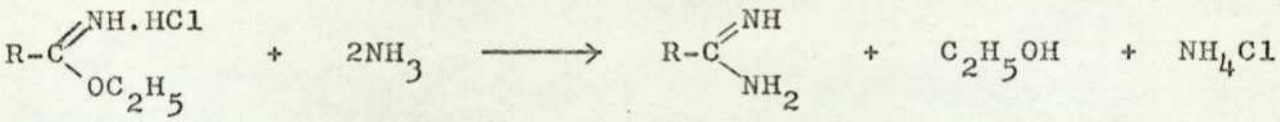
$$R\text{-}\underset{\underset{OR'}{|}}{C}\text{=}NH.HCl + H_2O \longrightarrow RCOOR' + NH_4Cl \qquad .....(B)$$

$$R\text{-}\underset{\underset{OR'}{|}}{C}\text{=}NH.HCl + 2R'OH \longrightarrow RC(OR')_3 + NH_4Cl \qquad .....(C)$$

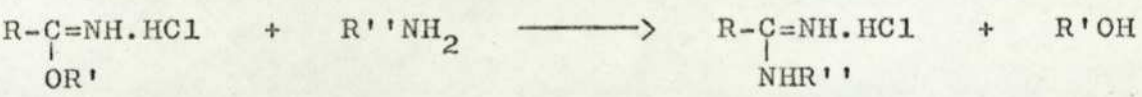
Of these reactions the hydrolysis of the hydrochlorides

to esters is particularly relevant to the present work. The original Pinner synthesis[1] must always suffer from the use of an aqueous medium for the preparation of the imidate from its hydrochloride. The hydrolysis is acid catalysed,[27] so that the use of potassium carbonate is advantageous, while the low temperature and high concentration of the aqueous solution are both designed to minimise hydrolysis.

2) Imidate hydrochlorides react with ammonia at room temperature to give amidines:-

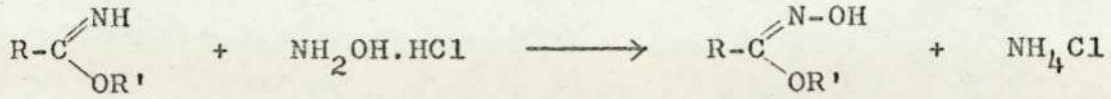


Extension of the above reaction to primary amines can be used as a preparative route to mono-substituted amidines.[27,65]

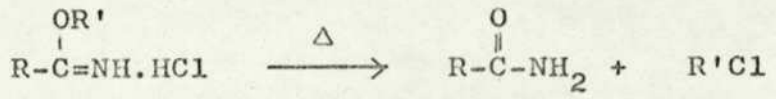


3) N-chlorosubstituted imidates are formed by the action of sodium hypochlorite on an imidate hydrochloride.[66]

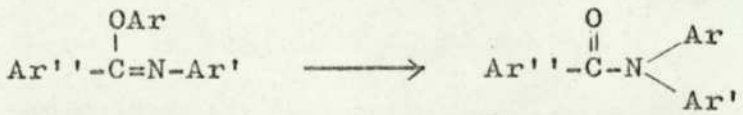
4) N-hydroxy imidates are formed by the action of hydroxylamine hydrochloride on a free imidate, usually in ethereal solution:-[66]



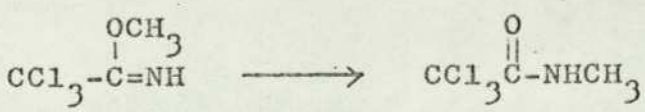
5) When imidate hydrochlorides are heated, cleavage occurs. This reaction, known as the Pinner fission, has been studied, amongst others, by McElvain[67] and Cramer[68] and is thought to invclve nucleophilic attack by the chloride ion on the protonated imidate:-



6) The thermal conversion of N-aryl benzimidates to N-aroyl diphenylamines is known as the Chapman rearrangement[69-71]



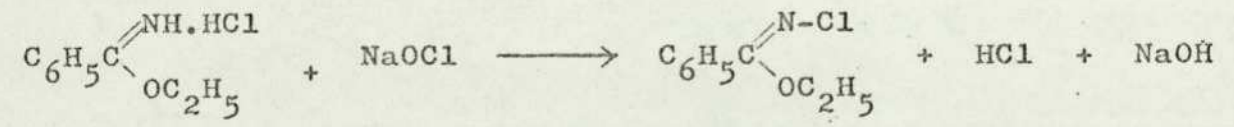
Cramer and Hennrich[72] studied the extension of this reaction to trichloroacetimidates, and found that boron trifluoride acted as an excellent catalyst.



D. SYNTHESIS OF N- HALOGENO-IMIDATES

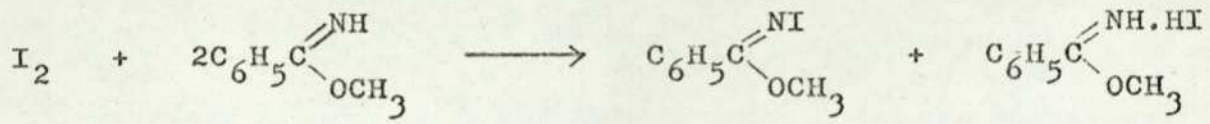
Many references in the literature are made to imidoyl chlorides (R.C(=N.R).X)and it has been decided to briefly define and contrast these compounds with the N-halogeno-imidates. In the imidoyl halides, the halogen group is attached to the carbon atom of a C=N bond and not to the nitrogen atom as in the N--halogeno-imidates. In the imidoyl chlorides the reactivity of the halogen is akin to that in acid chlorides, and as such they provide useful intermediates in the synthesis of numerous nitrogen containing derivatives. They are also employed as intermediates in several classical reactions including the Gattermann, Houben-Hoesch and Vilsmeier-Haack syntheses.[73] In contrast the N-halogeno-imidates, are a relatively neglected group of compounds, which would appear to be more stable than the parent imidate.

Preparatively, the most successful method is due to Stieglitz.[74,75] In the original preparation, ethyl benzimidate hydrochloride[74] was treated with sodium hypochlorite solution. This method was extended by Hilpert,[76] and later Houben and Schmidt[66,77,78] to include other N-chloro and N-bromo imidates.



Despite this early interest the N-halogeno-imidates are not well characterised.[79]

An alternative method of preparation, due to Wheeler and Walden,[80] involves the reaction between two molecules of an iminoester with one molecule of halogen (specifically iodine or bromine). The reaction yields the N-halogeno-imidate together with the hydrohalide of the imidate.



The reaction is slow; the above reaction mixture requires warming on a water bath for several days and careful purification of the product is required.

More recently Baumgarten et al[81] treated free iminoesters with t-butyl hypochlorite to give N-halogenoimidates, but the yield obtained was less than by the Steiglitz method.

E. SPECTRA OF IMIDATES

Amongst compounds containing the azomethine grouping, the imidates in particular remain spectroscopically neglected possibly on account of their difficulty of preparation. N.M.R. data have only been included in two previous studies and the results of these will be discussed in Chapter 3C together with the N.M.R. data obtained in the present study.

Data are available for the ν (C=N) of a variety of compounds (Table 1).

Table 1

Carbon-Nitrogen stretching wavenumber positions of various molecules containing the azomethine grouping.

Compound or group of compounds	Band position or wavenumber spread (cm^{-1})	Reference
Imidoyl chloride	1689	(82)
Aromatic Schiff Bases e.g. N benzlidineaniline	1613-1630	(83)
Cyclic imidic esters	1650-1670	(84)
Aldimines	1674-1664	(85)(87)
Formaldoxime	1642	(86)
N hydroxyl methyl benzimidate	1630	(88)
N benzoyloxy methyl benzimidate	1620	(88)

These data, and the compilations by Fabian, Legrand and Poirier[89,90] show a remarkable consistency in the wavenumber position of the ν(C=N) peak. More recently, Melendez and Sanchez del Olmo[91] have studied the influence of substituents on the wavenumber position of the ν(C=N) mode in seventeen imines (R-N=CR'R''). A reduction of 20-30cm^{-1} was observed for each phenyl group introduced. This information was useful in confirming the position of the ν(C=N) vibration in methyl and ethyl benzimidates. Fabian and Legrand[89] quote the wavenumber position of the ν(C=N) in N-(n-propylidene)-n-propylamine in carbon tetrachloride and chloroform respectively as 1673 and 1671cm^{-1} and suggest that the ν(C=N) mode is little affected in position by the nature of the solvent. A similar finding was made by Suydam.[87]

Spectrally the ν(C=N) mode would thus seem to be well characterised and this is no exception in the imidate systems. The importance of the ν(C=N) and ν(NH) bands from a structural point of view, however, has led workers to study these bands exclusively. Much of the data available was recorded many years ago.

Historically, the work of Kohlraush and Seka[92] in the field of imidates is of major importance. Their original paper includes data on ethyl and n-propyl acetimidates, ethyl propionimidate, and methyl and ethyl benzimidates. By comparison with the Raman spectra of esters and amides, the position of the ν(C=N) mode was established in the range

1648-1655cm^{-1} for the five imidates, whilst the ν(NH) mode was identified at 3327-3336cm^{-1}. Whilst no further assignment was attempted, Kohlraush and Seka gave complete unassigned spectra.

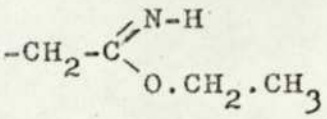
Early infra-red studies by Lenormant[93] and Gierer,[94] and Raman studies by Sannie and Poremski[95,96] were mainly concerned with the evidence of resonance in amides. Other early Raman work by Shigorin and Syrkin[97] on the C=N band, was later extended to include the imidate hydrochlorides.[98] Kirman and Laurent[85] observed a Raman band in imidates at 1655cm^{-1}.

After these early studies which were chiefly aimed at elucidating the structure of imidates, very little was published concerning imidate spectra until 1960.

Cramer et al,[57] prepared a number of trichloro-acetimidates by the base catalysed reaction of alcohols with trichloro-acetonitrile. The infrared spectrum was measured in each case, in what was essentially a paper on organic synthesis, in order to characterise the products of reaction. Cramer identifies two bands in the spectrum at 2.98 $\pm$ 0.01μ (3336cm^{-1}) and 6.00 $\pm$ 0.02μ (1667cm^{-1}) as the ν(NH) and ν(C=N) modes. Shvekhgeimer and Shul'man[52] quote bands at 1675 and 3353cm^{-1} in $CCl_3.C{=}NHOCH_2CCl_3$, trichloroethyl trichloroacetimidate.

The spectra are not discussed in detail and these appear to be the only papers which mention the spectra of the trichloro acetimidates.

Reynaud and Moreau[37] investigated the infra-red and N.M.R. spectra of seven ethyl esters of aliphatic imidates in the region 3400-1300cm^{-1}. The data is presented in tabular form to show the similarity in position between the bands in various imidates and assignment is made of the ν (NH) (3275-3340cm^{-1}) and ν (C=N) vibrations (1640-1646cm^{-1}). The remaining eight bands in the region 1500-1300cm^{-1} were assigned as characteristic of the grouping:-



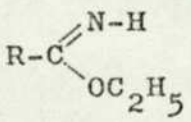
The paper provides some useful information on the higher wavenumber bands, but provides little assistance to the assignment of the skeletal bands. With the limited spectral range covered, many of the important bending modes of the molecule cannot be identified for comparison purposes, from the data.

Spinner[99] assigned the infra-red spectrum of methyl acetimidate hydrochloride and a detailed assignment of the free imidate appeared in 1967.[100] This latter assignment follows the assignment of the imidate by Prichard.[49] This was by far the most extensive work on the imidate spectra up to this time. By comparison of the N-chloro and N-hydroxy ethyl acetimidates with the parent compound, spectral trends and possible skeletal bands could be identified for the first

time.

Whilst Prichard concentrated on the acetimidates, a group of workers in France have studied the benzimidates and phenylacetimidate systems. Early work by Baccar et al[101-105] on the preparation and properties of benzimidates, phenylacetimidates and their derivatives culminated with the publication of a Thesis by Baccar in 1967.[63]

Included in this work were, however, preliminary spectral studies of eleven imidates of the type:-



where R = C_6H_5 (I), p-ClC_6H_4 (II), p-$CH_3C_6H_4$ (III), m-$CH_3C_6H_4$ (IV), p-$NO_2C_6H_4$ (V), o-$N\equiv C.C_6H_4$ (VI), β-$C_{10}H_7$ (VII), C_6H_5-CH=CH- (VIII), $C_6H_5CH_2$ (IX), p-$ClC_6H_4CH_2$ (X), o-$ClC_6H_4CH_2$ (XI)

The method of presentation of spectral data suggests that Baccar was mainly interested in the preparative chemistry of the imidates. N.M.R. spectra were presented in the liquid state and in carbon tetrachloride solution for four imidates (I, III, IX and XI), but no reference was made to

the shift of the imino hydrogen in solution. The infra-red spectra are mainly presented in diagramatic form, but, the position and intensity of the ν(C=N) and ν_{01}(NH) and its overtone are tabulated. Anharmonicities calculated from $2\nu_{01}-\nu_{02}$, were found to be of the same order (152-162cm^{-1}), in all the imidates studied.

Baccar's work appears, from subsequent publications to be part of an extensive study of the benzimidates and phenylacetimidates being undertaken at Toulouse University. Two papers by Pujol and Mathis[106,107] deal with solvent effects on the infra-red spectra of imidates. In the first paper,[106] the position of the ν(NH) band of the ethyl esters of butyrimidic(I), benzimidic(II), and phenylacetimidic(III) imidates was measured in fifteen solvents. A Bellamy, Hallam and Williams plot (B.H.W.) was made of the relative shift (νhexane - νsolvent)/νhexane, for the three imidates against pyrrole as a standard. From the slopes of these plots it was found that the acidity of the imidates increased in the order I<II<III. Pujol and Mathis noted that, in pyridine solution, ethyl phenylacetimidate exhibited two bands in the ν(NH) region. This was interpreted in terms of two stable conformations of the imidate in the liquid phase and this hypothesis will be discussed later (Chapter3B) in the light of the present work on solvent effects.

In the second paper,[107] solvent effect studies are extended to cover various substituted ethyl benzimidates.

A B.H.W. type plot was again made, using the data for the ethyl butyrimidate[106] as the standard in place of pyrrole. This produces a more linear plot as would be expected. There appears to be a rough correlation between the slope of these plots and the Hammett factor of the substituent. Neither paper, however, contains any ascertion to the mechanism of the shift or the degree of hydrogen bonding which prevails. It is also unfortunate that liquid phase and vapour phase values are not included for comparison.

The data originally obtained by Baccar[63] appears in a later paper[108] in which the results are discussed in greater detail. The N.M.R. data is used to support the hypothesis of two stable conformations in ethyl phenyl-acetimidate on the evidence of the splitting of the methylene group in carbon tetrachloride solution. A low temperature N.M.R. study might provide better evidence as to the existence of conformations in solution. These authors also used the work of Lumbroso et al[109] on the dipole moments of imidates to support their argument, and this, too, may be criticised, principally because the authors omitted to include structures with free rotation of the ethoxy grouping about the ether linkage in their calculations. Further observations, for example the lowering of the wavenumber position of the ν(C=N) in the benzimidates by 20cm^{-1}, endorse earlier ascertions. These authors also include data on imidates in a second paper[110] which draws the spectra of imidates into perspective with those

of their derivatives.

In the light of the spectral evidence which existed on commencement of the present work in 1969, it was decided to study imidates in four groups which can broadly be classified as:-

I Aliphatic imidates

II Benzimidates

III Phenylacetimidates

IV Trichloroacetimidates

The study was to involve vapour and liquid phase infrared spectra, solvent effect studies on the υ(NH) and υ(C=N) modes, dipole moment and N.M.R. studies, from which it was anticipated that a closer understanding of the spectra and structure of these compounds would result.

In the aliphatic imidates only ethyl propionimidate was fully studied as Prichard[49] had already obtained reliable data in a form suitable for comparison. In the trichloroacetimidates, where pure samples were more easily prepared, methyl, ethyl and n-propyl esters were prepared in order to observe if there was a linear shift in any of the lower wavenumber skeletal modes with the ester substituent.

Attempts were made to prepare some N-chloro derivatives as there appeared to be only one previous assignment of an N-chloro imidate.[49] Baccar[63] shows the spectrum of N-chloro ethyl benzimidate diagramatically but no measurements of the wavenumber positions of bands or assignments are given,

although later[110] the ν(C=N) mode is assigned at 1600cm^{-1}. Very few assignments of υ(N-Cl) modes have been made.

CHAPTER 2

Preparation of Imidates-

Experimental details.

A. PURIFICATION OF REAGENTS

The cyanides used in the preparation described in Chapter 2B were dried over phosphorus pentoxide and distilled from the drying agent. The alcohols were dried by a Grignard type reaction[111] in which a quantity of the alcohol was refluxed with magnesium and iodine. After the bulk of the iodine had reacted, as indicated by a slight paling of the solution, reflux was continued for two hours, before distillation of the dry alcohol. The diethyl ether was stored over sodium wire and decanted before use.

The majority of the solvents used for the solvent effect studies were stored over 0.5nm molecular sieve, which was heated for at least one day in an oven at 393K and cooled in a desiccator before use. Spectroscopic grade solvents were used whereever possible, otherwise the purest grade available was purified by a standard method. Carbon disulphide was used without any drying because molecular sieve appeared to cause decomposition of this solvent.

Chloroform was purified by passing repeatedly through a tower containing alumina, Brockmann activation 1, which had been stored in an oven for at least 24 hours at 393K before use. The spectrum of the purified chloroform was recorded before use.

Pyridine was stored over potassium hydroxide pellets and redistilled before use.

By using this scheme of drying the solvent effects on the ν(ND) mode of methyl trichloroacetimidate-d_1 were successfully measured. The additional precaution of storing the solvents in a dry box with their desiccants for two days before use was made. The carbon disulphide was dried with molecular sieve for this experiment alone, but the contact time with the desiccant was limited to one day only. From this it was concluded that the drying scheme was sufficient. All the experiments relating to a particular solute were performed on one occasion using the same instrumental settings throughout. An accuracy of $\pm 1 cm^{-1}$ was associated with the measurement of any sharp peak, by using the equipment described in Chapter 2C, while the error may approach $\pm 5 cm^{-1}$ with very broad bands.

B. PREPARATION

1. Methyl Trichloroacetimidate

This was prepared by the original method described by Steinkopf.[54] Trichloroacetonitrile was refluxed with an excess of dry methyl alcohol (approximately 2:1 by volume), and the mixture heated under reflux for two days. During the period of reflux a drying tower packed with a mixture of phosphorus pentoxide and glass wool was attached to the head of the column to prevent moisture from reaching the reaction mixture. At the end of this period the reaction mixture had taken on a pale pink hue and the pungent odour of the cyanide had disappeared. The excess alcohol was then distilled off at atmospheric pressure, using a pig to facilitate solvent collection and connection of a drying tower. The residual liquid was fractionally distilled under reduced pressure as the liquid showed signs of decomposition near its boiling point at atmospheric pressure. A final redistillation under reduced pressure was performed on the middle fraction of the above distillation.

Methyl trichloroacetimidate is a colourless liquid with a sweet terpenoid odour.

Boiling point	(1mm Hg)	308K	
Boiling point	(761mm Hg)	424-427K	
Literature value	(760mm Hg)	421-422K	(54)

n_D^{298} 1.4763

A sample of material was analysed using an F and M, Carbon, Hydrogen Nitrogen Analyser, Model 185, with the following results:-

Carbon 20.5% Nitrogen 8.4% Hydrogen 2.7%

Theoretical percentages:-

Carbon 20.4% Nitrogen 7.9% Hydrogen 2.3%

Oxygen 9.1% Chlorine 60.3%

2. Ethyl Trichloroacetimidate

Cramer et al[57] prepared ethyl trichloroacetimidate using potassium tetrabenzloxyaluminate as a catalyst for the reaction between ethyl alcohol and trichloroacetonitrile. Using the method outlined in 2.B.1, and potassium carbonate as catalyst, a high yield of the imidate was prepared, the reaction mixture being a wine-red colour on completion of the reaction.

Ethyl trichloroacetimidate is a colourless liquid with an odour reminiscent of the methyl ester.

Boiling point	(5mm Hg)	317K	
Literature value	(13mm Hg)	330.5K	(57)
	n_D^{298}	1.4661	

Results of elemental analysis:-

Carbon 24.9% Hydrogen 3.09% Nitrogen 7.05%

Theoretical percentages:-

Carbon 25.2% Hydrogen 3.15% Nitrogen 7.35%

3. n-Propyl Trichloroacetimidate

The method utilised in 2.B.1 was again followed using n-propyl alcohol, trichloroacetonitrile, and potassium carbonate as catalyst. The inclusion of catalyst (1g. to 1molar quantities) was sufficient to ensure complete reaction as was evidenced by the absence of the pungent odour of trichloroacetonitrile. The inclusion of the catalyst served to make the final vacuum distillation stage more difficult, due to increased bumping. By using a packed column, the middle fraction was collected and redistilled under reduced pressure, various fractions being collected. Each fraction was checked by obtaining its infra-red spectrum.

n-propyl trichloroacetimidate is a colourless liquid which possesses the same sweet terpenoid odour as the methyl and ethyl esters.

Boiling point	(1mm Hg)	307-309K	
	(2mm Hg)	315K	
	(748mm Hg)	411K	
Literature value	(12mm Hg)	344K	(57)
	n_D^{293}	1.4618	

No C, H, N data were available for this material. The spectral and physical data presented are consistent with the expected properties of n-propyl trichloroacetimidate.

4. Methyl Trichloroacetimidate-d_1

The method outlined in 2.B.1 was repeated using methanol-d_1, CH_3OD. The reaction was expected to proceed to give methyl trichloroacetimidate in which deuteration had occured at the imino nitrogen, this compound being referred to as methyl trichloroacetimidate-d_1 throughout.

The procedures associated with the exclusion of moisture were again followed. The final product was stored in a dry box and all operations concerned with the preparations of samples for spectroscopic studies were performed therein. The infrared solvent studies were performed using solvents dried over molecular sieves and stored in a dry box for a period of not less than 48hours. The stability of the resulting product to isotopic exchange appeared to vary between the samples prepared, presumably due to the presence of impurities which catalysed the exchange.

Boiling point (1mm Hg) 308K

Only one distillation was performed due to the small volume of sample available in each case. The odour of the deuterated material appeared to be identical to that of the non-deuterated form. Elemental analyses were not performed, however, a sample was left to exchange in air, whence it was found to assume a spectrum indistinguishable from that obtained for methyl trichloroacetimidate.

5. Methyl Benzimidate

20g of methanol, 61.5g of benzonitrile and 100g of ether were placed together in a two-necked round-bottomed flask. The flask was cooled by an acetone-dry ice bath and hydrogen chloride gas was passed into the reaction mixture at a rate sufficient to ensure that the temperature was maintained at or below 253K, until the weight of the flask had increased by approximately 20g. The flask was then left stoppered in a refrigerator at 273K for several days to allow the hydrochloride to crystallise.

The ether was decanted off, and the hydrochloride washed with chilled ether to remove any unreacted starting materials and the cake was broken up (the flask was cooled by an ice/salt mixture at this stage).

Another flask was filled with 200ml of ethyl ether and cooled to 253K by an acetone/dry ice bath. Ammonia gas was slowly bubbled through the ether and the hydrochloride added, again care being taken to ensure that the temperature did not rise appreciably above 253K. Fumes of ammonium chloride were evolved, both from reaction with the hydrochloride and with excess trapped hydrogen chloride gas. The reaction was continued until, after the addition of all the hydrochloride, and continued bubbling of ammonia, no more ammonium chloride was seen to be evolved. A little of the liquor was removed and checked for alkalinity with moistened litmus paper. The mixture was rapidly filtered, the filtrate being dried over

anhydrous sodium sulphate for 24hours. The excess ether was distilled off on a water bath at atmospheric pressure using a drying tower to prevent moisture entering the distillation equipment. The residue in the flask was distilled under reduced pressure and the fractions collected.

Methyl benzimidate is a colourless liquid, with a characteristic odour, slightly phenolic in nature.

Boiling point	(1mm Hg)	316-318K
Boiling point	(767mm Hg)	479-481K
n_D^{295}	1.5436	

Distillation at atmospheric pressure was accompanied by decomposition, as was instanced by darkening (reddening) of the kettle residue.

Results of an elemental analysis:-

Carbon 71.73% Hydrogen 6.15% Nitrogen 10.36%

Oxygen (by difference) 11.76%

Theoretical percentages:-

Carbon 71.09% Hydrogen 6.71% Nitrogen 10.36%

Oxygen 11.84%

6. Ethyl Benzimidate

This was prepared as described in 2.B.5 using ethyl alcohol and benzonitrile as the reactants. The product was a colourless liquid with a pleasant, slight phenolic odour.

Boiling point	(1mm Hg)	315-316K

The results of a C, H, N elemental analysis were :-

Carbon 73.1% Nitrogen 9.55% Hydrogen 7.51%

Oxygen (by difference) 9.84%

Theoretical percentages:-

Carbon 72.4% Nitrogen 9.40% Hydrogen 7.38%

Oxygen 10.74%

7. Ethyl Phenyl Acetimidate

This was prepared by the method described in 2.B.5 using phenyl acetonitrile and ethanol as the starting materials. The product was a colourless liquid with a pleasant odour.

Boiling point (10mm Hg) 399K

(764mm Hg) 499K with decomposition

n_D^{290} 1.5125

The results of an elemental analysis were:-

Carbon 73.84% Nitrogen 8.51% Hydrogen 8.06%

Oxygen (by difference) 9.59%

Theoretical percentages:-

Carbon 73.62% Nitrogen 8.59% Hydrogen 7.98%

Oxygen 9.82%

8. Ethyl Propionimidate

Ethyl propionimidate was prepared by the method described in 2.B.5 using propionitrile and ethyl alcohol as the starting materials. The imidate was quite unstable as evidenced by the presence of increasing amounts of carbonyl impurity in the

infra-red spectrum which appeared on standing, even with storage of the imidate in a desicator.

Ethyl propionimidate is a colourless liquid with an odour similar to impure acetamide.

Boiling point (13mm Hg) 327K

A C, H, N analysis to support the spectral evidence proved unsatisfactory as the sample was too volatile and too unstable to give consistent peaks for any of the elements.

It was decided to make use of the ester impurity present in the imidate after standing as a criterion of purity. By using a six foot, $\frac{1}{4}$" polyethylene glycol column, at 313K, a GLC was performed to give two peaks, 9.5cm and 14.7cm along the chart. A mass spectrum of both components was run on an A.E.I. M.S.20 spectrometer using identical scale settings for both spectra. Using the Nitrogen 28 and Oxygen32 peak it was possible to show that the mass numbers of these components corresponded to 101 and 102 respectively. These figures correspond to the atomic masses of ethyl propionimidate and ethyl propionate, the latter being the smaller of the two peaks in the GLC.

9. Methyl Acetimidate

This was prepared in the manner described in 2.B.5, using methyl alcohol and acetonitrile as the starting materials. This compound had already been extensively studied by Prichard[49,100] and was prepared to obtain data for solvent

effect studies on the imino stretching mode in the infra-red spectrum. The infra-red spectrum was consistent with published data.[100]

10.. N-Chloro Ethyl Benzimidate

Ethyl benzimidate hydrochloride was prepared as described in section 2.B.5. After washing with ether, the crushed hydrochloride was added to an excess of a 10% sodium hypochlorite solution maintained at or near 273K by an ice-salt bath.

On the addition of the hydrochloride, bubbling occured and a yellow oil separated. The impure N-chloro ethyl benzimidate was extracted with three 50ml portions of ether and dried over anhydrous sodium sulphate before removal of the ether on a water bath. Distillation under reduced pressure yielded a colourless liquid with an almond-like odour and lachrymatory powers.

Boiling point (1mm Hg) 340-342K

n_D^{296} 1.5424

On heating at atmospheric pressure (758mm Hg), the liquid steadily darkened to give a dark red liquid. Distillation was continued until 433K at which temperature the spectrum of the product showed strong ν (C≡N) and ν (C=O) peaks, and further distillation was thought to bear little information on the boiling point of the pure product.

To augment the spectral evidence a sodium fusion was

performed.[113] The results confirmed the presence of nitrogen and chlorine and the absence of sulphur.

Results of the C, H, N analysis were:-

Nitrogen 7.42%. Carbon 58.7% Hydrogen 5.35%

Theoretical percentages:-

Nitrogen 7.63% Carbon 58.86% Hydrogen 5.45%

Oxygen 8.72% Chlorine 19.35%

11. N-Chloro Ethyl Propionimidate

N-chloro ethyl propionimidate was prepared by the method described in 2.B.10 using ethanol and propionitrile. It is a colourless liquid with a pungent fish-like odour and has lachrymatory powers.

Boiling point (4mm Hg) 304K

(758mm Hg) 415-417K

n_D^{298} 1.4400

Elemental analysis gave:-

Carbon 44.29% Hydrogen 7.53% Nitrogen 9.58%

Theoretical percentages:-

Carbon 44.28% Hydrogen 7.38% Nitrogen 10.33%

Oxygen 11.81% Chlorine 26.20%

12. N-Chloro Methyl Trichloroacetimidate

An attempt was made to prepare the N-chloro derivative for comparison purposes. Preparation of the hydrochloride

was unsuccessful. The instability of the hydrochloride was found to be consistent with the work of Shvekhgeimer and Shul'man[52] who showed that alkyl trichloroacetimidate hydrochlorides are completely unstable at room temperature.

13. N-Chloro Methyl Acetimidate

The preparation followed the method described in 2.B.10. The product was a colourless liquid, with an unpleasant fish-like odour and lachrymatory properties. It appeared quite stable.

Boiling point	(17mm Hg)	335-336K
	(751mm Hg)	380-381K
n_D^{298}	1.4345	

Results of the duplicate elemental analysis were unreliable. Separate analyses below indicate the range encountered:-

Hydrogen 5.24%	Carbon 33.07%	Nitrogen 12.99%
Hydrogen 6.00%	Carbon 33.02%	Nitrogen 13.49%

Theoretical values:-

Hydrogen 5.58%	Carbon 33.49%	Nitrogen 13.2%

C. INSTRUMENTAL AND EXPERIMENTAL TECHNIQUES

1. N.M.R. Spectra

The N.M.R. spectra were recorded on a Perkin Elmer R10 instrument. Samples of pure liquid were recorded using T.M.S. (1%) as an internal standard. In each case an attempt was made to perform all the measurements on one solute in one solvent, i.e. at all solute concentrations, during the course of a day. In this way, it was hoped that bias errors, bias being used here in a statistical sense, would affect all readings equally and the trend itself would then be a true one. In the plots presented in 3.C some gaps occur where remeasurement of the results at a later occasion revealed a larger spread than the $\pm$0.02ppm accepted.

All samples were allowed to reach the temperature of the magnet before readings were taken, this was generally a period of 15-30 minutes during which the position of the T.M.S. peak was seen to shift against the field, equilibrium being deemed to have been reached when the T.M.S. peak could be stabilised on 10ppm (τ scale).

2. Infra-red Spectra

All spectra in the region 4000-400cm^{-1}, with the exception of that of methyl trichloroacetimidate, were measured on a Perkin Elmer 457 spectrometer. For the methyl

trichloroacetimidate a Beckmann I.R.9 instrument was used for the liquid and solvent effect spectra and a Grubb Parsons G.S.2 double beam grating spectrometer for the vapour spectra. The accuracy of the Beckmann I.R.9 instrument is probably greater, although the wavenumber position of the peaks did not vary by more than $\pm 1cm^{-1}$ from the values obtained later for methyl trichloroacetimidate, except in the region 1900-$2700cm^{-1}$ where no calibration was performed.

The liquid phase spectra were measured over the range $4000-600cm^{-1}$ as a film between potassium bromide or sodium chloride discs. The former were useful in allowing the relative intensities of peaks below $600cm^{-1}$ to be compared, while the sodium chloride plates generally produced a better base line in the region $4000-3000cm^{-1}$. The region $2800-1800cm^{-1}$ was also investigated using 0.1mm, 0.025mm and 1.0mm cells. All absorptions observed in this region were very weak. The intensity of the peaks in the remainder of the spectrum has been classified into very strong(v.s.), strong (s), medium(m), weak(w) and very weak(v.w.). The spectrum of the plates was recorded before each measurement. The spectrometer was calibrated for each run using the following wavenumber positions as standards:-

Indene:- $3139.5cm^{-1}$, $1361.1cm^{-1}$, $1018.5cm^{-1}$, $830.5cm^{-1}$, $590.8cm^{-1}$, $381.4cm^{-1}$.

Polystyrene:- $2850.7cm^{-1}$, $1583.1cm^{-1}$, $1154.3cm^{-1}$, $906.7cm^{-1}$.

These peaks were chosen from those suggested for calibrating spectra,[114] as being of suitable shape and intensity for reproducible calibration. Spectra were recorded initially using a medium scan speed in order to determine the approximate positions of the peaks and their intensities. The regions containing peaks were then investigated using the x10 SLOW expansion provision on the spectrometer. By using this provision the scale was expanded to $1cm^{-1}$/mm in the region $4000-2000cm^{-1}$, and $0.5cm^{-1}$/mm in the region below $2000cm^{-1}$. Measurement of the spectra was made from wavenumber marks which occured every $100cm^{-1}$ in the region $4000-2000cm^{-1}$ and every $50cm^{-1}$ below $2000cm^{-1}$. Each spectrum was scanned three times, using different samples of the imidate if available and the average position of each peak found. Because of the proximity of certain peaks to the wavenumber mark it was necessary to switch off the marker in the vicinity of the peak. Care must be excercised when using polystyrene for calibration purposes. The polystyrene peak near $1600cm^{-1}$ is quoted at $1601.4cm^{-1}$ [114] whereas Plyler[115] quotes its value as $1603cm^{-1}$. With sharp peaks, the accuracy is estimated as being within $\pm 2cm^{-1}$ in the region $4000-2800cm^{-1}$ and $\pm 1cm^{-1}$ in the region $1800-400cm^{-1}$. For broad peaks, band centers are always subject to greater measuring errors especially if the peak is asymmetric in outline. In the region $2800-1800cm^{-1}$ the peaks observed were generally broad and weak and no calibration was performed. Regular calibration of the spectrometer over a

prolonged period showed that the calibration of any peak was seldom outside $\pm 2cm^{-1}$ of the standard value[114] in the region $4000-2800cm^{-1}$ or $\pm 1cm^{-1}$ in the region $2000-400cm^{-1}$.

The region $600-250cm^{-1}$ was investigated as a liquid film between polythene plates. The procedure detailed previously with respect to scale expansion, wavenumber marking, and calibration was followed in a similar manner. Samples were also sent to the Physico-Chemical Measurements Unit (P.C.M.U.) for infra-red spectra in the region $400-40cm^{-1}$. A Beckmann-R.I.I.C. model FS720 interferometer was used to measure the spectrum of the pure liquid between polythene plates. Where peaks were observed in the region $400-250cm^{-1}$, the results obtained on the 457 Spectrometer have been prefered, for while P.C.M.U. were able to give a spectrum of the plates used, they were unable to perform any spectral calibration.

The solution spectra quoted are for 1% solutions of the imidate in carbon tetrachloride solution unless otherwise stated. 1mm balanced cells were used wherever possible and a blank spectrum was run first to find the fluctuation in the base line and to find the areas of low spectral energy. It was found necessary to dilute the solution further in all cases to observe the strong band in the region $1700-1600cm^{-1}$. The peaks obscured by the strong carbon tetrachloride absorption were observed using a 1% solution of cyclohexane or n-hexane.

The vapour spectra were run in a 10cm path length cell manufactured by Beckmann-R.I.I.C. The cell, which had

potassium bromide windows, could be evacuated and samples injected with a hypodermic needle through a serum cap without destroying the vacuum. The body of the cell contained a heating coil, and by using a Variac it was possible to control the temperature of the cell within limits of $\pm 5^{\circ}C$ over a period of time. In a typical experiment, the cell was heated to $110^{\circ}C$ and the Variac altered to maintain this temperature. After evacuation the sample was injected and allowed to evaporate into the cell. A temperature in the range $100-120^{\circ}C$ was found to produce sufficient vapour to allow spectra to be measured. The major difficulties encountered were firstly, decomposition of the sample due to the high temperature used, accelerated by loss of vacuum from the cell, and secondly condensation of the sample on the windows, the spectrum then being recorded as that of the liquid. The cell was re-evacuated and refilled regularly in order to obtain the vapour spectrum of the pure compound. The vapour concentration also had to be limited to prevent condensation on the potassium bromide plates, and as such most of the medium-weak to weak peaks in the liquid phase could not be observed against the background noise.

Solvent effects on the infra-red spectra were performed on all the parent imidates in the region $3400-3200cm^{-1}$ and on certain imidates in the region $1690-1600cm^{-1}$ using solvents which did not have strong absorbances in these regions.

For the region $3400-3200cm^{-1}$ solute concentrations were

uniformly kept at 1% $^{v}/v$, at which concentration solute-solute interactions were deemed negligible, and because of the medium-weak nature of the peak in this region, it was found necessary to use a 1mm path length. At this path length the energy in solvents such as dioxan, was too low for the spectral bands to be measured. It would appear that Pujol and Mathis[106,107] must have used higher solute concentrations and shorter path lengths in order to obtain measurements in dioxan. The solvents used were dried and purified as described in Chapter 2.A. In each case, a complete solvent effect study on a particular solute band, was performed during the course of a day to overcome calibration errors which may have occured with the day to day variance of the spectrometer. The 3139.5cm^{-1} Indene peak was used for calibration of the spectrometer in the 3400-3200region in all cases and the 1583.1cm^{-1} peak of polystyrene for the calibration of the 1690-1600cm^{-1} region. Both calibration peaks lie outside the immediate region of the solute peaks, however, on the basis of the general linearity of the calibration throughout the whole spectral region from 4000-600cm^{-1} on this particular model, extrapolation of the calibration into the regions under investigation was considered reasonable.

The 1690-1600cm^{-1} region was investigated using a 1mm cell, with a variable path cell in the reference beam. Solutions of approximately 1% $^{v}/v$ concentration were prepared and then diluted until an optimum concentration was reached, at which

the position of the peak could be accurately measured.

The experimental details of the dipole moment work are included in the section on the dipole moments of the imidates (Chapter 3.E).

D. SAMPLE STORAGE AND STABILITY

From experience it was found to be sufficient to store the imidate samples in stoppered flasks in a dessicator filled with silica gel. A dry box was used for all the work associated with methyl trichloroacetimidate-d_1.

The imidates were found to be relatively stable to hydrolysis at room temperature. Difficulty was mainly found at the distillation stage of the preparation. The imidates based on aliphatic nitriles were easily converted into N-alkyl amides during distillation. In each case distillation was performed at reduced pressure in order to lower the still-head temperature.

The trichloroacetimidates and benzimidates could be stored for periods of up to one month, when slow hydrolysis would occur. The acetimidates and phenyl acetimidates were much less stable. The difficulty in the distillation stage and the inavailability of preparative GLC equipment meant that work on these samples had to be performed rapidly.

The N-chloro compounds were found to be at least as stable as their parent compounds and for the N-chloroacetimidate in particular a definite increase in stability was noted enabling easier purification.

Neither the parent compounds, nor the N-chloro derivatives were seen to react with any solvent investigated at room temperature. The accuracy of the vapour spectra suffers from

the instability of all the compounds at elevated temperatures. To enable the whole spectrum to be obtained it was necessary to evacuate the cell once a sufficiently high temperature had been reached, evaporate a fresh sample of imidate, and measure the peaks before the substance decomposed. This procedure was repeated until complete spectra had been recorded.

CHAPTER 3

Structure and spectra of imidates-

Special Topics

A. INTRODUCTION

With the original aim of studying the effect of substituents on the spectra and physical properties of the imidates, it is easier to discuss certain features of the results for the imidates as a whole, rather than to consider each imidate separately. The N.M.R. spectra (3.C) and solvent effects on infra-red spectra (3.B) will be discussed in relation to the intermolecular and intramolecular bonding characteristics of the imidates.

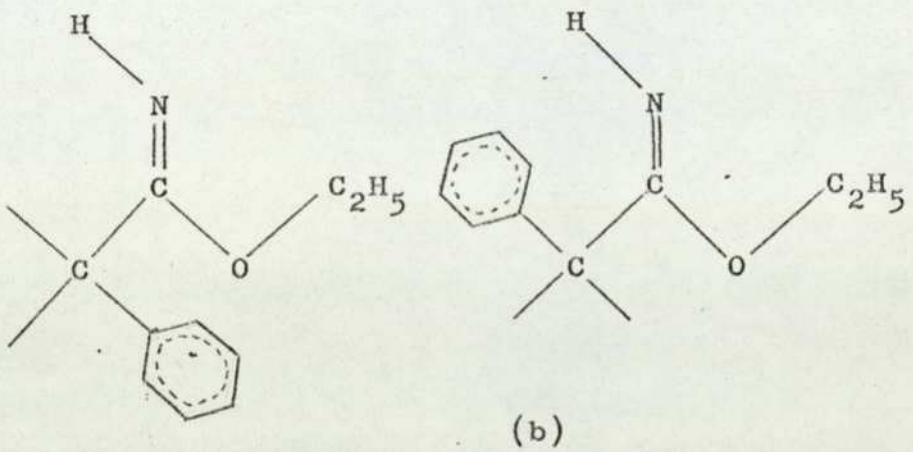
The lack of knowledge of the skeletal modes in the imidates has prompted a comparison of the imidate spectra (3.D), in order to allow a complete spectral assignment where possible (Chapter 4).

Discussion of the possible configurations of the compounds is to be found in (3.E). Correlations between the infra-red solvent shift data and the probable conformation are also made in this section.

B. SOLVENT EFFECTS ON THE INFRA-RED SPECTRA

The only data previously available on solvent effects on the infra-red spectra of imidates in the region of the nitrogen hydrogen stretching mode, ν NH, are due to Pujol and Mathis.[106,107] The measurement of the wavenumber positions of all the peaks in the spectrum of the majority of the imidates has been measured in carbon tetrachloride solution. These results, presented in the Assignment section (Chapter 4), demonstrate that only the position of the ν(NH) peak is greatly affected by the solvent. Pujol and Mathis have studied the effects of solvent on the ν NH mode of ethyl benzimidate, ethyl butyrimidate, ethyl phenylacetimidate and the ethyl esters of p-nitro, p-methyl, m-chloro and m-methyl benzimidates.

Pujol and Mathis[106] discuss the solvent effects on ethyl phenylacetimidate. The results are interpreted in terms of the two conformations shown in Fig. 2.



(a) (b)

Fig.2

The structure Fig.2(a) is assigned to a band at 3340cm^{-1} in hexane and 3267cm^{-1} in pyridine. The structure Fig.2(b) is assigned to a band at 3325cm^{-1} in hexane and 3317cm^{-1} in pyridine.

The results obtained by Pujol and Mathis for ethyl benzimidate are given in Table 12. These results were not discussed in relation to the preferred structure for the imidate.

In the first paper, Pujol and Mathis[106] produce Bellamy, Hallam and Williams (BHW) plots[116] for the wavenumber shift of the νNH of three imidates relative to the position of the νNH band in hexane, using the data for pyrrole as reference. The slopes of these plots are compared in order to determine the relative acidity of the imidates. Pyrrole appears to be a poor choice as the imino hydrogen is strongly intermolecularly hydrogen bonded and the plots illustrated in the paper would seem to bear out this ascertion. The later paper[107] represents an improvement in that the BHW plots of a variety of phenyl substituted ethyl benzimidates use the data for ethyl butyrimidate from the earlier paper[106] as reference. It would, however, seem equally as useful to plot the values relative to the parent compound, ethyl benzimidate.

Prichard[49] presented vapour and liquid spectra of methyl acetimidate, methyl trichloroacetimidate and ethyl acetimidate, but no solvent effect studies. In methyl and ethyl acetimidate the large frequency shift in the ν(NH) in going from the

liquid to the vapour phase is indicative of an intermolecularly bonded imino group. In the methyltrichloroacetimidate system the much smaller shift led Prichard to suggest that the imino group was not involved in intermolecular bonding. This ascertion suggests two possibilities, intramolecular bonding or steric hinderance and to obtain a clear idea of the bonding which existed in the liquid phase it was decided to study four classes of imidates, aliphatic, trichloroacetimidates, benzimidates and phenylacetimidates.

1. Simple Aliphatic Imidates

Two imidates were studied in this group, methyl acetimidate (Table 2) and ethyl propionimidate (Table 3). In the present study the ν(NH) mode in the liquid phase of methyl acetimidate was found at 3320, this comparing with a value of 3273cm^{-1} quoted by Prichard.[49] The band is extremely broad and asymmetric on the lower wavenumber side, the band stretching with very little decrease in intensity to below 3270cm^{-1}. Thus the actual position of the band is open to interpretation. This is also the case in ethyl propionimidate, where the presence of the carbonyl impurity was often a problem in the preparation. The band was measured at 3327cm^{-1} in this imidate but there was a distinct shoulder as shown (Fig.3, see over) and the band shape was again indicative of an intermolecularly bonded system. Kohlraush and Seka[92] quote peaks

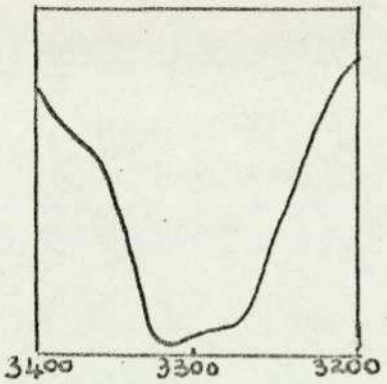


Fig.3 NH region of Ethyl Propionimidate

in ethyl propionimidate at 3330cm^{-1} (3) and 2975cm^{-1}(7) in the spectrum of ethyl propionimidate.

The relatively large shifts from the vapour value to the liquid value of 43.5cm^{-1} to 90.5cm^{-1} (methyl acetimidate) and 82cm^{-1} in ethyl acetate[49] again suggests intermolecular bonding, although the shift was smaller in ethyl propionimidate, where condensation and decomposition of the imidate made accurate measurement of the vapour spectrum extremely difficult.

One obvious conclusion from the data in Tables 2 and 3, is that the imino group stretching mode is much less susceptible to solvent shifts than the corresponding vibration in pyrrole[117] where, for example, a shift of 42cm^{-1} was observed in going from hexane to benzene.

In imidates the nitrogen atom is sp^2 hybridised to give three equivalent orbitals, one of which contains a lone pair of electrons. The difference in hybridisation and the resultant presence of the azomethine grouping must be responsible for the dramatic reduction in the sensitivity of the NH grouping to solvent effects. Conjugation of the lone pair with the azomethine grouping, could produce the situation depicted below (Fig. 4).

Table 2

Solvent effects on the (NH) mode of Methyl Acetimidate

Solvent*	Position (cm^{-1})	Shift from vapour value (cm^{-1})	Shift from n-hexane (cm^{-1})
Vapour	3372) (a) 3355)		
n-Hexane	3343	20.5	
Carbon tetrachloride	3341.5	22.0	1.5
Cyclohexane	3341	22.5	2.0
Tetrachloroethylene	3340	23.5	3.0
Trichloroethylene	3337	26.5	6.0
Chloroform	3335.5	28.0	7.5
Dichloromethane	3334	29.5	9.0
Nitrobenzene	3332.5	31.0	10.5
Toluene	3331.5	32.0	11.5
Ethyl acetate	3330	33.5	13.0
Acetone	3323 b	40.5	20.0
Di-n-butyl ether	3322 b	41.5	21.0
Pyridine	3267 b	96.5	76.0
Pure liquid	3320 b) 3273 (a))	43.5 90.5	23.0 70.0

(a) Ref (49) b broad

* Vapour and liquid values are included for comparison

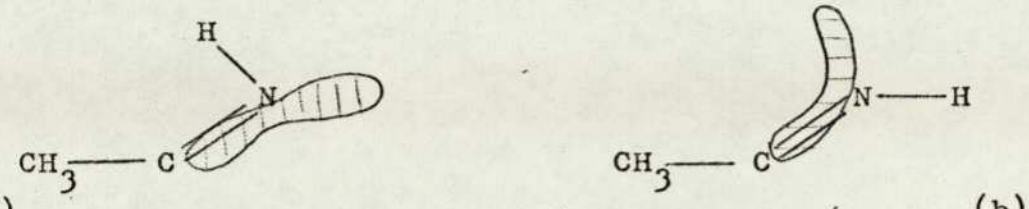
Table 3

Solvent effects on the ν(NH) mode of Ethyl propionimidate

Solvent*	Position (cm^{-1})	Shift from vapour value (cm^{-1})	Shift from n-hexane (cm^{-1})
Vapour value	3358 ± 10		
Cyclohexane	3342	16.0	+1.5
n-Hexane	3340.5	17.5	
Carbon tetrachloride	3340.5	17.5	0
Tetrachloroethylene	3340	18.0	-0.5
Trichloroethylene	3336.5	21.5	-4.0
Carbon disulphide	3336	22.0	-4.5
Chloroform	3335	23.0	-5.5
Dichloromethane	3333	25.0	-7.5
Nitrobenzene	3332.5	25.5	-8.0
o-Dichlorobenzene	3332.5	25.5	-8.0
Benzene	3332	26.0	-8.5
Toluene	3330	28.0	-10.5
Anisole	3328.5	29.5	-12.0
Bromoform	3328	30.0	-12.5
Ethyl acetate	3326.5	31.5	-14.0
Acetonitrile	3324.5	33.5	-16.0
n-Butyl ether	3324 b	34.0	-16.5
Methyl ethyl ketone	3320.5 b	37.5	-20.0
Ethyl ether	3320	38.0	-20.5
Pure liquid	‡3327 b	31.0	-13.5

* Vapour and liquid values are included for comparison

‡ Asymmetric on the lower wavenumber side.



(a) (b)

Fig. 4

It is anticipated that this electron cloud will effectively screen the imino grouping from the solvent molecules, at least from approach in one direction, allowing only relatively weak intermolecular bonding. Small solvent shifts would then be expected to occur, except with the more polar solvents, e.g. pyridine. In ethyl propionimidate the higher liquid value may be consistent with slight steric hinderance which would exist in the configuration (Fig.5), although there would appear to be no energetic reason for accepting this, as the most favourable structure.

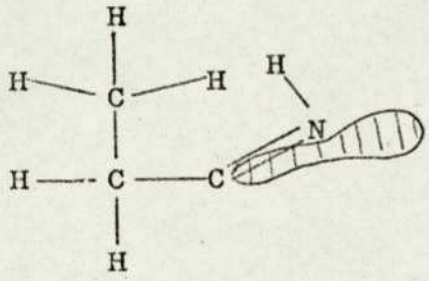


Fig. 5

2. Trichloroacetimidates

In the trichloroacetimidates (Tables 4-7), the shift in going from the vapour phase to the pure liquid is significantly less (24-27cm^{-1}) than in the acetimidates and propionimidates, the liquid band having a much sharper profile. Only in the n-propyl trichloracetimidate is there a slight

shoulder at 3325cm^{-1} on the main absorption at 3347cm^{-1}. The wavenumber position of the νNH mode in the liquid phase of methyl trichloroacetimidate has been compared with the wavenumber position of the mode in the solvents given in Table 4. For methyl trichloroacetimidate only relatively non polar solvents such as hexane, carbon tetrachloride and carbon disulphide shift the position of the peak to higher wavenumbers whilst benzene, chloroform and bromoform, for example, all shift the peak to slightly lower wavenumbers, and this trend is thought to be consistent with a weak intramolecular bond existing within the compound. (Fig.6)

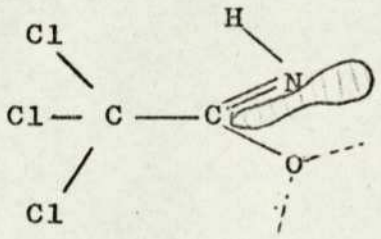


Fig. 6

The strength of the intramolecular bond depends on the distance of approach of the hydrogen and chlorine atoms and this in turn varies with the position of the oxygen lone pair electrons. The bond is not expected to be strong, a conclusion supported by the N.M.R. studies in chloroform solution.[118] Here the molecules can move to the most favourable distance for intermolecular bonding to occur between hydrogen and chlorine atoms on neighbouring molecules. Kaiser, however, has shown that chloroform is only weakly self associated in the liquid phase.

A study of the effect of carbon tetrachloride/pyridine solvent mixtures on the ν(NH) mode of methyl and n-propyl

Table 4

Solvent effects on the ν(NH) mode of Methyl Trichloroacetimidate

Solvent*	Position (cm^{-1})	Shift from vapour value (cm^{-1})	Shift from n-hexane (cm^{-1})
Vapour	3373.0		
n-Hexane	3356.9	16.1	
Cyclohexane	3355.8	17.2	1.1
Carbon tetrachloride	3352.1	20.9	4.8
Tetrachloroethylene	3351.3	21.7	5.6
Carbon disulphide	3346.7	26.3	10.2
o-Dichlorobenzene	3345.8	27.2	11.1
Toluene	3344.3	28.7	13.6
Dichloromethane	3344.2	28.8	13.7
Benzene	3344.1	28.9	13.8
Chloroform	3344.1	28.9	13.8
Nitrobenzene	3342.8	30.2	15.1
1,2-Dichloroethane	3342.8	30.2	15.1
Anisole	3341.8	31.2	16.1
Bromoform	3338.3	34.7	19.6
Liquid value	3345.6	27.4	11.3

* Vapour and liquid values are included for comparison

Table 5

Solvent effects on the υ(NH) mode of Ethyl Trichloroacetimidate

Solvent*	Position (cm^{-1})	Shift from vapour value (cm^{-1})	Shift from n-hexane (cm^{-1})
Vapour value	3371		
n-Hexane	3354	17.0	
n-Heptane	3354	17.0	0
Di-n-butyl ether	3352	19.0	2.0
Diethyl ether	(3352 (3312wsh	19.0	2.0
Cyclohexane	3351.5	19.5	2.5
Tetrachloroethylene	3351.5	19.5	2.5
Carbon tetrachloride	3351	20.0	3.0
Trichloroethylene	3348	23.0	6.0
Pure liquid	3347	24.0	7.0
Carbon disulphide	3344.5	26.5	9.5
Dichloromethane	3343.5	27.5	10.5
Benzene	3342	29.0	12.0
Pyridine	(3342 (3244wsh	29.0	12.0
Nitrobenzene	3340	31.0	14.0
Anisole	3336.5 b	34.5	17.5
Ethyl acetate	3335 b	36.0	19.0
Acetonitrile	3334 b	37.0	20.0

b broad wsh weak shoulder

* Vapour and liquid values are included for comparison

Table 6

Solvent effects on ν(NH) mode of n-propyl trichloroacetimidate

Solvent*	Position (cm^{-1})	Shift from vapour values (cm^{-1})	Shift from n-heptane (cm^{-1})
Vapour	3372		
n-Heptane	3353.5	18.5	
n-Butyl ether	3352.5	19.5	1.0
Ethyl ether	(3352 (3306.5	20.0	1.5
Cyclohexane	3351.5	20.5	2.0
Carbon tetrachloride	3350.5	21.5	3.0
Tetrachloroethylene	3349.5	22.5	4.0
Pure liquid	(3347 (3325sh	25.0	6.5
Trichloroethylene	3346.5	25.5	7.0
Carbon disulphide	3345.5	26.5	8.0
o-Dichlorobenzene	3344.5	27.5	9.0
Dichloromethane	3342.5	29.5	11.0
Benzene	3342.5	29.5	11.0
Toluene	3342	30.0	11.5
Chloroform	3342	30.0	11.5
Nitrobenzene	3341.5	30.5	12.0
Anisole	3336.5 b	35.5	17.0
Bromoform	3335 b	37.0	18.5
Acetonitrile	3331.5	40.5	22.0
Ethyl acetate	3329 b	43.0	24.5

b broad sh shoulder

* The vapour and liquid values are included for comparison.

Table 7

Solvent effects on the ν(NH) mode of Methyl Trichloroacetimidate deuterate

Solvent*	Position (cm^{-1})	Shift from vapour values (cm^{-1})	Shift from n-heptane (cm^{-1})
Vapour value	2493.5		
n-Heptane	2482	11.5	
Carbon tetrachloride	2480.5	13.0	1.5
Cyclohexane	2478	15.5	4.0
Carbon disulphide	2477	16.5	5.0
Trichloroethylene	2476.5	17.0	5.5
Liquid value	2476	17.5	6.0
o-Dichlorobenzene	2475.5	18.0	6.5
Chloroform	2475	18.5	7.0
Benzene	2474.5	19.0	7.5
Toluene	2473.5	20.0	8.5
Bromoform	2470.5	23.0	11.5
Acetone	2463 b	30.5	19.0
Methyl ethyl ketone	2459.5 b	34.0	22.5
Ethyl acetate	2455 b	38.5	27.0

b broad

* Vapour and liquid values are included for comparison.

A weak overtone band was observed in bromoform(2500), n-heptane(2507), cyclohexane(2505), carbon disulphide(2504), o-dichlorobenzene(2504), carbon tetrachloride(2507.5), and in the pure liquid(2501).

trichloroacetimidates (Table8), are also thought to be consistent with an intramolecularly bonded species.

Table 8

Data from the mixed solvent studies of the ν NH mode in methyl and n-propyl trichloroacetimidates in carbon tetrachloride/ pyridine solutions.

Methyl Trichloroacetimide		n-Propyl Trichloroacetimidate	
$\%CCl_4$	Position (cm^{-1})	$\%CCl_4$	Position (cm^{-1})
100	3352	100	3350.5
85	3350	80	3349
70	3347	60	3346.5
55	3347	40	3345.5vw
40	3346.5vw	20	3343.5vw
20	3345.5vw	0	3335 vw
0	3344 vw		

vw very weak

The solvent effects on methyl trichloroacetimidate d_1 (Table7), serve to confirm the assignment, and demonstrate the lower sensitivity of the ν(ND) mode to solvent effects relative to the corresponding ν(NH) mode.[119]

3. Phenyl acetimidate

Data for methyl and ethyl phenyl acetimidates is given in Tables

9 and 10. For methyl phenylacetimidate, only the solvent effects have been performed and the spectrum has not been assigned, the solvent effects being included to support the values presented for ethyl phenylacetimidate.

The values presented in the present study do not agree with the values published by Pujol and Mathis.[106] These authors use 0.2M solutions which would be equivalent to 1-2% $^{w}/_{w}$. In the present study 1% $^{v}/_{v}$ solutions were prepared and further dilution was undertaken to check that no further shifting of the νNH band occured. The NH band, itself, is a relatively weak absorption and in some cases it was necessary to use the (x10) scale expansion factor in order for accurate wavenumber measurement to be made. It was found impossible to obtain measurements in solvents such as dioxan and dimethyl sulphoxide as there was insufficient energy available at the required wavenumbers. Values were obtained by Pujol and Mathis in these solvents, and, in the case of ethyl benzimidate, in triethylamine.

Whilst some asymmetry was observed in the νNH mode in the majority of the solvents studied, a doublet was only observed in the case of pyridine.

For comparison purposes, the data of the present work is tabulated with the results of Pujol and Mathis in Table 11.

Pujol and Mathis appear to have mathematically separated the bands in several of the solvents e.g. hexane and carbon tetrachloride. There appears little reason for this separation,

Table 9

Solvent effects on ν(NH) mode of Methyl Phenyl Acetimidate

Solvent*	Position (cm^{-1})	Shift from n-heptane (cm^{-1})
n-Heptane	3331.5	
Cyclohexane	3329	2.5
Carbon tetrachloride	3327.5	4.0
Tetrachloroethylene	3327.5	4.0
Di-n-butyl ether	3326sh	5.5
Ethyl ether	3325.5sh	6.0
Benzene	3325.5	6.0
Ethyl acetate	3325	6.5
Nitrobenzene	3325sh	6.5
Toluene	3324.5	7.0
Carbon disulphide	3322.5	9.0
Anisole	3321.5	10.0
Trichloroethylene	3321.5	10.0
Methyl ethyl ketone	3321.5	10.0
o-Dichlorobenzene	3321.5	10.0
Acetonitrile	3321	10.5
Dichloromethane	3319	12.5
Chloroform	3318.5sh	13.0
Pyridine	3317.5,3270-75	13.5,61.5-56.5
Benzaldehyde	3315sh	16.5
Pure liquid	3321,3275wsh	10.5,56.5

w weak sh shoulder on lower wavenumber side

* The liquid value is included for comparison

Table 10

Solvent effects on ν(NH) mode of Ethyl Phenyl Acetimidate

Solvent*	Position (cm^{-1})	Shift from n-heptane (cm^{-1})
n-Heptane	3331.5	
Cyclohexane	3329	2.5
Carbon tetrachloride	3327.5	4.0
Tetrachloroethylene	3327.5	4.0
Di-n-butyl ether	3326as	5.5
Ethyl ether	3325.5as	6.0
Benzene	3325.5	6.0
Ethyl acetate	3325	6.5
Nitrobenzene	3325b	6.5
Toluene	3324.5	7.0
Carbon disulphide	3322.5	9.0
Anisole	3321.5	10.0
Trichloroethylene	3321.5	10.0
Methyl ethyl ketone	3321.5	10.0
o-Dichlorobenzene	3321.5	10.0
Pure liquid	3321,3275w	10.5,56.5
Acetonitrile	3321	10.5
Dichloromethane	3329.5sh,3319	2.0,12.5
Chloroform	3318.5	13.0
Pyridine	3317.5,3270-75	13.5,61.5-56.5
Benzaldehyde	3315b	16.5

b broad as asymmetric on lower wavenumber side sh shoulder

* The liquid phase value is included for comparison purposes

Table 11

Solvent effects on the νNH mode of methyl and ethyl phenyl acetimidates

Solvent	Ethyl phenyl acetimidate (a)	Ethyl phenyl acetimidate (b)	Methyl phenyl acetimidate (b)
Hexane	3325-3340	3331.5	3331.5*
Carbon tetrachloride	3324-3337	3327.5	3327.5
Carbon disulphide	3318-3329	3323.5	
Chloroform	3319-3328	3320	3318.5
Benzene		3324.5	3325.5
Acetonitrile	3319-3327	3321	3321
Pyridine	3317-3267	(3316 (3274	(3317.5 (3270-75

(a) Ref 106 (b) Present work * n heptane solution

for although the bands are asymmetric, the asymmetry appears no greater in the case of the phenyl acetimidates than in the benzimidates which the same authors accept as a single peak, even in pyridine.

The solvent effects, as presented in the present work, are reasonably explained by the weak intramolecularly bonded complex.(Fig.7) The shift from the vapour value to the pure liquid value, and the small solvent shift observed is akin to the observations for the trichloroacetimidates. The uniformly small shift may be an extension of the electronic hindrance proposed in the acetimidates, as additionally the

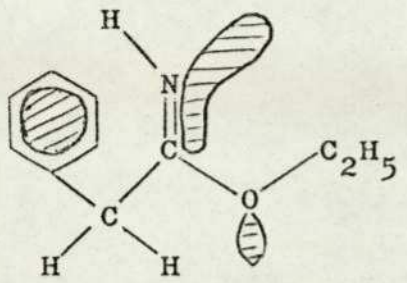


Fig.7

solvent is hindered by the π cloud on the benzene ring. This appears to be the most favourable structure as the areas of highest electron density are subject to the least interaction in this conformation.

The doubling of the υ(NH) mode in the liquid phase is thought to be due to an overtone of the υ(C=N)(2x1646 = 3292). The carbonyl group is known to give a measureable overtone and it is reasonable that the C=N band overtone may be likewise observed. In the pure liquid and pyridine, where the wavenumber position of the υNH fundamental is close to the overtone, the overtone may be involved in Fermi resonance.

This explanation is preferred to the suggestion of two conformations, both stable in solution. For methyl benzimidate where the liquid spectrum also shows a distinct shoulder on the lower wavenumber side in the infra-red spectrum, an N.M.R. study revealed sharpening of this band on cooling. The acceptance of one configuration in the benzimidates and phenyl acetimidates would appear logical.

4. Benzimidates

Data has previously been published for the solvent effects on the imino group of benzimidates in the infra-red.[106,107]

Table 12

Solvent effects on the υ(NH) mode of ethyl benzimidate[1]

Solvent*	Position (cm^{-1})	Shift from n-hexane (cm^{-1})	Shift from vapour value (cm^{-1})
Vapour	3363		
n-Hexane	3350		13
Carbon tetrachloride	3346	4	17
Chloroform	3340	10	23
Benzene	3340	10	23
Carbon disulphide	3339	11	24
Nitromethane	3339	11	24
Acetonitrile	3336	14	27
Acetone	3334	16	29
Dioxan	3327	23	36
Dimethyl sulphoxide	3290	60	73
Pyridine	3289	61	74
Triethylamine	(3346 (3292	4 58	17 71
Dimethyl formamide	3309	41	54
Liquid	(3327 (3298sh	23 52	36 65

[1] data from ref. 106 sh shoulder

* Vapour and liquid values from the present study are included for comparison.

Table 13

Solvent effects on the υ(NH) mode of methyl benzimidate

Solvent *	Position (cm^{-1})	Shift from vapour value (cm^{-1})	Shift from n-hexane (cm^{-1})
Vapour	3364		
n-Hexane	3351	13	
Cyclohexane	3349	15	2
Carbon tetrachloride	3347	17	4
Tetrachloroethylene	3347	17	4
Trichloroethylene	3346	18	5
Dichloromethane	3346	18	5
o-Dichlorobenzene	3344	20	7
Carbon disulphide	3342	22	9
Toluene	3342	22	9
Chloroform	3342	22	9
Nitrobenzene	3342	22	9
Benzene	3341	23	10
Ethyl acetate	3340b	24	11
Anisole	3339	25	12
Bromoform	3336	28	15
Acetonitrile	3336b	28	15
Methyl ethyl ketone	3335	29	16
Ether	3332b	32	19
Pure liquid	3336)	28	15
	3298sh)	66	53

cont.

Table 13(cont.)

Solvent	Position (cm^{-1})	Shift from vapour value (cm^{-1})	Shift from n-hexane (cm^{-1})
Benzaldehyde	3325b	39	26
Di-n-butyl ether	3346-3330b		
Acetone	3333b	31	18
Pyridine	3285b	79	66

b broad sh shoulder

* Vapour and liquid values are included for comparison

The results of these authors for ethyl benzimidate are given in Table 12 and will be discussed together with the present results for methyl benzimidate(Table 13). As discussed in Chapter 1.E, Pujol and Mathis, have made BHW plots of their data to show a broad similarity between the ν(NH) mode in various imidates. The main disadvantage with the BHW plot is that a reasonable plot of virtually any XH dipole can be obtained, against the NH band of pyrrole, whether it is a ν(OH) mode, or, as in this case the ν NH of a differently hybridised system. Plots using the ν NH mode of ethyl butyrimidate[107] are more acceptable, and the demonstrated variation in the slopes of the plots suggests a variation in the acidity of the proton with the inductive power of the substituent.

Pujol and Mathis[106] discuss the relative acidity of benzimidates, butyrimidates and phenyl acetimidates, but

although they discuss briefly the existence of two bands in triethylamine solution, there is no discussion of the bonding in the liquid phase of the benzimidates.

The data in Tables 12 and 13, shows good positional agreement between the two imidates. The results of the vapour phase and liquid phase spectra of ethyl benzimidate , from the present study, are included with Pujol and Mathis' data in Table 12.

The benzimidates, would appear, structurally, to present an intermediate position between the acetimidates and trichloroacetimidates. The shift from the vapour phase measurement to the pure liquid value is only slightly larger than for methyl trichloroacetimidate. If, however, a comparison is made of the wavenumber position of the peak in the liquid phase with the position of the band in solution, it is found (Table 13) that the band position corresponds to that in bromoform, an obviously polar solvent. From the solvent effects on methyl acetimidate and ethyl propionimidate, it is obvious that even in an intermolecularly bonded system the νNH mode is, in comparison to pyrrole, affected very little by solvation. Taking these factors into account, and the results of the N.M.R. solvent effects (Chapter 3C) it would appear that some form of steric hinderance, would most reasonably, account for the observed effects.

The most probable structure is illustrated in Fig.8. Although the imino group is not bonded in any way to the ring

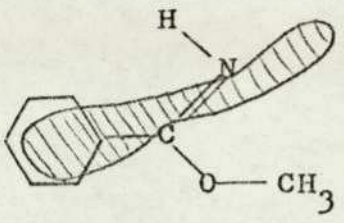


Fig.8

it will be sterically protected by the ring and the electron cloud.

In hexane and other non-polar solvents, the compound will exist as the free imidate, and the shift to the vapour phase will be relatively small. In solution the hinderance both sterically and electronically to bond formation will mean that the solvent shifts will be relatively small. In the pure liquid, there is electronic opposition to intermolecular bonding and the band occurs at a higher wavenumber than in ethyl acetimidate and ethyl propionimidate. Only very polar solvents such as dimethyl sulphoxide and pyridine can overcome the electronic opposition and shift the band below $3300cm^{-1}$.

The shoulder on the ν(NH) peak at $3298cm^{-1}$ in the liquid phase infra-red spectrum, is most probably, an overtone. The imino peak of methyl benzimidate, sharpens in the N.M.R. on cooling, which would seem to allow only one configuration in solution. The original Raman data[92] quotes only one band in the region, but it is not clear whether the sensitivity of measurement in this early work would have allowed observation of the weaker overtone.

5. <u>The ν(C=N) mode</u>

Solvent effects on the ν(C=N) mode of two imidates are

reported (Tables 14 and 15).

Table 14

Solvent effects on the spectrum of methyl benzimidate in the region 1600-1700cm^{-1}

Solvent	Position (cm^{-1})			
	Strongest band		Side bands	
Hexane	1643		1636	1628
Acetonitrile	1640	1649	1636	1627
Trichloroethylene	1640	1649	1636	1629
Tetrachloroethylene	1640		1635	1627
Dichloromethane	1638	1648	1634	
Chloroform	1636	1649		1628

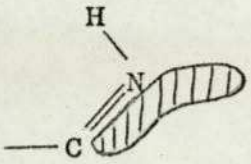
The υ(C=N) absorption is a very strong and broad band in all cases and associated with it are several shoulders. These could be due to overtone modes or retention of the vibrational structure of the band in the liquid phase. The further possibility, however, that one of the side bands might be due to the in-plane imino bending mode, β(NH), prompted a study of this band. Fabian and Legrand[89] report the position of N-(n propylidene)-n-propylamine in carbon tetrachloride and chloroform, and the position of the band at 1673cm^{-1} and 1671cm^{-1} respectively, suggested that the υ(C=N) mode would not be strongly affected in its position by the solvent.

Table I5

Solvent effects on the spectrum of n-propyl trichloroacetimidate in the region 1600-1700cm^{-1}

Solvent	Position (cm^{-1})		
	Strongest bands		Side bands
n-Heptane	1665.5	1663	1652
Cyclohexane	1664	1661.5	1651.5
Tetrachloroethylene	1663		1651.5
Pure liquid	1663		1652
Carbon tetrachloride	1663		1651.5
Trichloroethylene	1662.5		1651.5
Dichloromethane	1661.5		1651.5
Toluene	1661		1652
Carbon disulphide	1661	1662	1651.5
Chloroform	1660	1662.5	1651.5
o-Dichlorobenzene	1660	1662.5	1652
Bromoform	1659.5		1652.5

The results for n-propyl trichloroacetimidate (Table15) and methyl benzimidate (Table 14), show a regular variation in the position of the mode with solvent polarity. No significant change in the position of the side bands was noted with solvent polarity and hence these are thought to be due to overtone modes. The shift is thought to result from bonding of the solvent with the conjugated lone pair on the



nitrogen, and the relatively small shift is assumed to be due to the hinderance of the imino hydrogen.

6. The νNCl mode

Table 16 presents the solvent effects on the 732cm^{-1} band in the spectrum of N-chloro methyl acetimidate. The solvents used were limited to those given in Table 16, because many compounds absorb strongly in this region. The results appear to justify the assignment, the shifts following the solvent order observed for ν(C-Cl) studies by Hallam and Ray.[120] A similar study on N-chloro ethyl benzimidate in the region 650-750cm^{-1} failed to produce any useful information.

Table 16

Solvent effects on the ν(NCl) mode of N-chloro methyl acetimidate

Solvent	Position (cm^{-1})
Cyclohexane	732
Pure liquid	732
Carbon disulphide	731.5
Tetrachloroethylene	731.5
Ethyl ether	731
Trichloroethylene	730.5
Acetone	730.5
Ethyl acetate	730
Di-ethyl ketone	729.5
NN-dimethyl formamide	727.5
Dioxan	726.5
Methyl ethyl ketone	725.5

C. Nuclear Magnetic Resonance Studies

1. Introduction

Very little published work is available on the N.M.R. spectra of imidates. The earliest work, due to Reynaud and Moreau[37] dealt with the O-ethoxy aliphatic imidates. The spectra were measured in deutero chloroform solution (no concentration given) and T.M.S. was used as a reference. The imino absorption was assigned to a single broad band centered in the region 2.90p.p.m. (ethyl acetimidate) to 3.06p.p.m. (ethyl i-valerimidate), in the seven imidates studied. No data on the pure liquids were included.

The results of Bacaar et al[63,108] (Table 17), have been converted to the τ scale, to allow comparison with the present work. The data presented in the later paper,[108] extends to benzimidates and phenyl acetimidates. Reynaud and Moreau[37] used deuterochloroform solutions for their study and thus a direct comparison cannot be made.

2. Assignments

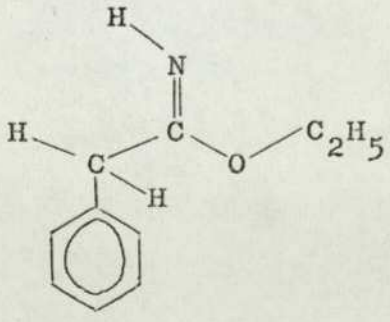
The results given in Table 18 are τ values(p.p.m.) for the pure liquid, the reproducibility being $\pm$ 0.03p.p.m. Positional and multiplicity evidence only, exists for n-propyl trichloroacetimidate and ethyl phenyl acetimidate.

Reference to the spectrum of n-propyl propionate[121] revealed peaks attibuted to the propoxy grouping as follows:-

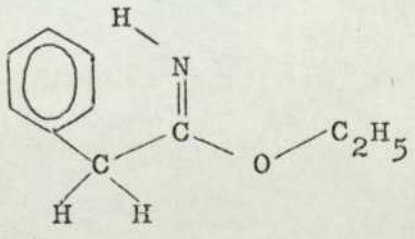
CH_3 9.05 $-(CH_2)-$ 8.40 $O-CH_2$ 5.96

These values are consistent with the assigned values for n-propyl trichloroacetimidate.

The N.M.R. spectrum of ethyl phenyl acetimidate is less well characterised. There is little evidence for the existence of the imino peak in the N.M.R. spectrum. From the position of the imino absorption in the other imidate studies, it may be expected that the peak occurs in the region 1.50-3.0p.p.m. The present study accepts a very weak peak at 1.54p.p.m. as being the imino peak. Baccar et al, suggest that the peak lies at 2.9p.p.m. This would, however, appear a remarkable measurement as the same authors also quote the strong benzene peak at 2.86p.p.m. No integration evidence is included. The asymmetry of the methylene peak at 6.60p.p.m.[63] or 6.55p.p.m., from the present work, presents a difficult problem for interpretation. Baccar proposed the existence of two separate conformations in solution (Fig. 9)



(a)



(b)

Fig. 9

Table 17

Published N.M.R. assignments due to Baccar et al.[63,108]

Compound		Position(p.p.m.)	
		Pure liquid	CCl_4 soln.
Ethyl benzimidate	NH	1.7	2.3
	C_6H_5	2.25-2.75	2.4-2.65
	CH_2	5.58	5.68
	CH_3	8.68	8.62
Ethyl m-toluimidate	NH	1.8	2.35
	C_6H_5	2.6-2.9	2.65-2.95
	CH_2	5.61	5.7
	CH_3	7.82	7.65
	CH_3	8.68	8.64
Ethyl phenyl acetimidate	NH	2.9	3.28
	C_6H_5	2.86	2.83
	CH_2	5.83	5.28
	CH_2	6.60*	6.60-6.43
	CH_3	8.85	8.74
Ethyl o-chloro phenyl acetimidate	NH	2.8	3.29
	C_6H_4	2.88	2.83
	CH_2	5.87	5.93
	CH_2	6.46-6.37	6.53-6.36
	CH_3	8.82	8.79

* Asymmetric on low field side.

Table 18

N.M.R. assignments of various imidates.

Compound		Position (p.p.m.)	Multiplicity	Integral
Ethyl	NH_2	2.76	Singlet	1
propionimidate	OCH_2	5.93	Quartet	2
	CH_2	7.83	Quartet	2
	CH_3	8.79	Multiplet	6
Methyl	NH	1.52	Singlet	1
trichloroacetimidate	OCH_3	6.06	Singlet	3
Ethyl				
trichloroacetimidate	NH	1.62	Singlet	1
	OCH_2	5.65	Quartet	2
	CH_3	8.64	Triplet	3
n-Propyl	NH	1.74	Singlet	-
trichloroacetimidate	OCH_2	5.74	Triplet	-
	CH_2	8.27	Sextet	-
	CH_3	8.89	Triplet	-
Methyl benzimidate	NH	1.68	Singlet	1
	C_6H_5 o	2.25	Multiplets	2
	m,p	2.68		3
	OCH_3	6.13	Singlet	3
Ethyl	NH	1.54	Singlet	-
phenyl acetimidate	C_6H_5	2.82	Singlet	-
	OCH_2	5.81	Quartet	-

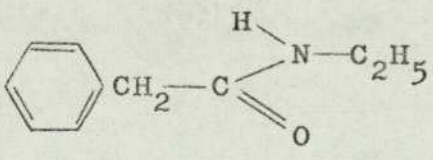
cont.

Table 18 continued.

Compound		Position (p.p.m.)	Multiplicity	Integral
Ethyl	CH_2	6.55*	Singlet	-
phenyl acetimidate	CH_3	8.83	Triplet	-
Ethyl benzimidate	NH	1.61	Singlet	1
	C_6H_5 o	2.16	Multiplet	2
	m,p	2.60	Multiplet	3
	OCH_2	5.53	Quartet	2
	CH_3	8.68	Triplet	3
N-chloro methyl	OCH_3	6.24	Singlet	1
acetimidate	CH_3	7.83	Singlet	1
N-chloro ethyl	OCH_2	5.87	Quartet	2
propionimidate	CH_2	7.44	Quartet	2
	CH_3	8.80	Multiplet	6
N-chloro ethyl	C_6H_5 o	1.92	Multiplet	2
benzimidate	m,p	2.82-2.57	Multiplet	3
	OCH_2	5.69	Quartet	2
	CH_3	8.73	Triplet	3

* Asymmetric on low field side.

This explanation is used for both the infrared and N.M.R. spectra. In the infrared spectrum, the present work suggests an intramolecularly bonded species, attributing the weak shoulder to an overtone. If we are to accept the stability of the intrabonded species we must also accept that dilution with carbon tetrachloride, will shift the equilibrium away from the intermolecularly bonded species towards the intramolecular species, in a similar way to the formation of a monomeric alcohol species on dilution. Although Baccar quotes a very weak side band on the ν NH peak in carbon tetrachloride solution, this was not observed in the infrared dilution studies undertaken in the present work. In the N.M.R. spectrum of ethyl phenyl acetimidate, Baccar, quotes a dilution value of the phenyl acetimino methylene in solution, which shows distinct splitting of the band in carbon tetrachloride solution. If dilution reduces the proportion of the intermolecular species, one would expect the asymmetry of the methylene peak to disappear in carbon tetrachloride. In the present study, a similar asymmetry was observed in carbon tetrachloride. Water was added to the sample, this showed that the peak could not be due simply to an aqueous impurity. It is thought more probable that the second band could be due to an N-ethyl phenyl acetamide impurity. This impurity,



formed on distillation, would manifest itself in the carbonyl peak observed

in the infrared spectrum, while in the N.M.R., the position of the imino absorption and the asymmetry of the methylene absorption could be attributed to this impurity.

Table 19 presents the position of the imino absorption in the liquid phase of the imidates studied.

Table 19

Position of the imino absorption in the N.M.R. spectra of some imidates.

Imidate	Position (p.p.m.)
Ethyl propionimidate	2.76
Methyl trichloroacetimidate	1.52
Ethyl trichloroacetimidate	1.62
n-Propyl trichloroacetimidate	1.74
Methyl benzimidate	1.68
Ethyl benzimidate	1.61

It is obvious from this data that the position of the imino absorption is at a higher field in ethyl propionimidate than in the benzimidates and trichloroacetimidates. The observed difference would appear to be sufficient to suggest that the imino group is essentially in a different environment in ethyl propionimidate.

The infrared solvent effect evidence suggests that ethyl propionimidate is intermolecularly bonded, the trichloroacetimidates intramolecularly bonded and the benzimidates

probably sterically hindered. As a result of this observation, a survey was made of the effect of intramolecular bonding on chemical shift. The compounds which appear to have received the greatest attention are the phenols.[122-125] Here it is well established that substitution with a nitro group in the ortho position can cause the formation of a strong intramolecular hydrogen bond. In the phenols comparison has been made between the position of the hydroxyl proton chemical shift for the various phenols at infinite dilution in carbon tetrachloride. This allows comparison between free and intrabonded species. Table 20 gives a typical set of results for this type of study.

Table 20

N.M.R. shift (p.p.m.) down field of the hydroxyl proton from the position in phenol (all measurements at infinite dilution in carbon tetrachloride).[125]

Compound	Shift (τ scale, p.p.m.)
5-Nitrosalicylaldehyde	-8.70
o-Nitrophenol	-8.46
o-Chlorophenol	-1.17
o-Bromophenol	-1.15

The shift of the intrabonded species is to considerably

lower fields, and the relatively stronger intrabonding in the o-nitrophenols is well shown by the above results.

It is thus reasonable to expect that in the liquid phase of the trichloroacetimidates the intramolecularly bonded imino grouping will occur at a lower field relative to the intermolecularly bonded ethyl propionimidate. The chemical shift values of 1.52p.p.m. (methyl trichloroacetimidate) and 2.76p.p.m. (ethyl propionimidate) appear to support the formation of a weak intramolecular bond, as would the small upfield shift of 0.2p.p.m. observed on the dilution of methyl trichloroacetimidate (5% solution in carbon tetrachloride).

In the benzimidates, the conjugation associated with the benzene ring may be extended to encompass the C=N grouping. This would appear a reasonable assumption as the ν C=N mode is shifted in the infrared in the benzimidates by approximately 20-30cm^{-1} for each phenyl group introduced. The compound will then be approximately planar, and the electron clouds represented as follows:- (Fig. 10).

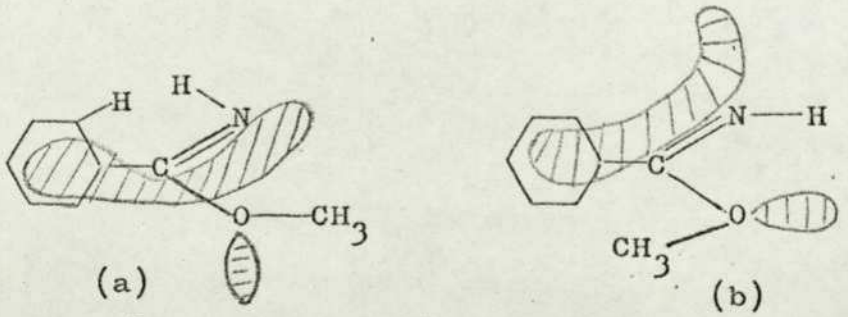


Fig. 10

In either of the configurations, but particularly in configuration 10(a) the imino proton can be affected by the ring current and the resonance shifted to low fields. The low field resonance of the imino proton in the benzimidates may then be a function of the electronic environment consequent on the presence of the benzene ring and not due to the formation of an intramolecular bond.

3. Low temperature study

A temperature effect study on the N.M.R. spectrum of methyl benzimidate was undertaken to further establish the possible existence of two configurations in the liquid phase. On cooling, however, the peak rapidly sharpened, in agreement with the intramolecular structure proposed. At -20°C, however, the compound froze and to continue the study it was decided to dissolve the compound in chloroform. An upfield shift in the position of the imino peak was noticed, and it was decided to pursue N.M.R. solution studies on two imidates to investigate this effect more fully.

4. N.M.R. solution studies

A. Introduction

In a magnetic field, the actual field H, at a nucleus, can be related to the applied field H_0:-

$$H = (1 - \sigma)H_0 \qquad (1)$$

where σ is the screening constant.

Buckingham[126] has shown that when an X-H bond is subjected to an electric field E, the screening constant is effectively altered, the change $\Delta\sigma$, being given by:-

$$\Delta\sigma = -kE\cos\theta - k'E^2$$

$$= -kE_Z - k'E^2 \qquad (2)$$

where k is a constant of the bond along which $E\cos\theta$ or E_Z, the projection of the local field E, acts. For protons $k>>k'$. ($k \sim 2\times10^{-12}$ and $k' \sim 10^{-18}$ e.s.u.).

When the field is along the X-H direction, it effectively draws electrons from the proton and the resonance occurs at lower fields. In solution, polarization of neighbouring solvent molecules produces an electric field and it is expected that the shielding constant will be altered and the resonance shifted.

Attempts to calculate the electric field, which may induce large solvent shifts with polar solutes, have generally taken the dielectric permittivity as the important solvent parameter. The position may be complicated by the induction of a secondary field in the solvent due to the influence of the permanent dipole moment of the solute, this further modifying the electron distribution in the solute.

The electric field, or reaction field R, as it is commonly termed at the centre of a cavity in a medium of constant

dielectric ($\mathcal{E}$) is given by:-[127,128]

$$R = \rho(\mathcal{E})\mu$$

where μ is the dipole moment of the solute molecule, and where $\rho(\mathcal{E})$ depends on the shape of the cavity.

In its simplest form, where a spherical cavity is considered,[131] the reaction field can be shown to be given by:-

$$R = \frac{(n^2 - 1)(\mathcal{E} - 1)}{3\alpha(\mathcal{E} + n^2/2)} \cdot \mu \qquad (3)$$

where α is the polarisability and n the refractive index of the solvent. Extensions to ellipsoidal cavities have been made.[129]

Buckingham[130] considered the observed screening constant in solution to be the sum of the screening constant for the isolated molecule, σ_{gas}, and a contribution due to the presence of the solvent, $\sigma_{solvent}$.

$$\sigma_{solvent} = \frac{H_0 - H}{H_0} \qquad (4)$$

where H_0 is the applied field strength producing resonance in an isolated gas molecule, and H is the field required to produce resonance at the same frequency in solution.

Buckingham considers the solvent contribution, $\sigma_{solvent}$, as being made up of four smaller contributions, as follows:-

$$\sigma_{solvent} = \sigma_b + \sigma_a + \sigma_w + \sigma_E \qquad (5)$$

The contribution σ_E, known as the polar effect, in the original paper, is equivalent to the reaction field effect, and is calculated using equations (2) and (3).

σ_b is the contribution due to the bulk susceptibility of the medium. Buckingham considers the solute molecule as existing in a cavity of constant magnetic permittivity μ^*. By using this parameter or the volume susceptibility ($\chi_v = \frac{1}{4\pi}(\mu^* - 1)$), the effective magnetic field at the cavity may be calculated.

σ_a arises from the anisotropy of the molecular susceptibility of the solvent molecules. Buckingham cites the high field shifts induced by aromatic solvents as examples.[132,134] Benzene rings have large induced magnetic moments only when the ring is perpendicular to the field. The disc-like shape of the benzene ring allows a closer approach in configuration (a) Fig. 11, and as the secondary magnetic field is proportional to the inverse third power of the separation, the effect of configuration (a) is likely to be dominant. The field at the solute proton will be diminished by the effect of the ring and hence a higher field will be required for



(a) (b)

Fig. 11

resonance. It is also suggested that low field shifts will be expected in rod shaped molecules (eg. carbon disulphide) where the largest diamagnetic susceptibility is along the axis of the rod.

The final term σ_w, the van der Waals term, is due to interactions between solvent and solute molecules. Interactions between solvent and solute molecules will perturb the electronic structure of the solute molecules and hence alter the screening of the solute in solution.

Two effects are recognised as contributing to σ_w.

a) Interaction will cause distortion of the solute molecules from their equilibrium configuration. As the electrons are attracted by the nuclei of neighbouring molecules, this distortion is probably an expansion, diminishing the diamagnetic screening, leading to a shift of the resonance to lower field strengths.

b)Time-dependent symmetry distortions due to "buffeting". This effect has been shown to be unimportant in the case of methane, but for molecules in which sideways attack is possible eg. hydrogen chloride, acetylene or hydrogen cyanide, a larger shift to lower fields can occur as a result of negative paramagnetic screening.

N.M.R. Solvent effect studies have been used to investigate a variety of structural problems. Happe[135] has used solvent effect studies in cyclohexane to investigate the complex formed between pyrrole and pyridine. Dilution studies

have been used to investigate various chemical equilibria, for example, the monomer-tetramer equilibrium in diethylamine[136] and the acceptor, donor equilibrium between chloroform and nitrogen bases,[137] and chloroform and acetone.[138] Comparison of the chemical shifts of a variety of compounds, particularly those containing hydroxyl groupings, at the same dilution in an inert solvent,[122,216] have been used to yield data on the strength of intramolecular bonding. The role of benzene as a solvent has been extensively studied, both shielding and deshielding effects being noted and accounted for by the geometry of the solute-solvent 'complex'.[139] Self association in halo-alkanes has been established[140] and the enthalpy associated with hydrogen bond formation between an amine and chloroform has been calculated using the van't Hoff equation.[141] For a comprehensive coverage of the literature the extensive review article by Laszlo[142] is suggested.

B. Results and discussion

The method employed in this work was evolved to overcome the experimental difficulties, in particular the necessity to use small samples, and also the limitation of the R10 instrument.

Lengthy discussions are presented in the literature[142] on the use of internal and external standards in N.M.R. spectroscopy. As with the infrared studies the shift from the gas phase value is considered by many the best criteria

but it suffers from the impracticability of its measurement. The use of an external reference requires a susceptibility correction[143] to account for the difference in magnetic susceptibility between the reference and the sample. The most common external reference would appear to be water, and so shifts both up field and down field of the reference standard are obtained.

Table 21

Results of a self association study of chloroform.

Solvent	Dilution shift (p.p.m.)	Reaction field shift (p.p.m.)	Self association
n-Hexane	-0.29	-0.078	-0.21
Cyclopentane	-0.29	-0.074	-0.22
Cyclohexane	-0.29	-0.071	-0.22
Carbon tetrachloride	-0.29	-0.062	-0.23
Dioxan	-0.28	-0.064	-0.22
Triethylamine	-0.28	-0.055	-0.22
Diethyl ether	-0.23	-0.007	-0.22
Acetone	-0.15	+0.066	-0.22

In the present work, an internal reference standard was chosen. The internal reference standard may be affected in its position by the solvent. For the present study tetramethyl silane (T.M.S.) was added as a 1% solution in the

solvent as the reference, but shifts were also considered relative to the protons of the methoxy methyl group (methyl trichloroacetimidate) and the o-phenyl proton (ethyl benzimidate). It is suggested that the reaction field effect can be eliminated by subtraction,[132] as the whole molecule is equally affected by the field, and this correction has been used, for example, in the dilution studies on aniline, where the amino group shift was considered in respect to the para ring proton.[144]

Kaiser[118] in a self association study of chloroform, prefers to calculate the reaction field contribution to the shift(Table 21). Clearly the results demonstrate the applicability of the calculation in this case.

The chloroform molecule approximates in its shape to the Onsager model. In the imidates the open structure of the molecules would seem to preclude the idea of a point dipole and it is questioned whether it would be better to consider the dipole moment of each bond separately and calculate a reaction field localised around the particular bond.

For the present study methyl trichloroacetimidate and ethyl benzimidate were chosen. In each case six solvents of varying polarity were taken although the solvents themselves were not the same in both cases. For each study the spectrum of the pure liquid was run in triplicate and volumetric dilution studies were then performed continuously, again in triplicate, until a dilution was reached at which the imino

group absorption became too weak for accurate measurement, or in the case of the benzimidates, was submerged below the stronger phenyl group absorption.

Figures 12-15, show graphically the results of the dilution studies performed in methyl trichloroacetimidate. From these plots, the position of the imino group at infinite dilution was obtained by extrapolation. Similar plots of the effect of solvents on the position of the methyl group were performed, and extrapolated to give the dilution shift as quoted in Table 22, where positive values indicate a shift to higher field strength. The final column, 'corrected shift', is the difference between the dilution shifts for the imino and methyl groups, from which, it is hoped, the reaction field component is eliminated.

Table 22

N.M.R. solvent effect study of methyl trichloroacetimidate

Solvent	Dilution shift(p.p.m.)		Corrected shift
	NH	CH_3	
Carbon tetrachloride	+0.22	0	+0.22
Tetrachloroethylene	+0.15	0	+0.15
Trichloroethylene	+0.16	+0.2	+0.14
Cyclohexane	+0.20	+0.9	+0.11
Acetonitrile	-0.22	+0.1	-0.23
Dimethyl sulphoxide	-0.83	*	-0.83*

* The dilution shift for the imino group has not been corrected,

as the methyl group absorption in the imidate became obscured by the solvent.

The results for ethyl benzimidate are much more difficult to present, due to the presence of the benzene vibrations into which the imino absorption was frequently shifted. Acetone appeared to exert no influence on the imino resonance. Reliable results were only obtained for dimethyl formamide and dimethyl sulphoxide(Fig. 16). The results are given in Table 23. The quoted shift is that at the lowest concentration of solute at which the peaks remained observable.

Table 23

Solvent effects on the imino group of ethyl benzimidate

Solvent	Final solute concentration	Shift		Corrected shift
		NH	o proton	
Dimethyl sulphoxide	0%ext.	-0.49	-0.04	-0.45
Dimethyl formamide	50%	-0.31	-0.09	-0.22
Acetone	2%	+0.03	0	+0.03
n-Heptane	40%	+0.34	+0.15	+0.19
Cyclohexane	25%	+0.39	+0.16	+0.23
Trichloroethylene	50%	+0.44	+0.04	+0.40
Chloroform	60%	+0.31	+0.08	+0.23

ext. - extrapolated

In methyl trichloroacetimidate the relatively small shifts observed in carbon tetrachloride, trichloroethylene and cyclohexane are consistent with the intramolecularly bonded species previously proposed. Acetonitrile was not used in the infrared solvent studies on methyl trichloroacetimidate but in ethyl trichloroacetimidate a shift to lower wavenumbers relative to the pure liquid value was observed and this would seem to suggest that acetonitrile is able to break the intramolecular bond and form a more stable solvent-solute complex. In dimethyl sulphoxide the large shift observed is indicative of a strong complex involving the imino group.

The solvent effects on ethyl benzimidate are less easily explained.

Solvent effects on the N.M.R. spectrum of methyl trichloroacetimidate.

Fig. 12

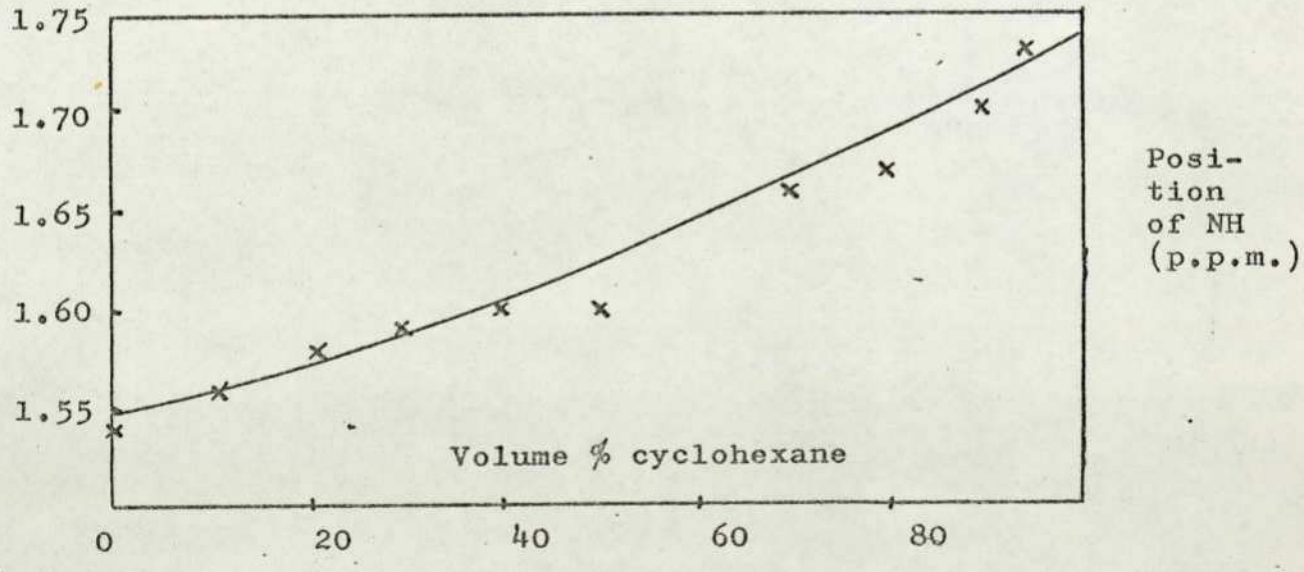


Fig. 13

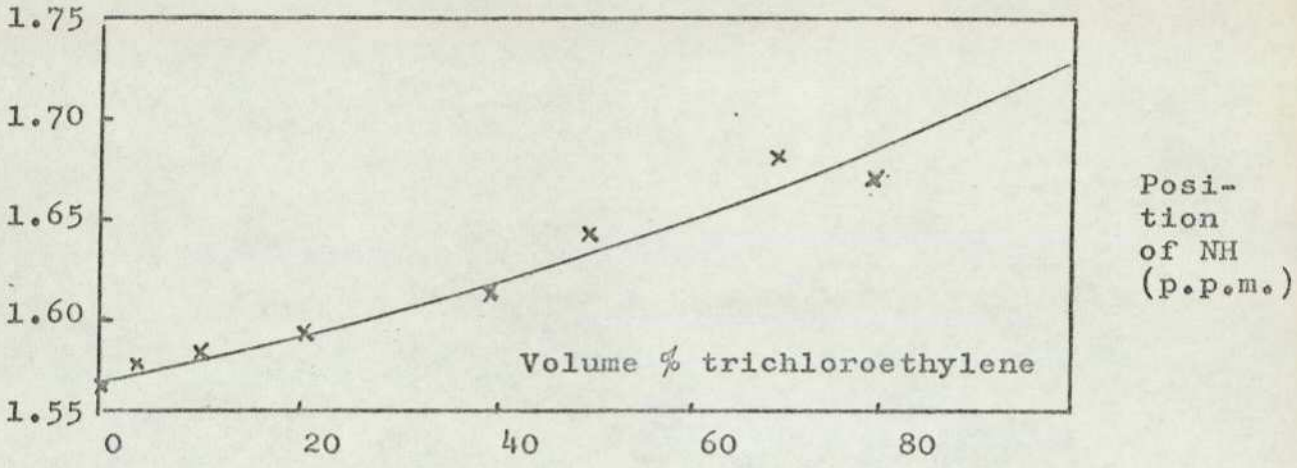
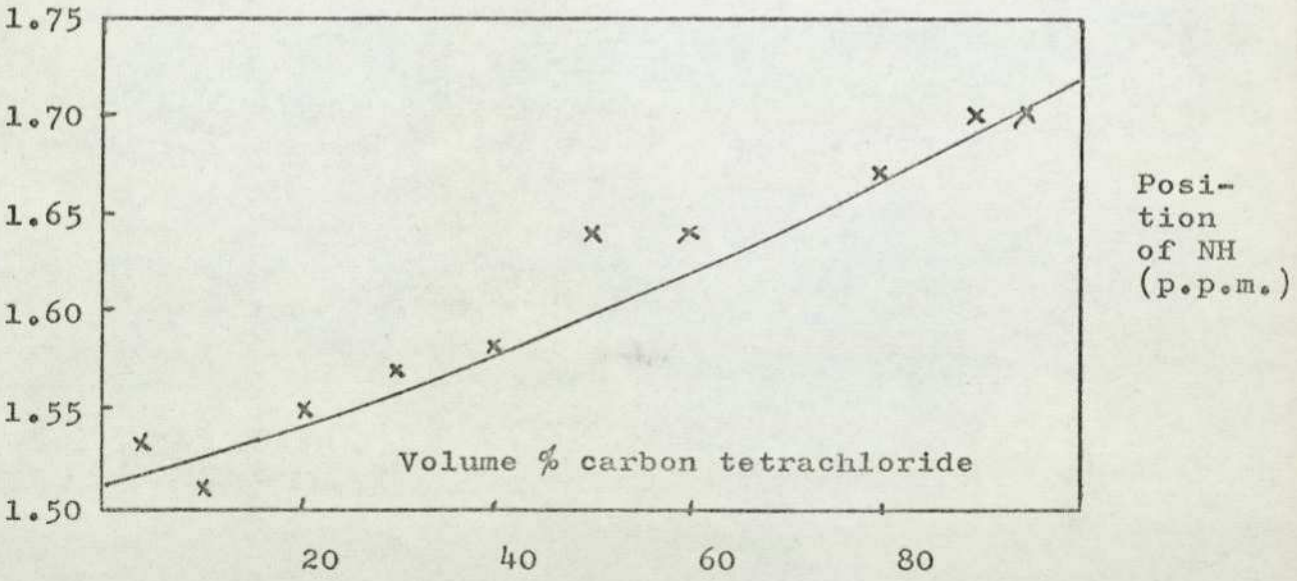
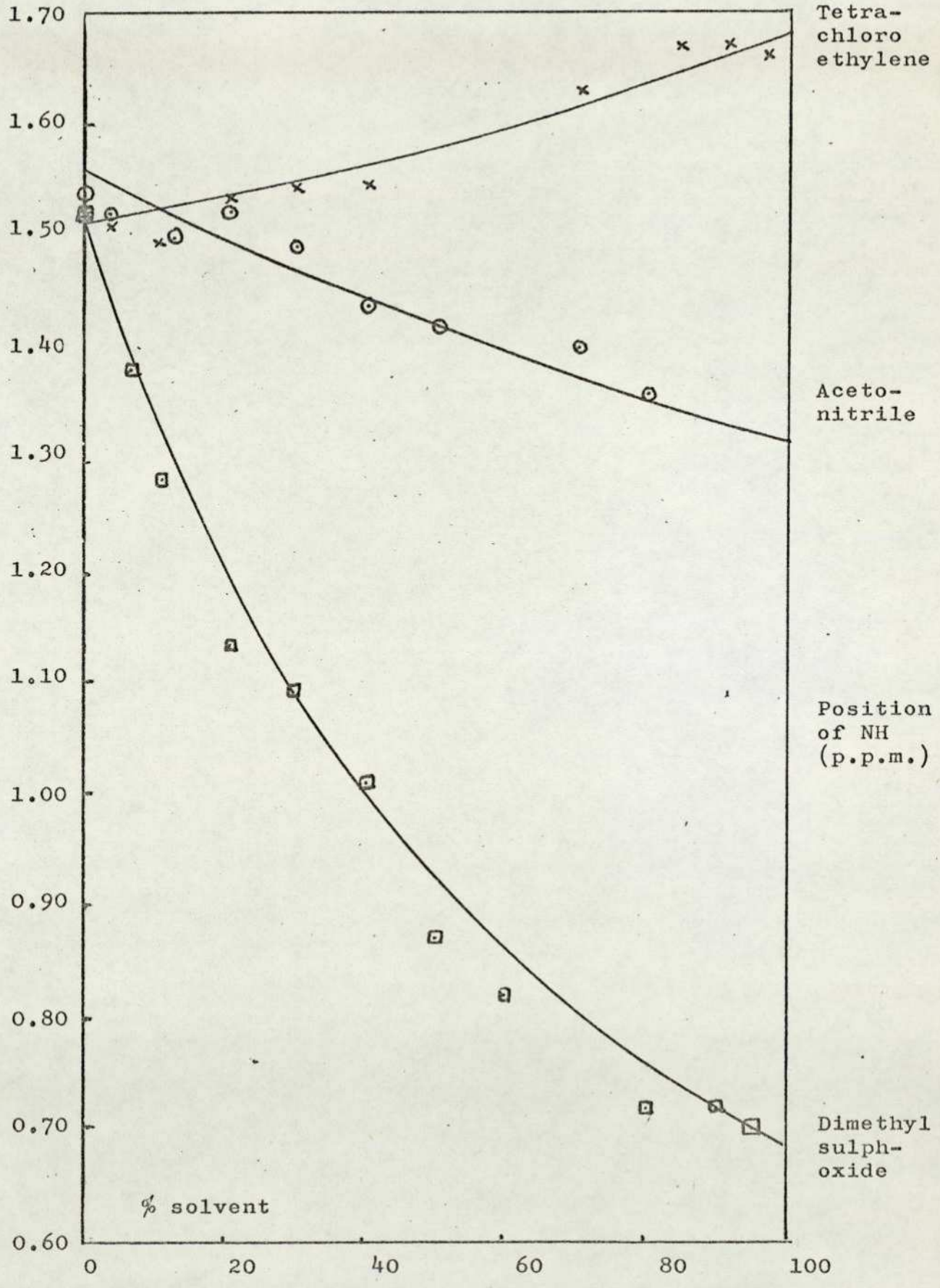

1.75
1.70
1.65
1.60
1.55
0
20
40
60
80
Volume % trichloroethylene
Position of NH (p.p.m.)

Fig. 14


1.75
1.70
1.65
1.60
1.55
1.50
20
40
60
80
Volume % carbon tetrachloride
Position of NH (p.p.m.)

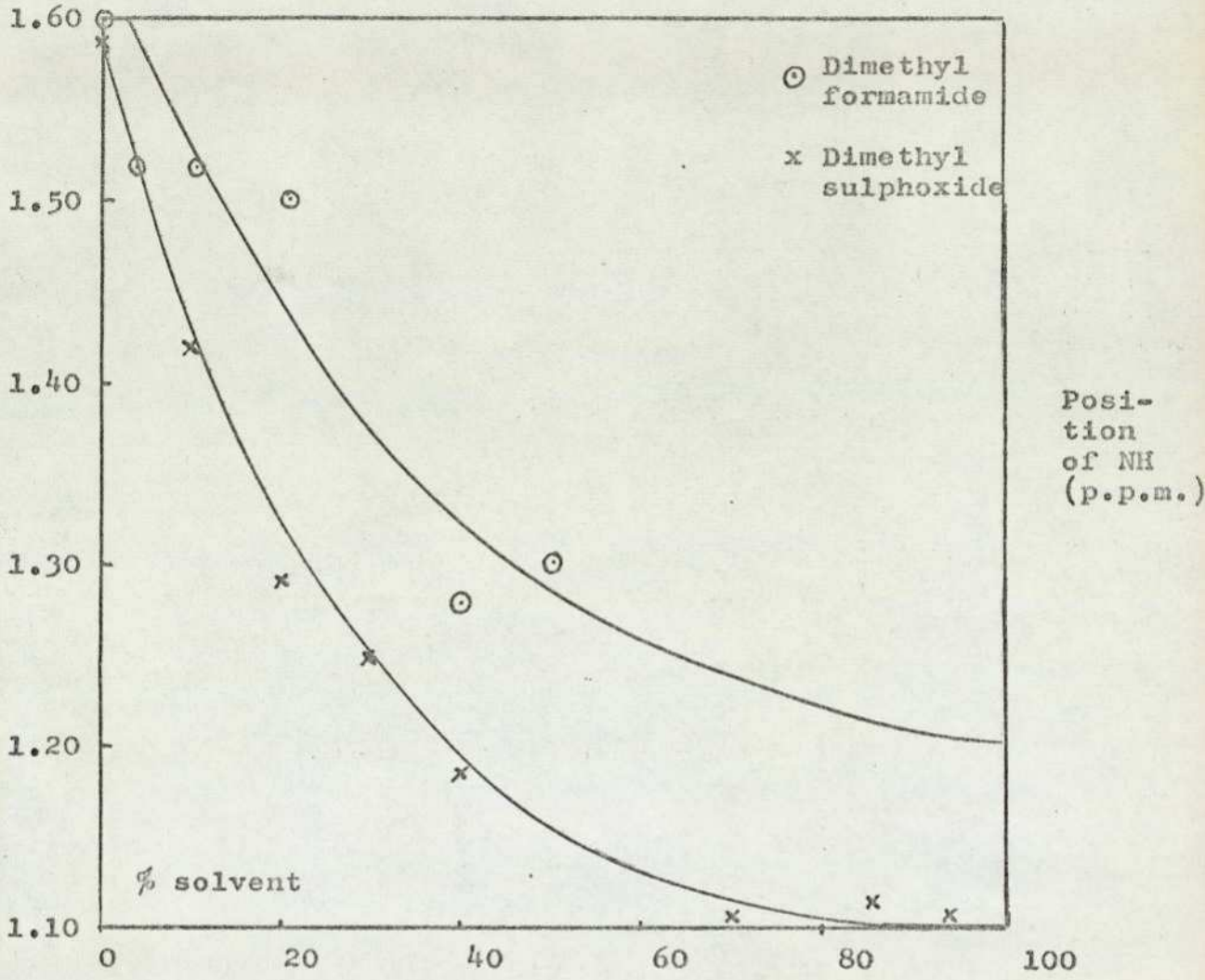
Solvent effects on the N. M. R. spectrum of methyl trichloro-acetimidate.

Fig. 15



Solvent effects on the N.M.R. spectrum of ethyl benzimidate

Fig. 16



The upfield shifts are greater than for the trichloroacetimidate but conversely the downfield shift in dimethyl sulphoxide is smaller. The problem is the difficulty of finding literature data for comparison. In the nitrophenols,[123] the dilution shift in carbon tetrachloride solution for the m and p nitro phenols was of the order of +5p.p.m. while for the o-nitro phenols a shift of -0.5 to 1.5p.p.m. was observed. In the dimethyl phenols,[145] however, shifts for the 2,6; 2,4; and 3,4; compounds were respectively +0.1p.p.m., -1.3p.p.m. and -2.5p.p.m.

On this basis, the results for ethyl benzimidate have

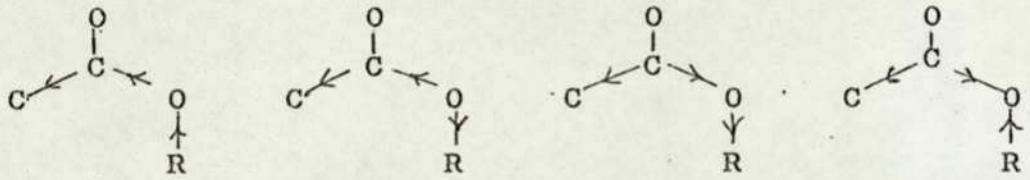
been interpreted in terms of steric hindrance. The up field shifts in the nonpolar solvents studied are relatively small, but being greater than in the trichloroacetimidate where intramolecular bonding is established. The down field shift in dimethyl sulphoxide is less than in the trichloroacetimidate because of the steric hindrance of the benzene ring.

D. Skeletal Modes in the Infrared Spectrum

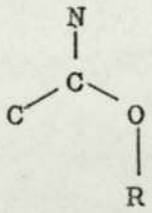
Examination of the spectra of various imidates and N-chloro acetimidates, revealed peaks in the 1350-800cm^{-1} region which could not be assigned to simple "group modes".

The existence of these 'skeletal' modes had previously been recognised by Prichard,[49] who found four bands which were not coincident with those of methyl acetimidate and which were regarded as being due to mixed modes.

For esters, Jones and Sandorfy[146] had postulated a series of vibrations of the type.



Prichard, suggested that, in the case of the imidate system, mixing may be described in terms of the five particle system:-



This five particle system could be considered as two coupled three particle systems, each having associated with them, a pseudosymmetric and pseudoantisymmetric vibration, which could lead to the following mixed vibrations (Fig. 17).

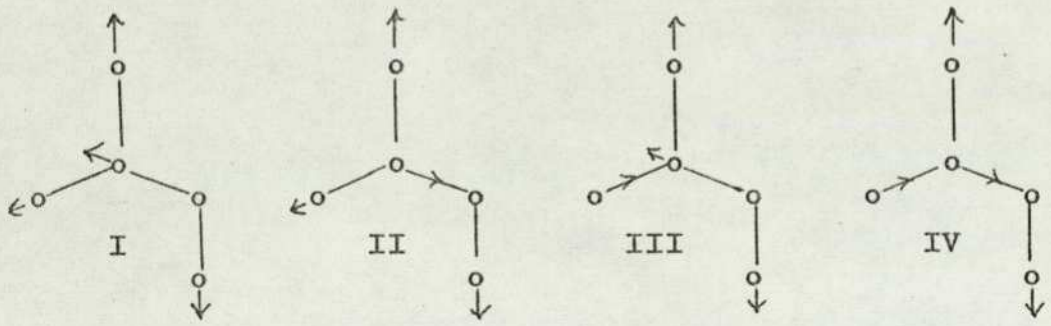


Fig. 17

For methyl trichloroacetimidate, Prichard tentatively assigned the four peaks, which have been measured at 1314, 1083, 1009 and 906cm^{-1}, in terms of the four vibrations I to IV. Prichard, however, did not assign these wavenumbers to the specific modes except to suggest that the two strongest bonds, which occured at 1314 and 1083cm^{-1}, may be associated with the pseudoantisymmetric vibrations III and IV and the two weaker bands at 1009 and 906cm^{-1} with the pseudosymmetric modes I and II.

As considerable mixing had been noted by Miyazawa et al[147] between the modes of N-methyl acetamide on the basis of a force field calculation, the previous hypothesis was accepted as a distinct possibility. Data for a variety of imidates and N-chloroimidates were compared to discover if

any trends could positively identify the mixed modes.

For convenience, the four modes will be denoted A, B, C and D in descending order of wavenumber position. It will be convenient to discuss mode B first.

1. Mode B

Consider the five atom skeleton as enumerated in Fig. 18.

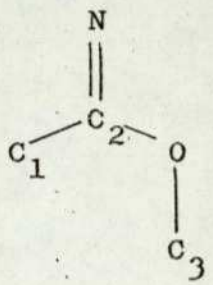


Fig. 18

The position of any vibration of the skeleton will be affected by the substituents on C_1, C_3 and the nitrogen atom. Table 24 shows the influence of substituents on the wavenumber position of mode B.

With the exception of methyl acetimidate the mode is little affected by the substituent on the nitrogen atom. Being a mixed mode the degree of mixing may vary in such a manner that the mode will be principally characteristic of either of the constituent vibrations.

Nolin and Jones assigned a mode, which is essentially a C-O-C stretching vibration, in methyl acetate at $1047cm^{-1}$ [148] and in ethyl acetate at $1046cm^{-1}$. [149] As aliphatic ethers also exhibit an antisymmetric stretching vibration in this region it appears that mode B is essentially a ν_{as}(C-O-C) vibration. The band is at a higher wavenumber in imidates and it is as reasonable to associate the raising of the band position with induction of partial double bond character into the C-O-C

grouping. It may also be due to coupling with the higher wavenumber ν(C=N) vibration.

2. Mode A

This is the highest wavenumber vibration. The effects of substituents on the C_1 atom (Table 25), the C_3 atom (Table 26) and the imino nitrogen (Table 27) have been examined. The infrared activity of mode A is associated with the substituents on the nitrogen atom and the carbon atom C_1. In methyl and ethyl acetimidate where there are low mass substituents on C_1 and the nitrogen, the mode is not observed, but in the corresponding N- chloro- derivative it absorbs strongly. The clearest substituent effect may be observed between methyl trichloroacetimidate and its N-deuterate, where there is a straight mass effect with the absence of the electronic effect associated with the introduction of a more electronegative substituent. This shift is consistent with a mode which is principally a ν[(C-C)=N] vibration and the minor importance of the ν_s(C-O-C) mode is illustrated by the lack of a definite trend with the nature of the alkyl substituent on C_3 (Table 26). The appearance of the mode at higher wavenumbers in the benzimidates may be due to conjugation of the C-C=N group with the benzene ring.

3. Mode C

Data are presented in Table 28 for the position of mode C

in various imidates. The important features of the data which aid assignment may be outlined as follows:

(a) The substituent on C_3 has very little influence on the position of the band.

(b) Where comparison is possible, for example between two imidates with similar nitrogen substituents, the wavenumber position of acetimidates > propionimidates > benzimidates ≈ phenyl acetimidates > trichloro-acetimidates. The mode accordingly appears to be affected by the mass of the substituent on C_1.

(c) The mass effect of the nitrogen substituent is difficult to assess as there is an accompanying electronic effect on substituting a chlorine or hydroxyl group. On deuteration there is a distinct shift in the position of the band although the direction of the shift is surprising in relation to the shift observed with the C_1 substituent (see (b) above).

These observations are consistent with mode C being principally a $\nu[(C\text{-}C)\text{-}X]$ vibration.

The strong absorption at 1057cm^{-1} in methyl and ethyl acetimidate, assigned by Prichard[49] to the rocking ($C\text{-}CH_3$) and $\nu(C\text{-}C)$ of the $CH_3\text{-}C{=}N$ group could be assigned to vibration II, the assignment being consistent with the vibrations in N-chloro- and N-hydroxy acetimidates.

Prichard[49,100] recognised the existence of a skeletal

mode below 1000cm^{-1}. The vibration has been established from the present study as being basically a ν_s(C-O-C) mode. A survey of the assignments of ν_s(COC) and skeletal modes by Prichard[49] was made and the assignments of the five compounds studied are given in Table 29.

Table 29

The position of the ν_s(C-O-C) and skeletal modes in some imidates.

Imidate	Position	Assignment	Reference
Methyl trichloroacetimidate	905cm^{-1}	Skeletal	49
Ethyl acetimidate	850cm^{-1}	ν_s(C-O-C)	49
Methyl acetimidate	974cm^{-1}	ν_s(C-O-C)	100
N-hydroxy ethyl acetimidate	985cm^{-1}	Skeletal	49
N-chloro ethyl acetimidate	948cm^{-1}	Skeletal	49
	860cm^{-1}	Skeletal	49

The extreme range in the position of the mode in the above assignments has led to their reapraisal.

The mode is principally ν_s(C-O-C), so that useful comparison may be made with the position of the mode in other compounds. Nolin and Jones[148] found a band at 844cm^{-1} in methyl acetate, which was strong enough to suggest a skeletal motion involving significant participation of at least one polar group, probably the carbonyl carbon atom or the methoxyl

oxygen atom.

Prichard[100] assigned the strong band at 848cm^{-1} in methyl acetimidate to a ν(C-C) mode and a band of similar intensity at 850cm^{-1} in ethyl acetimidate to a ν_s(C-O-C) mode. This latter assignment is supported by the work of Kohlraush and Seka[92] who found a fairly strong band at 844cm^{-1} in the Raman effect. Comparison may be made with the Raman effect of dimethyl ether, where the ν_s(C-O-C) band is stronger than the ν_{as}(C-O-C) band.

The ν(C-C) mode, is very sensitive in its position to its environment as may be observed from the data of Mecke and Spiesecke,[150] Table 30.

Table 30

The position of the ν(C-C) mode in some compounds.

Compound	Position (cm^{-1})
Monothioacetic acid	993
Acetyl chloride	955
Dithioacetic acid	903
Acetamide	878
Acetyl fluoride	813
Acetone	780
Thioacetamide	717

Prichard[49] quotes a range of 1200-800cm^{-1} for the ν(C-C) mode and 1000-800cm^{-1} for the ν_s(C-O-C) mode and it is possible that the band at 974cm^{-1} in methyl acetimidate is in fact a ν(C-C) mode.

The assignment of Mode D to the weak band at 905cm^{-1} in methyl trichloroacetimidate[49] is also subject to revision. This band is rather weak in comparison to the skeletal vibrations in other imidates and also occurs at a significantly higher wavenumber. The strong band in the spectrum at 827cm^{-1} was assigned to an overtone of the band at 407cm^{-1}, but it would appear from its position and intensity that this band is better assigned to Mode D, the band at 906cm^{-1} being an overtone or difference band.

The final assignment of bands in various imidates to mode D are given in Table 31. The wavenumber position of the band is raised in the N-chloro and N-hydroxy derivatives presumably due to changes in bond order.

Table 24

The position of mode B in the spectrum of some imidates.

Substituent				Position	Reference
C_3	C_1		N	(cm^{-1})	
Methyl	Acetimidate		H	1102[1]	49
Methyl	Acetimidate		Cl	1072	
Ethyl	Acetimidate		H	1096s	49
Ethyl	Acetimidate		Cl	1094m	49
Ethyl	Acetimidate		OH	1093m	49
Ethyl	Propionimidate		H	1089vs	
Ethyl	Propionimidate		Cl	1085vs	
Methyl	Trichloroacetimidate		H	1083vs	
Ethyl	Trichloroacetimidate		H	1078vs	
n-Propyl	Trichloroacetimidate		H	1082vs	
Methyl	Trichloroacetimidate		D	1085m	
Methyl	Benzimidate		H	1077vs*	
Ethyl	Benzimidate		H	1075vs*	
Ethyl	Benzimidate		Cl	1110s, 1094m	
Methyl	Phenyl acetimidate		H	1088vs	
Ethyl	Phenyl acetimidate		H	1091vs	

[1]Mode shifted to 1090 in carbon tetrachloride solution

*May be assigned to other vibrations.

Table 25

The position of Mode A in the spectrum of some imidates.

Substituents			Position	Reference
C_1	C_3	N	(cm^{-1})	
CH_3 (acetimidate)	CH_3	H	*	49
	CH_3	Cl	1293vs	
	C_2H_5	H	*	49
	C_2H_5	OH	1302vs	49
	C_2H_5	Cl	1293vs	49
C_2H_5 (Propionimidate)	C_2H_5	H	1278s	
	C_2H_5	Cl	1297vs	
C_3H_7 (Butyrimidate)	C_2H_5	H	1295	37
CCl_3 (Trichloroacetimidate)	CH_3	H	1314vs, 1295s.sh	
	C_2H_5	H	1311vs	
	nC_3H_7	H	1309vs	
	CH_3	D	1283vs	
C_6H_5 (Benzimidate)	CH_3	H	1343vs	
	C_2H_5	H	1329vs, 1297m	
	C_2H_5	Cl	1306, 1288vs	
$C_6H_5CH_2$ (Phenyl acetimidate)	C_2H_5	H	1341s	

* No peak observed in the appropriate region.

Table 26

The position of mode A in the spectrum of some imidates.

Substituents			Position	Reference
C_3	C_1	N	(cm^{-1})	
CH_3	CH_3	H	*	49
	CH_3	Cl	1293vs	
	CCl_3	H	1314vs, 1295s.sh	
	CCl_3	D	1283vs	
	C_6H_5	H	1313vs, 1343vs	
C_2H_5	CH_3	H	*	49
	CH_3	OH	1302vs	49
	CH_3	Cl	1293vs	49
	C_2H_5	H	1278s	
	C_2H_5	Cl	1297vs	
	C_3H_7	H	1295vs	37
	CCl_3	H	1311vs	
	C_6H_5	H	1329vs, 1297m	
	C_6H_5	Cl	1306, 1288vs	
	$C_6H_5CH_2$	H	1341s	
C_3H_7	CCl_3	H	1309vs	

* No peak observed in the appropriate region.

Table 27

The position of mode A in the spectrum of some imidates.

Substituents			Position	Reference
N	C_1	C_3	(cm^{-1})	
H	CH_3	CH_3	*	49
	CH_3	C_2H_5	*	49
	C_2H_5	C_2H_5	1278s	
	C_3H_7	C_2H_5	1295	37
	CCl_3	CH_3	1314vs,1295s.sh	
	CCl_3	C_2H_5	1311vs	
	CCl_3	nC_3H_7	1309vs	
	C_6H_5	CH_3	1343vs	
	C_6H_5	C_2H_5	1329vs, 1297m	
	$C_6H_5CH_2$	C_2H_5	1341s	
Cl	CH_3	CH_3	1293vs	
	CH_3	C_2H_5	1293vs	49
	C_2H_5	C_2H_5	1297vs	
	C_6H_5	C_2H_5	1306, 1288vs	
OH	CH_3	C_2H_5	1302vs	49
D	CCl_3	CH_3	1283vs	

* No peak observed in the appropriate region.

Table 28

The postition of Mode C in the spectrum of some imidates.

Substituents			Position	Reference
C_3	C_1	N	(cm^{-1})	
Methyl	Acetimidate	H	1057s*	49
Methyl	Acetimidate	Cl	1049s	
Ethyl	Acetimidate	H	1057s*	49
Ethyl	Acetimidate	Cl	1048s	49
Ethyl	Acetimidate	OH	1056s	49
Ethyl	Propionimidate	H	1032sm	
Ethyl	Propionimidate	Cl	1028s	
Methyl	Trichloroacetimidate	H	1009s	
Ethyl	Trichloroacetimidate	H	1028s	
n-Propyl	Trichloroacetimidate	H	1000s	
Methyl	Trichloroacetimidate	D	1026vs	
Methyl	Benzimidate	H	1028*m	
Ethyl	Benzimidate	H	1016m	
Ethyl	Benzimidate	Cl	1017s	
Methyl	Phenyl acetimidate	H	1018m	
Ethyl	Phenyl acetimidate	H	1030m	

* May be assigned to other modes.

Table 31

The position of Mode D in some imidates.

Substituents			Position	Reference
C_3	C_1	N	(cm^{-1})	
Methyl	Acetimidate	H	848s	49
Methyl	Acetimidate	Cl	876s	
Ethyl	Acetimidate	H	850m	49
Ethyl	Acetimidate	Cl	860s	49
Ethyl	Acetimidate	OH	902s	49
Ethyl	Propionimidate	H	858m,838m	
Ethyl	Propionimidate	Cl	869m	
Methyl	Trichloroacetimidate	H	827s	
Ethyl	Trichloroacetimidate	H	816s	
n-Propyl	Trichloroacetimidate	H	827vs	
Methyl	Trichloroacetimidate	D	852s	
Methyl	Benzimidate	H	823w*	
Ethyl	Benzimidate	H	873s,827s*	
Ethyl	Benzimidate	Cl	869s	
Methyl	Phenyl acetimidate	H	838m	
Ethyl	Phenyl acetimidate	H	841mw	

* May be assigned to other modes.

E. Dipole Moment Studies

The theory related to this section has been drawn extensively from two sources.[151,152] The procedure adopted for the measurements follows the standard method, which may be outlined as follows:-

(a) The dielectric permittivity and refractive index of dilute solutions of the solute in freeze dried benzene were measured at 298K.

(b) Plots of dielectric permittivity versus weight fraction and refractive index squared versus weight fraction were made and the slopes measured.

(c) These values were used to calculate the orientation polarisation $_{\mu}P_2$, as given by:-

$$_{\mu}P_2 = \frac{3M_2\alpha v_1}{(\varepsilon_1 + 2)^2} - \frac{3M_2 v_1 \nu}{(n_1^2 + 2)^2}$$

where α and ν are the slopes of the dielectric permittivity and refractive index squared plots respectively, M_2 the molecular weight of the solute, ε_1 and n_1 the dielectric permittivity and refractive index of the solvent respectively, and v_1 the specific volume of the solvent.

(d) The dipole moment of the solute is given by the equation

$$\mu = \sqrt{\frac{9kT.\ _{\mu}P_2}{4\pi N}}$$

where N is Avogadros Number, k the Boltzmann Constant and T the absolute temperature.

The dielectric permittivity was measured using a Dipolmeter DM01, manufactured by Wiss-Tech. Werkstätten, which works on the heterodyne beat principle.

1. Computer Program

The program in the Fortran language (Appendix 1) was devised to give an accurate value of the dipole moment. The program gave the dipole moment to seven places of decimals but the errors involved in the preparation of solutions and the measurement of dielectric permittivity and refractive index collectively could introduce an error which should be considerably less than 10% (this figure was arrived at by drawing best and worst lines through the points and estimating the effect on the total value). For this purpose the dielectric permittivity plot was weighted as the slope of this plot was generally an order of magnitude larger than the slope of the refractive index squared plot.

2. Suitability of the Program and Method

The dipole moment of a purified sample of chlorobenzene was determined by the method outlined above, using the program to calculate the dipole moment. The value of 1.58D obtained compares with a value of 1.59D given by Le Fevre,[151] (Refractivity Method) and values of 1.58D (Dielectric Permittivity)

and 1.52D (Microwave Absorption) given by Smith.[152]

In each case plots of refractive index squared versus weight fraction and dielectric permittivity versus weight fraction have been made to ensure linearity. The plots for ethyl propionimidate are given in Figs. 20 and 21. The format of the results obtained from the computer is given in Appendix 2.

3. Correlation of Dipole Moment measurements with the structure of Imidates.

Early dipole moment studies by Kumler and Porter[156] were used to provide important physical evidence to distinguish the imidates structurally from the isomeric N-alkyl amides R.CO.NHR'.

In saturated carboxylic acids dipole moment data can be used to establish a favoured trans planar structure[157] and it was concluded that dipole moment data could be similarly used to establish favoured configurations in imidates.

The dipole moments of very few imidates appear to have been measured (Table 32). Interpretively they offer a system which is less easily studied, chiefly because of the uncertainty in the value of the azomethine dipole moment. Additionally the hybridisation of the nitrogen would seem to rule out a planar structure, and it is necessary to assume that the moments lie in plane to allow simple calculations to be performed. Kalakowski[158] studied ethyl p-bromobenzimidate by

x-ray crystallography but did not measure any bond angles.

Dipole moment evidence for the imidate structure has been given by Exner et al[160] and Lumbroso and Bertin.[109,161] Exner et al studied ethyl benzimidate and ethyl p-nitro benzimidate and calculated the dipole moments of six possible configurations, accepting free rotation of the ethoxy group about the carbonyl bond. Lumbroso and Betin accepted only four possible structures. Their first paper deals with ethyl acetimidate and ethyl benzimidate[109] while the later paper[160] includes these same imidates, together with ethyl p-nitro benzimidates and ethyl p-propoxy benzimidate.

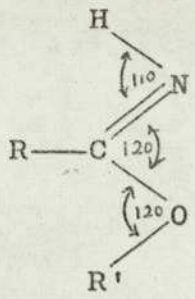
The present study adopted six structures. These will be described in terms of the position of the imino hydrogen (cis or trans) and the ethoxy ethyl group (cis', trans' or free') relative to the functional group R, from the parent nitrile, as depicted in Fig. 22, together with the bond angles used in the calculations.

The following data has been employed in the calculation of the dipole moment of the structures below for the imidates given in Table 33:-

a) A dipole moment of the $Cl_3C.C$ grouping was calculated from that of chloroform,[162] i.e. 1.05D. Taking the aliphatic CH bond moment as -0.3D, the moment of the $CCl_3.C$ group was calculated as being approximately 1.35D along the C-C axis in the direction of the chlorine atoms.

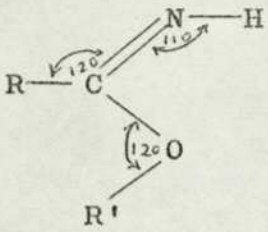
b) The moments of the $C-O-CH_3$ and $C-O-C_2H_5$ groupings

22a)



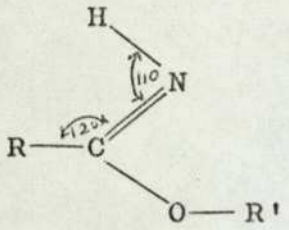
cis cis'

22b)



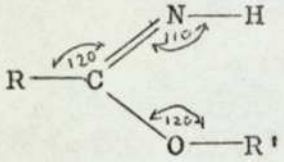
trans cis'

22c)



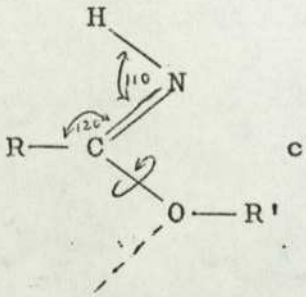
cis trans'

22d)



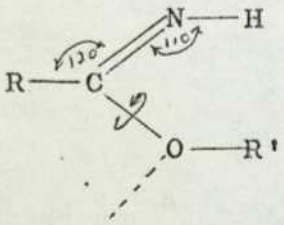
trans trans'

22e)



cis free'

22f)



trans free'

were taken as being the same at the dipole moments of dimethyl and methyl ethyl ethers,[162] i.e. 1.25D. This would suggest that the dipole moments of the methyl and ethyl imidates should be approximately equal unless there is a different

favored conformation in the two homologues. The calculations given in Table 33 apply equally to ethyl and methyl imidates.

c) The dipole moment of the imino group was taken as 1.31D.[152]

d) The moment of the carbon hydrogen dipole was taken as o.3D in the sense (C→H), where the arrow points to the negative end, and 0.4D in the reverse sense (C←H) in the aromatic systems. This is consistent with the data and discussion presented by Smith.[159]

e) The calculation of the moment of ethyl p-nitro benzimidate was undertaken in duplicate using values for the nitro grouping of 4.0D and 4.5D as this range was suggested by Exner.

f) From the discussion by Sandorfy,[163] the dipole moment of the C=N bond has been taken as 1.0D. Smyth[164,166] estimated the dipole moment of the C=N bond as 0.9D. Sastry and Curl[165] measured the dipole moment of N-methyl methylenimine $CH_2=NCH_3$ as 1.53D (gas phase microwave measurement), from which the C=N dipole can be estimated as 1.0D, this latter value being adopted for the present studies. From this data, the value of 1.8D taken by Exner for the C=N moment would appear rather high.

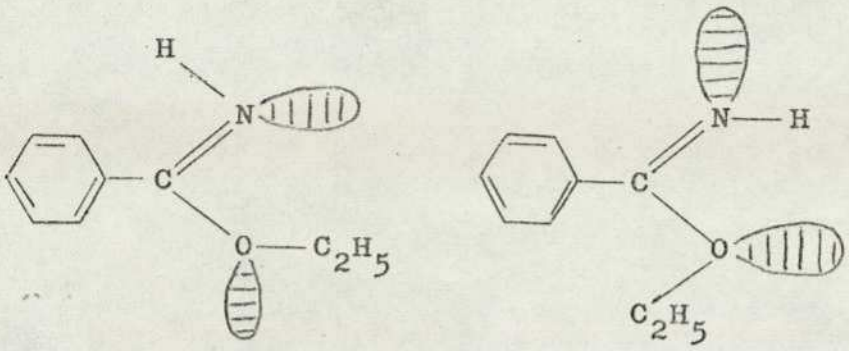
Lumbroso and Bertin accepted only four structures, presumably cis cis', cis trans', trans cis', and trans trans'. This uncertainty exists from the earlier paper[109] in which the cis trans' structure (Fig. 22c) is depicted with an arrow

suggesting free rotation, whilst in the later paper, no arrow is depicted, and in neither paper is there any mention of free rotation. It is very difficult to assess the usefulness of these papers as the second contains a recalculation of the data in the first paper into which the added refinement of a mesomeric effect in the O-C=N grouping is introduced.

4. Conformations of ethyl p-nitro benzimidate and ethyl benzimidate.

Table 34, contains the values of the dipole moments calculated for the six conformations of the benzimidates from the present work and previous workers.

Comparison of the data in Table 34 shows the inadequacy of a theoretical approach to the dipole moments of complex systems. To analyse the data, it was considered a reasonable assumption that the structure favored in both systems would be the same, and hence the calculated value must agree relatively closely with the experimentally determined moment in both cases. The cis cis', cis free', trans free' and trans trans' can be immediately dismissed on this account. As may be noted, the results from the three workers agree most closely in the p-nitro compound, this being indicative of the dominant effect of the nitro group moment on the vectorial summation. The remaining two structures, cis trans' and trans cis', would appear from the dipole moment values to be equally favorable. These structures can be represented as follows:-



cis trans'

trans cis'

The lone pair on the nitrogen and oxygen are both situated, in energetically favorable positions. In the trans cis' structure the imino hydrogen could partially bond with the π cloud of the benzene ring but with the imino hydrogen in this position free rotation of the ethyl group would appear feasible. The trans cis' would favour interaction of the imino hydrogen with the lone pair on the oxygen, but the fact that methyl acetimidate is intermolecularly bonded, would seem to rule out this possibility. In the trans cis' there would appear to be the possibility of steric hinderence by the imino hydrogen on the ethoxy group.

5. Conformations of methyl and ethyl trichloroacetimidates

The situation is simplified by the existence of only one set of calculations. The experimentally measured dipole moments of methyl trichloroacetimidate 1.04D, and ethyl trichloroacetimidate 1.21D are both lower than any of the calculated values. The three structures in which the imino

Table 34

Dipole moment calculations for the conformation of ethyl benzimidate and ethyl p-nitro benzimidate.

	Ethyl benzimidate				Ethyl p-nitro benzimidate			
Conformation	(a)	(b)	(c)	(d)	(e)	(f)	(b)	(d)
cis cis'	3.0	2.57	3.2	3.2	1.42	1.91	1.50	1.7
trans cis'	1.4	1.83	2.1	2.6	3.70	4.18	3.69	4.0
cis trans'	1.64	0.7	1.3	1.2	3.38	3.72	3.4	(3.0)
trans trans'	1.49	1.47	0.9	1.7	5.49	5.99	5.23	5.1
cis free'	2.65	1.91			2.35	2.81	2.62	
trans free'	0.125	1.66			4.18	4.68	4.83	
μ exp		1.7	1.54	1.54			3.80	

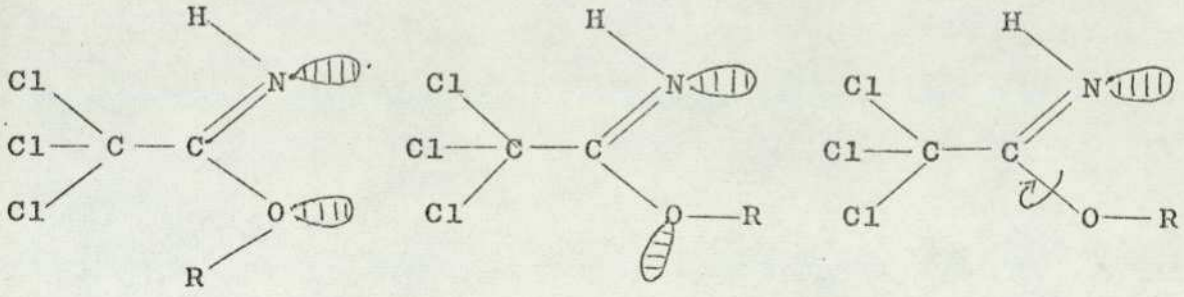
All measurements are given in Debye units

c) Ref. 109 d) Ref. 161 b) Ref. 160

a), e) and f) are from the present work. Data (e) employs a value of 4.0D for the nitro grouping and (f) uses 4.5D. The present calculation is applicable to methyl benzimidate for which a value of 1.95D was measured.

group is cis to the trichloro grouping are the three favoured structures from the calculations. These are represented in Fig. 23.

Fig. 23



cis cis' 1.24D cis trans' 1.37D cis free' 1.36D

An attempt to simulate the system in model form suggested that, in the trichloroacetimidate system, the imino hydrogen may be sterically hindered by , or hydrogen bonded to, the chlorine atoms. There appears to be little difference energetically to favour the cis cis' structure over the cis trans' structure. In the cis cis' structure, the extra energy associated with the repulsion between the lone pairs on the oxygen and nitrogen atoms, may be counterbalanced by the energy gained from the reduction of the C=N-H bond angle, bringing the imino hydrogen into closer proximity with the chlorine atoms. In the cis trans' structure the position of the oxygen and nitrogen lone pairs, relative to each other, is apparently more favourable. Simply on the basis of the cis cis' and

cis trans' structures being equally favourable, the cis free' structure will be accepted as most closely approximating to the true structure.

6. Conformations of ethyl acetimidate

As with ethyl benzimidate and p-nitro ethyl benzimidate, two sets of data due to Lumbroso and Bertin exist, and these are tabulated with the calculated values from the present work in Table 35.

Table 35

Dipole moment calculations for the conformations of ethyl acetimidate.

Conformation	(a)	(b)	(c)
cis cis'	2.3	2.9	3.6
trans cis'	1.11	2.0	2.8
cis trans'	1.28		1.6
trans trans'	1.97	1.2	1.5
cis free'	2.06		
trans free'	0.48		
μ	1.78*	1.42	1.42

a) Present work b) Ref. 109 c) Ref. 161

* Value for ethyl propionimidate.

The results in Table 35 only serve to emphasise the poor

agreement between the present calculations and those of Lumbroso and Bertin. The infrared solvent effect study has suggested an intermolecularly bonded species but as the functional groupings in the propionimidates and acetimidates are small, eliminating possible steric hinderence and due to the apparent absence of any centre for intramolecular bonding, no inferences were drawn.

7. N-Chloro compounds

An attempt was made to correlate the data for the N-chloro compounds. From the Pauling electronegativities[167] of nitrogen and chlorine, which are both given as 3.0, it was anticipated that the N-chloro grouping would have a low dipole moment, in the range +0.5 to -0.5D. Using this criteria and the fact that the dipole moments of the compounds studied (Table 32) lay in the range 1.95 to 2.20D, calculations were performed which indicated that by varying the value of the N-Cl dipole from 0.5 to -0.5D, four of the possible structures could be accomodated, the exceptions being the cis trans' and trans trans'.

Table 32

Dipole moment studies of some imidates.



Table 33

Calculations of the dipole moments of some imidates.

Imidate	Conformation cis	trans cis'	cis trans'	trans trans'	cis free	trans free
Methyl trichloroacetimidate Ethyl trichloroacetimidate	1.24	1.41	1.37	2.90	1.36	1.53
Ethyl benzimidate Methyl benzimidate	3.0	1.40	1.64	1.49	2.65	0.125
Ethyl acetimidate Ethyl propionimidate	2.3	1.11	1.28	1.97	2.06	0.48
Ethyl p-nitro benzimidate (using μNO_2 = 4.0)	1.42	3.70	3.38	5.49	2.35	4.18
Ethyl p-nitro benzimidate (using μNO_2 = 4.5)	1.91	4.18	3.72	5.99	2.81	4.68

Dipole moments are given in Debye units throughout.

Plot of Dielectric permittivity against weight fraction of Ethyl propionimidate

Fig. 20

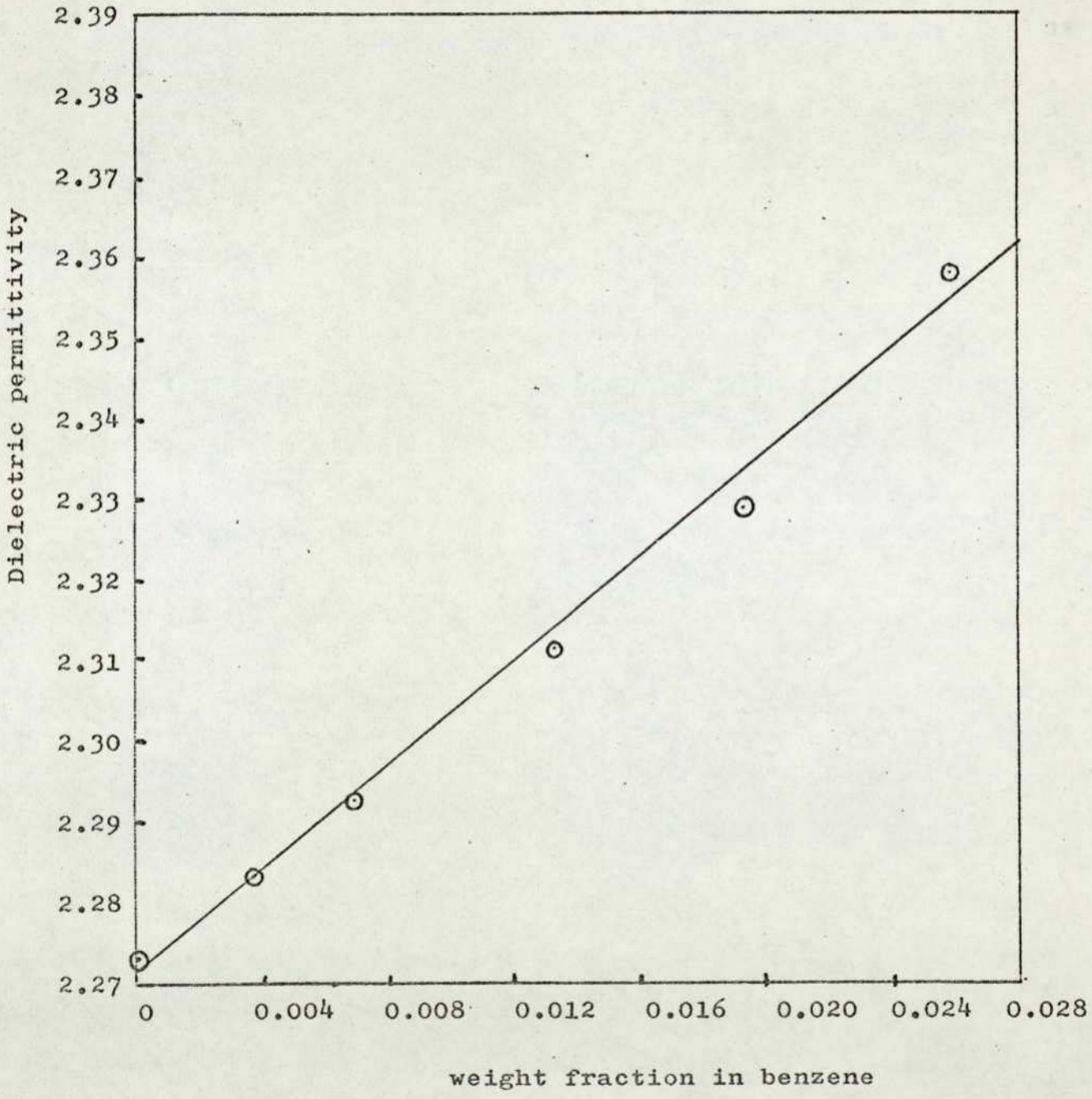
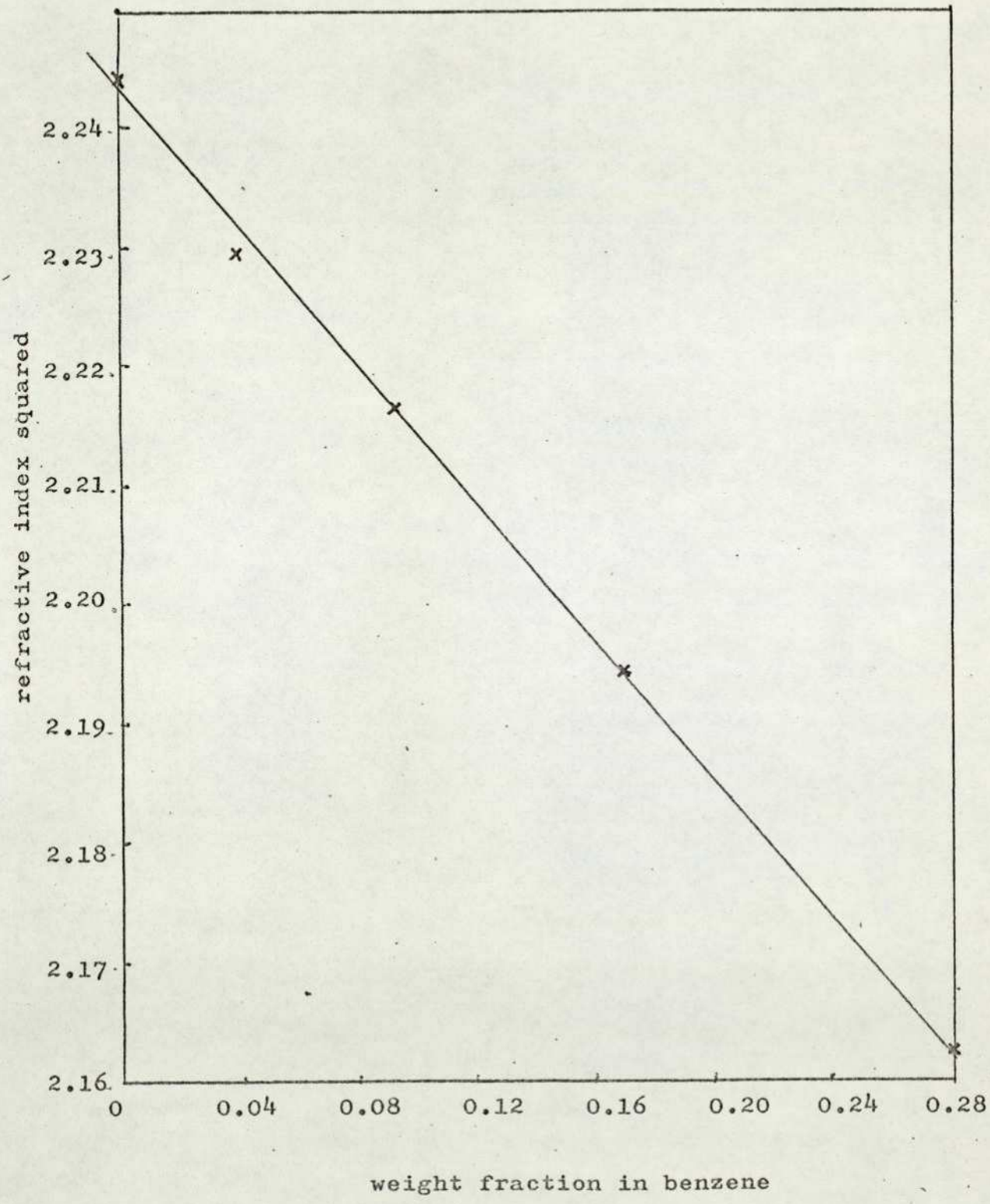


Fig. 21

Plot of refractive index squared against weight fraction of ethyl propionimidate



The positions of the absorption bands throughout this section are given in wavenumbers (cm^{-1}).

In discussing the assignments reference will be made to the liquid phase values unless otherwise stated as certain bands are too weak in the vapour phase spectra for accurate measurement.

The diagrams of the spectra given in this section will be for the liquid phase. The general position and relative intensity of the bands varies little between the liquid, vapour and solution spectra of the imidates with the exception of the ν NH mode. This mode has previously been discussed in detail (Chapter 3.B).

CHAPTER 4

Infrared Spectra - Assignments

A. Methyl Trichloroacetimidate

Methyl trichloroacetimidate would appear to be the only imidate for which the presence of specific skeletal modes has been recognised.[49] The present assignment extends the original assignment in the light of the extra information obtained from dipole moment studies, solvent shift studies, the knowledge of other imidate systems in which skeletal modes have been observed and the measurement of the far infrared spectrum.

Although for the convenience of the dipole moment calculations the methyl trichloroacetimidate system was considered as being planar, the probable arrangment of the atoms would eliminate all elements of symmetry, except perhaps a plane of symmetry involving the heavy atom skeleton, consequently, all modes are likely to be active in the infrared and Raman effect. Of the thirty (3N - 6) infrared active fundamental modes, there will be eleven (N - 1) stretching modes and nineteen (2N - 5) deformation modes. Without a force field calculation, which has not been undertaken due to the difficulty in obtaining accurate bond length data for the C=N bond, and without a Raman spectrum, assignment of the bands must always be tentative, particularly in the far infrared region in which larger shifts in band position with substitution are noted.

Assignment is made largely by comparison of the peaks in methyl trichloroacetimidate with the band positions in

molecules containing the same fundamental groups, in similar molecular environments, where possible. As there is only one plane of symmetry within the molecule the modes can be divided into two groups, those symmetric to the plane (a' species) and those antisymmetric to the plane (a'' species) of which there are nineteen and eleven respectively.

For convenience the modes associated with the chlorine and hydrogen atoms will be discussed first.

Associated with the CCl_3 and CH_3 groupings will be symmetrical and antisymmetrical stretching modes (ν_s and ν_{as}), symmetrical and antisymmetrical in plane bending modes (b_s and b_{as}), an in plane rocking mode and an out of plane rocking mode (wagging). Additionally there will be two torsional modes, one associated with the methyl group and the carbon - oxygen bond and the other associated with the CCl_3 group and the carbon - carbon bond.

For convenience the b_{as} and ν_{as} modes have been considered as being doubly degenerate, as would be the case with higher symmetry, as the splitting between the in and out of the plane antisymmetric modes is likely to be below the resolving power of the equipment. Thus eighteen modes have been postulated as follows:

$\nu_s CH_3$, $\nu_{as} CH_3$ (degenerate), $b_s CH_3$, $b_{as} CH_3$ (degenerate), rCH_3, wCH_3, $t(CH_3\text{-}C\text{-}O)$, $\nu_s CCl_3$, $\nu_{as} CCl_3$ (degenerate), $b_s CCl_3$, $b_{as} CCl_3$ (degenerate), $rCCl_3$, $wCCl_3$, and $t(CCl_3\text{-}C\text{-}C)$.

In addition there will be modes associated with the imino

group, the NH stretching, νNH, the in plane bending βNH and the out of plane bending γNH.

The remaining nine modes must be associated with the five atom skeleton (Fig. 24). These can be further divided into five bending and four stretching modes. The four stretching modes expected, $\nu C_1\text{-}C_2$, $\nu C_2\text{-}O$, $\nu C_3\text{-}O$, and $\nu C_2{=}N$, would appear to be considerably mixed and this mixing is discussed (Chapter 3.D). The bending modes can be divided into three a' species, namely C-O-C bending, O-C=N bending and C-C=N bending, and two a'' species, C-O-C torsion and CH_3-C-O out of plane bending.

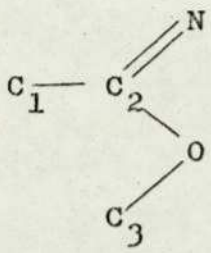


Fig. 24

The infrared spectrum of methyl trichloroacetimidate has been recorded in the range 4000-20cm^{-1} in the liquid phase and 4000-650cm^{-1} in the vapour phase. Previously[49], the complete solution spectrum in carbon tetrachloride solution, supplemented by carbon disulphide in the regions of solvent absorption had shown that only the peak occurring at 3346 in the liquid phase and 3373 in the vapour phase, and possibly the peak at 1253, in the vapour phase, were affected in their position by the choice of solvent. This study has not been repeated. The highest wavenumber absorption at 3373 in the vapour phase is characterised by its sharpness in both the vapour and liquid spectra. Comparison of the shape of this band with the corresponding band in methyl acetimidate (Chapter 3.B), suggests

the absence of intermolecular bonding in the liquid phase.

In the liquid phase there are five absorptions in the region 2800-3050, of which two peaks are expected to be attributable to the symmetric and antisymmetric stretching modes of the methoxy group. For comparison the data of Nolin and Jones[148] for methyl acetate and Prichard and Orville-Thomas[100] on methyl acetimidate is cited (Table 36).

Table 36

Assignment of the carbon hydrogen stretching region of methyl trichloroacetimidate

Assignment	Methyl acetate[a]	Methyl trichloroacetimidate	Methyl acetimidate[b]
Combination band	3026	3025	
Combination band	2999	2999	3005
ν_{as}CH of CH_3O	2957	2952	2948
Combination band	2905	2905	2902
ν_sCH of CH_3O	2846	2848	2853

[a]Ref. 148 [b]Ref. 100

The weak peaks in the region 1700-2800 are assigned to combination tones with the exception of the peak at 1773. This is almost certainly a carbonyl impurity. The intensity of the peak slowly increases in intensity on standing and may be indicative of sample decomposition to methyl trichloroacetate

or rearrangement to the N-methyl trichloroacetamide[72]. The carbonyl band of methyl trichloroacetate has been measured at 1776, by Josien and Callas[168].

The strong band at 1673 is assigned to the carbon nitrogen stretching mode, νC=N. The corresponding band occurs in methyl acetimidate[100] at 1660 and the raising in the wavenumber position of this band is similar, though not as marked as that observed with carbonyl groups adjacent to trichloro groupings (methyl acetate 1748, methyl trichloroacetate 1776).

An interesting feature of the spectrum of methyl trichloroacetimidate is the appearence of two strong bands at 1314 and 1295. The 1295 band may tentatively be assigned to the overtone of the ν_sCCl band at 652, which is involved in Fermi resonance with the stronger band at 1314.

This latter band is assigned, in common with the bands at 1083, 1009 and 827 to the skeletal modes of the imidate as described in Chapter 3.D.

The antisymmetric and symmetric in-plane bending modes of the methyl group can readily be assigned to the two bands at 1463 and 1439, the position being very close to the bending modes in other systems where the methyl group is attached to an oxygen atom (Table 37).

In the light of the evidence in Table 38 the wavenumber position of methyl group rocking mode, r(OCH_3) has been left unassigned, and the band at 1193, assigned by Prichard[49] to the rocking mode, is assigned for preference to the wagging

mode of the methyl group.

Table 37

Assignment of the in-plane bending carbon-hydrogen modes of methyl trichloroacetimidate

Compound	$b_{as}(CH_3)$	b_sCH_3	Reference
Methyl acetate	1456	1435	148
O-Methyl formhydroxamic acid	1464	1441	169
O, N-Dimethyl nitramide	1466	1403	170
O-Methyl hydroxylamine	1475	1439	171
Methyl acetimidate	1458	1447	100
Methyl trichloroacetimidate	1463	1439	

Table 38

Comparison of the rocking and wagging modes of the methoxy groups of various compounds.

Compound	$r(OCH_3)$	$w(OCH_3)$	Reference
O-Methyl hydroxylamine	1143	1212	171
O, N-Dimethyl hydroxylamine	1156	1215,1202	171
Trimethyl hydroxylamine	1086	1214	171
O-Methyl formhydroxamic acid	1124	1209	169
Methyl acetate	1248?	1187	172
Methyl formate	1230?	1168	172
Methyl acetimidate		1195	100

In the present work it had been hoped to assign the in plane NH bending mode, βNH, and recourse was made to the preparation of the N-deutero compound (Chapter 4.D), in order to observe isotopic shifts. Prichard[49] assigned the mode to a weak band at 1242 in methyl trichloroacetimidate but this band was not observed in the present study and may have been due to an impurity. Grivas and Taurins,[173] in assigning N-mono- and N-disubstituted- trichloroacetamidines, assigned a band at 1510-1525 in the alkyl and 1570-1550 in the aryl compounds to a deformation (NH) mode. This assignment was supported by the absence of a band in the NN-disubstituted derivatives. Barr and Haszeldine[174] and Hadzi and Skrbljak[175] also found bands in the same region assignable to the deformation (NH) mode. These were weak bands, however, whilst the bands observed by Grivas and Taurins were strong or very strong bands and resonance enhancement due to coupling was postulated. In the trichloroacetimidates no significant band in the region 1500-1600 was observed.

An assignment of an in-plane bending NH mode, substantiated by a normal coordinate treatment, is due to Miyazawa et al.[147] A band at 1299 was assigned to a mode which contained a contribution from the ν C-N mode. Other assignments of the βNH mode place the band even lower, at 1100 for primary and secondary amines,[176] at 1144 for pyrrole,[177] and at 903 for ethylenimine.[178] If compared with the relative intensity of the βOH and ν OH modes, it would seem reasonable to expect, in

the light of the medium intensity of the υNH mode, that the βNH mode will be a relatively weak vibration, and it is possible that this band is masked by other strong absorptions.

The most probable assignment of the βNH band in methyl trichloroacetimidate is a shoulder band at 1295, which possibly shifts to 1159 (ratio 1.12) or 1055 (ratio 1.23) in the deuterate. However, a band is observed in the same region in N-chloromethyl acetimidate which could contradict this assignment.

Table 39

The carbon chlorine stretching modes of the trichloro group in various molecules.

Compound	ν_{as}CCl	ν_{s}CCl	Reference
Trichloroacetonitrile	760	667	179
Methyl chloroform	786	490	180
Trichloroacetic acid	791	712	181
Trichloroacetamide	833	676	182
Trichloroacetimino methyl ether	832	650	183
Methyl trichloroacetimidate	797	650	184

The out of plane γ(NH) mode is left unassigned as it appears to have been masked by the very intense trichloro group absorption.

The two very intense bands at 798 and 652 are assigned to

the antisymmetric and symmetric carbon chlorine stretching modes respectively. This assignment is made by comparison with the data in Table 39.

The weak band at 682cm^{-1} is probably a fundamental associated with a bending mode of the heavy atom skeleton, O-C=N. Similar assignments have been made by Davies,Evans and Jones[185] for the 630 band in the spectrum of N-methyl acetamide and more recently by Miyazawa et al[147] for the 627 band in the same compound, in the latter case the force field calculations show considerable mixing of the vibrational modes which occur in N-methyl acetamide. This assignment is in agreement with bands observed by the author in the spectrum of n-propyl trichloroacetimidate at 679 and 674 in the spectra of methyl benzimidate.

With no Raman data available, the assignment of the spectrum below 600 must be extremely tentative. An obvious starting point was to draw together the data for all the imidates investigated. This revealed the presence of a band at 320-270 in every compound, which is assigned to a skeletal bending mode, possible involving the C-O-C grouping, as the position is fairly constant. Miyazawa et al[147] observed a band at 289 in N-methyl acetamide, assigned to the mixed mode 70% CH_3-N-C bending; 30% O=C-N. This evidence would appear to support a mode involving the basic five atom skeleton, and would suggest that the degree of mixing may be greater than was first anticipated. In methyl trichloroacetimidate this assignment is to the weak band at 288.

The band at 118 is thought to be due to a torsional mode of the molecule. Miller et al[186] found in halogeno substituted benzaldehydes that the torsional modes fell in the range 11-70cm^{-1}, while the torsional mode of 1,1,1,2 tetrachloroethane was assigned by Allen et al[188] to a band at 118 in the Raman spectrum of the liquid.

Either of the bands at 173 and 209cm^{-1} may provisionally be assigned to rocking modes of the trichloro group. Assignment of bands at 159 in 1,1,1,2 tetrachloroethane[188] and at 165 and 176 in pentachloroethane[188] substantiate this view. The evidence for the assignment of the band at 209 is less satisfactory, for whereas Lucazeau and Novak found a peak at 201 in the spectrum of trichloroacetaldehyde,[187] Nielson et al[189] found a deformation mode of the CCl_3 group at 224 in pentachloroethane.

The band at 345 is probably another CCl_3 mode, as corresponding bands occur at 340 in hexachloroethane[190] and 345 in methyl chloroform.[184]

A complete assignment of the spectrum of methyl trichloroacetimidate is given in Table 40, and the liquid phase spectrum is shown diagramatically in the range (4000-600) in Fig. 25.

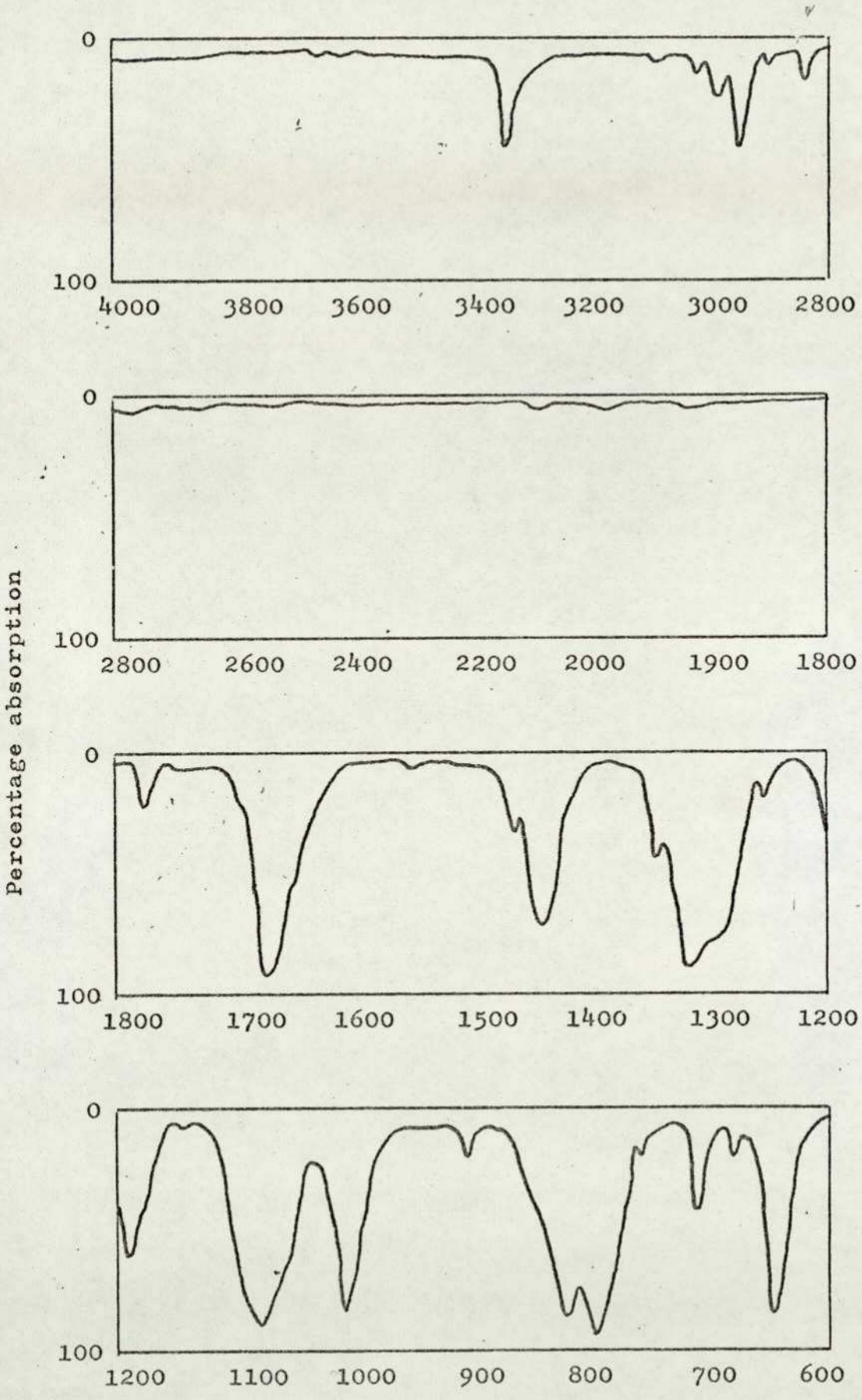


Fig. 25 Liquid phase infrared spectrum of methyl trichloro-acetimidate in the region 4000-600cm^{-1}

Table 40

Assignment of the infrared spectrum of methyl trichloroacetimidate.

Liquid	Vapour	Assignment
3346s	3373s	ν NH
3025m	3033m	combination band ($\nu_s CH_3$+173)=3021
2999m	3001m	combination band (νCN+1314)=2987
	2968vs.sh	
2952s	2962vs	$\nu_{as} CH_3$
	2958vs.sh	
2905w	2916w	combination band $b_{as} CH_3$+$b_s CH_3$=2902
2848m	2857m	$\nu_s CH_3$
2750w		combination band $b_{as} CH_3$+1314=2777
2575w		combination band $b_{as} CH_3$+1083=2546
2098vw		combination band 1083+1009=2092
1989vw		combination band 1083+906=1989
1773w	1790w	νCO impurity
1673vs	1675s	νC=N
	1652m,sh	
1496vw		combination band $\nu_{as} CCl_3$+682=1480
	1465m	$b_{as} CH_3$
1463m	1459m	
1439m	1442m	$b_s CH_3$
1314vs	1315vs	skeletal mode A
1295s.sh		βNH
1253w	1248w	combination band 1083+173=1256

Table 40 cont.

Liquid	Vapour	Assignment
1193m	1197m	wCH_3
1083vs	1089vs	skeletal mode B
1009s	1014s	skeletal mode C
906w	911w	combination band 118+798=916
827s	832s	skeletal mode D
798s	807vs	$\nu_{as}CCl_3$
714m		CCl_3 group combination band, 435+288=723
682w		δ(O-C=N)
652s	656m	$\nu_s CCl_3$
435w		? skeletal bending mode
407w		? 118+288=406
345w		$b_s CCl_3$
288w		skeletal bending mode (O-C=N)
209w		$rCCl_3$
173w		$rCCl_3$
118w		torsional

s. strong m. medium w. weak sh. shoulder v. very

B. Ethyl Trichloroacetimidate

The assignment of this imidate closely follows that of methyl trichloroacetimidate, and as such the discussion of the assignment will be mainly concerned with the modes involving the ethoxy grouping.

The work of Nolin and Jones[149] on ethyl acetate is used for comparison purposes. Peaks and assignments for ethyl acetate are given in Table 41, together with the corresponding peaks in ethyl trichloroacetimidate.

Table 41

Assignment of the carbon-hydrogen stretching region of ethyl trichloroacetimidate.

Ethyl acetate[a]	Ethyl trichloroacetimidate	Assignment
2982	2985	ν_{as}CH of ethoxy methyl
2962sh	2961sh	ν_{as}CH of ethoxy methylene
2939	2940	overtone
2906	2906	ν_{s}CH of ethoxy methylene
2873	2872	ν_{s}CH of ethoxy methyl

[a]Ref. 149

Nolin and Jones question their own assignment in only one respect in that the assignment of the bands at 2939 and

2873 may be reversed. From the spectrum of methyl acetate the above assignment would seem more realistic. Prichard[49] observed peaks in ethyl acetimidate at 2981, 2932, 2906 and 2870 which were assigned respectively to the $\nu_{as}CH_3$, $\nu_{as}CH_2$, $\nu_s CH_2$ and $\nu_s CH_3$ modes. The agreement with the present work is again good but the assignment of the 2932 may be better attributed to an overtone, as the $\nu_{as}CH_2$ band is only a relatively weak band and it may have been masked by the stronger $\nu_{as}(CH_3)$ band in ethyl acetimidate.

The band observed at 1745 would again appear to be a carbonyl impurity, this assignment being supported by the shift and increase in intensity of this band in the gas phase spectrum.

The spectrum of ethyl trichloroacetimidate shows six bands in the region 1320-1500. Comparison was sought with the position of bands in ethyl acetate[149] and various imidates and N-chloro imidates (Table 42).

Nolin and Jones[149] observed a peak at 1475 in the deuterated ethyl acetate derivatives which contained a methylene group but the intensity of the band was increased if a methyl group was adjacent to the methylene group. Thus this peak and the corresponding peaks in Table 42 may be assigned to a CH bending mode of the ethoxy group. Assignments of the bands in ethyl acetate at 1464, 1446 and 1393 to the scissoring CH_2 bCH_3 of the ethoxy group and $b_s CH_3$ respectively are also adopted for the corresponding bands in Table 42. The remaining

bands of ethyl trichloroacetimidate in this region are less satisfactorally assigned. The band at 1472 is probably an overtone, and, as it has no parallel in the four compounds in Table 42, it may be an overtone of a trichloro group stretching mode probably the symmetric stretch.

Table 42

The position of peaks in the region 1500-1320 of ethyl trichloroacetimidate and related compounds.

Ethyl trichloro-acetimidate	Ethyl acetate[a]	Ethyl acetimidate[b]	N-chloro ethyl acetimidate[b]	N-hydroxy ethyl acetimidate[b]
1477	1475	1481	1479	1481
1472				
1464	1464	1462	1468	1468
1445	1446	1443	1445	1444
	1430*			
1394	1393	1403	1395	1395
	1373*	1379	1376	1376
1369	1359	1330		

[a]Ref. 149 [b]Ref. 49 * CH_3CO modes.

The band at 1369 is assigned to the wagging motion of the methylene group. This is shifted to 1359 in ethyl acetate by

coupling with the ν_s(CH) of the CH_3CO grouping.

Of the bands in the region 1320-600, four bands at 1311, 1078, 1028 and 816 may be assigned to skeletal modes as discussed in Chapter 3. D, two at 796 and 649 to the $\nu_{as}CCl_3$ and ν_sCCl_3 modes respectively, and a further band at 714 to a b(O-C=N) mode on the basis of the assignment of methyl trichloroacetimidate. Additionally the βNH mode is tentatively assigned to a side band at 1294 on skeletal mode A. The remaining bands in the region are at 1174, 1159, 1116, 1093, 963, 947 and 881. The band at 1174 is probably a wagging mode of the methyl group. This mode occurs at 1193 in methyl trichloroacetimidate and at 1176 in ethyl acetimidate.[49] The bands at 1116 and 1093 have analogues at 1115 and 1093 in ethyl acetate. The former band is possibly a rocking mode of the methyl group, on the grounds of its intensity and shift in the deuterated ethyl acetates.[149] Of the remaining bands the peak at 947 may be a ν(C-C) mode of the ethyl group. A vibration at 922 is assigned in propane vapour[197] to this mode and there is a band at 938 in ethyl acetate which is left unassigned by Nolin and Jones.

Five peaks were identified below 600 but as the lowest of these bands was at 194, it would appear that the torsional mode was too weak to be observed.

The assignment of the 194 band to a $rCCl_3$ mode, and the 345 band to the b_sCCl_3 mode again follows the assignment of methyl trichloroacetimidate. The remaining bands are probably

skeletal bending modes, the band at 288 corresponding in position to a band in methyl trichloroacetimidate.

The liquid phase spectrum is shown diagrammatically in Fig. 26 and a complete assignment including gas phase and solution values is given in Table 43.

Table 43

Assignment of the spectrum of ethyl trichloroacetimidate.

Liquid	Vapour	Solution	Assignment
3347m	3371m	3351w	νNH
2985m	2991m	2986w	ν_{as}CH of ethoxy methyl group
2961m.sh		2964vw.sh	ν_{as}CH of ethoxy methylene group
2940mw	2946w	2940vw	combination band 1477+1464=2941
2906w	2914w	2906w	ν_{s}CH of ethoxy methylene
2873w		2872vw	ν_{s}CH of ethoxy methyl
2725vw			combination band
2610vw			overtone 2x1311=2622
2578vw			combination band 1116+1464=2580
2482vw			combination band 1311+1174=2485
2248vw			combination band 1174+1078=2252
2114vw			combination band 1028+1078=2106
1962vw			combination band 1311+649=1960
1857vw			combination band
1745mw	1780m		carbonyl impurity

cont.

Table 43 cont.

Liquid	Vapour	Solution	Assignment
1670s.sh	1672s		
1664vs		1664vs*	νC=N region
1653s.sh		1653m.sh*	
1635m.sh			
1477mw		1477w	ethyl group bending mode
1472mw.sh		1473w.sh	combination band 649+816=1465
1464mw			scissoring CH deformation of methylene group
1445mw		1445w	$b_{as}CH_3$
1394mw			b_sCH_3
1369m	1374m	1369m	ωCH_2
1311vs	1301s	1311s	skeletal mode A
1294s.sh		1294s.sh	βNH
1174mw		1174w	$\omega(CH_3)$
1159w.sh			combination band 816+345=1161
1116m		1115w	$r(CH_3)$
1093s.sh			combination band 816+274=1090
1078vs	1088s	1079s	skeletal mode B
1028vs	1032m	1029m	skeletal mode C
963mw	962w		combination band
947w			νC-C of ethyl group
881ms	884m		combination band
816s			skeletal mode D
796vs	806s	813s*	$\nu_{as}CCl_3$
714mw	713w		b(O-C=N)
649s	651m	651m*	ν_sCCl_3
378w			skeletal bending mode
345w			$b_s(CCl_3)$
288w			δ(O-C=N)
274w			skeletal bending mode
194w			$rCCl_3$
?			torsional mode

Solution spectra apply to carbon tetrachloride except those values marked * which apply to hexane.

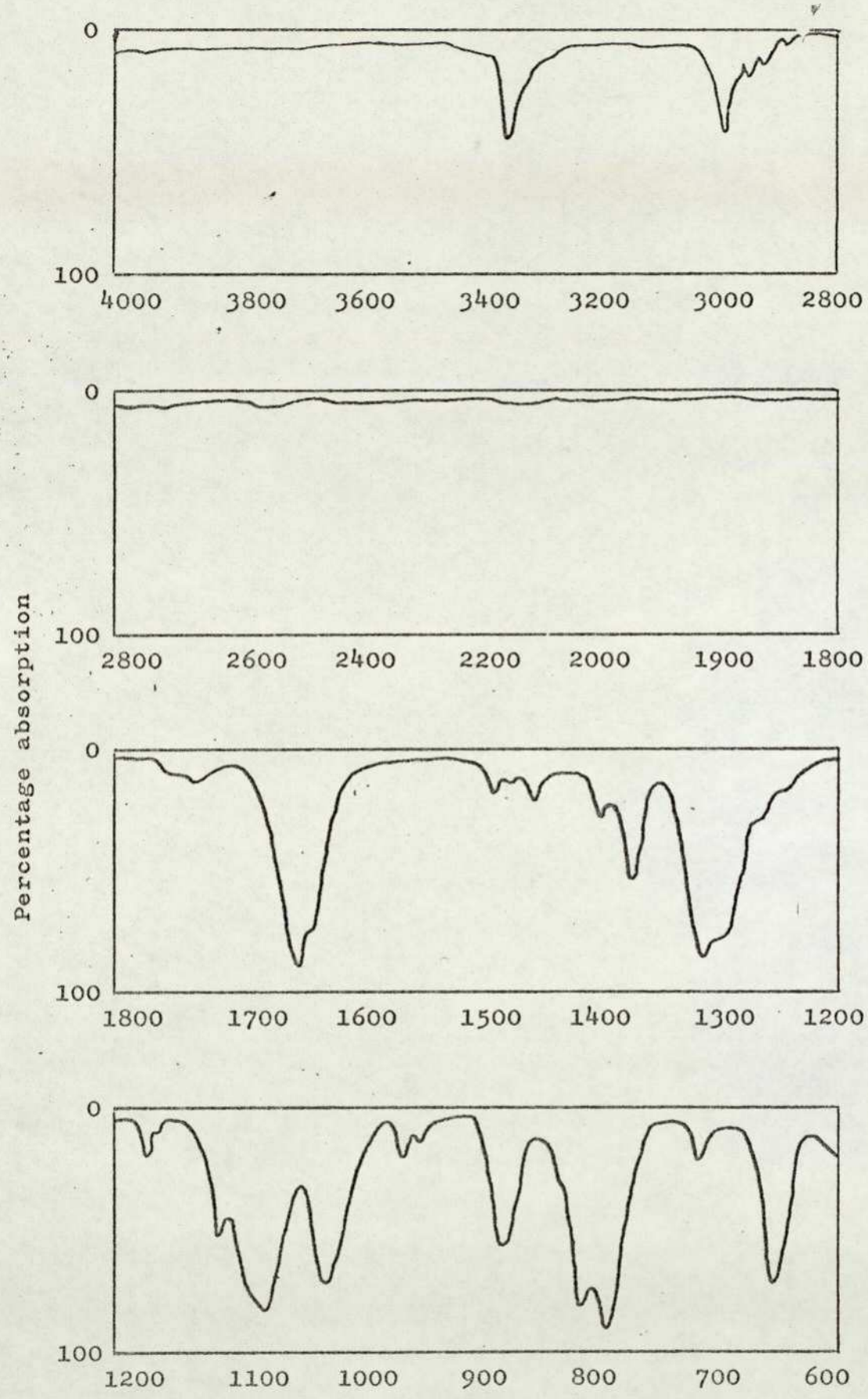


Fig. 26 Liquid phase infrared spectrum of ethyl trichloro-acetimidate in the region 4000-600cm^{-1}

C. n-Propyl Trichloroacetimidate

The assignment of the spectrum of n-propyl trichloroacetimidate was not undertaken in detail due to the lack of data for the n-propyl group. The division of the expected 48,(3N-6) modes in the spectrum, into 17,(N-1) stretching modes and 31,(2N-5) deformation modes, is complicated by the degeneracy and mixing of the vibrations. This is particularly so in the case of the n-propyl group vibrations, where many of the vibrations are superimposed. With no adequate data on the n-propyl grouping it was decided to record the spectrum of n-propyl acetate for comparison purposes.

From the observations of Nolin and Jones[148,149] it was anticipated that the spectrum of n-propyl acetate in the νCH region would be essentially that of the n-propyl group, with only a small contribution from the methyl group. The similarity in the wavenumber positions of peaks in n-propyl acetate and n-propyl trichloroacetimidate as presented in Table 44 would seem to support this assumption.

In the spectrum of n-propyl acetate, only four peaks were observed in the νCH region, suggesting that the peaks at 2928 and 2858 in n-propyl trichloroacetimidate are overtones. The two stronger and higher wavenumber peaks at 2973 and 2941 may reasonably be assigned to the antisymmetric stretching vibrations of the propoxy methyl group and the propoxy methylene groups respectively, whilst the weaker bands at 2895 and

2883 are assigned to the symmetric stretching modes of the methylene and methyl groups respectively.

Table 44

Comparison of the spectra of n-propyl acetate and n-propyl trichloroacetimidate in the region 3000-2800cm^{-1}.

n-propyl acetate	n-propyl trichloroacetimidate
2973s	2973vs
2944s	2941s
	2928s.sh
2897m.sh	2895m
2884m	2883m
	2858m

The band observed at 1745 is probably a carbonyl impurity, the position corresponding to the carbonyl band in n-propyl acetate (1744), although this may not be the impurity.

Bellamy[191] quotes the following positions for the carbon - hydrogen deformations in alkanes:-

C-CH_3	1450 ± 20cm^{-1}	(m)	antisymmetric
-CH_2-	1465 ± 20cm^{-1}	(m)	
-C-CH_3	1380 - 1370cm^{-1}	(s)	symmetric

In the region 1350-1500, the following bands (Table 45) were observed in n-propyl trichloroacetimidate and n-propyl acetate.

Table 45

Wavenumber positions of bands in the region 1350-1500 in n-propyl acetate and n-propyl trichloroacetimidate.

n-propyl acetate	n-propyl trichloroacetimidate
	1475m.sh
1467w	1468m
1457m	
1442m.sh	1440m
1391s	1391s
1378s.sh	1380m
1366s	

On this basis the bands at 1468, 1440 and 1391 are assigned to the scissoring CH_2 and the antisymmetric and symmetric deformation modes of the methyl group respectively.

The wagging CH_2 mode is assigned to a band at 1348. This is lower than the band position in ethyl trichloroacetimidate, 1369, and ethyl acetate, 1359, this mode being particularly sensitive to its environment.

Of the remaining bands below 1340, four bands at 1309, 1082, 1000 and 827 are assigned to skeletal modes and the $\nu_{as}CCl_3$ and $\nu_s CCl_3$ modes are assigned to bands at 798 and 645 on the basis of previous assignments. The shoulder at 1294 again remains a problem for although it could easily be assigned to a $\nu_s CCl_3$ group overtone, it may possibly be the

βNH mode.

The band at 1158 is probably a rCH_3 mode, a corresponding band occuring in propane at 1155.[192] The band at 982 is possibly an antisymmetric C-C stretching mode associated with the propyl chain. Brown and Sheppard[193] observed a band at 1029 in n-propyl chloride comparable to the mode. As discussed previously, the C-C stretching mode is very variable in its position and the band at 982 would appear to be the only band of sufficient intensity for assignment to this mode, although McMurray and Thornton[192] prefer a band at 923 in propane.

The assignment by the latter authors of a band at 870 on the basis of Raman evidence to the symmetrical stretch of the carbon chain is in agreement with the present observations.

The remaining bands below 600 are mainly left unassigned. The torsional band has probably not been recorded, as the lowest observed band at 215 is positionally consistent with a rocking CCl_3 mode. The band at 287 is again thought to be a skeletal mode of the five atom skeleton.

The assignment of the n-propyl trichloroacetimidate is given in Table 46, together with the vapour and solution values, and the liquid phase spectrum is shown diagramatically in Fig. 27.

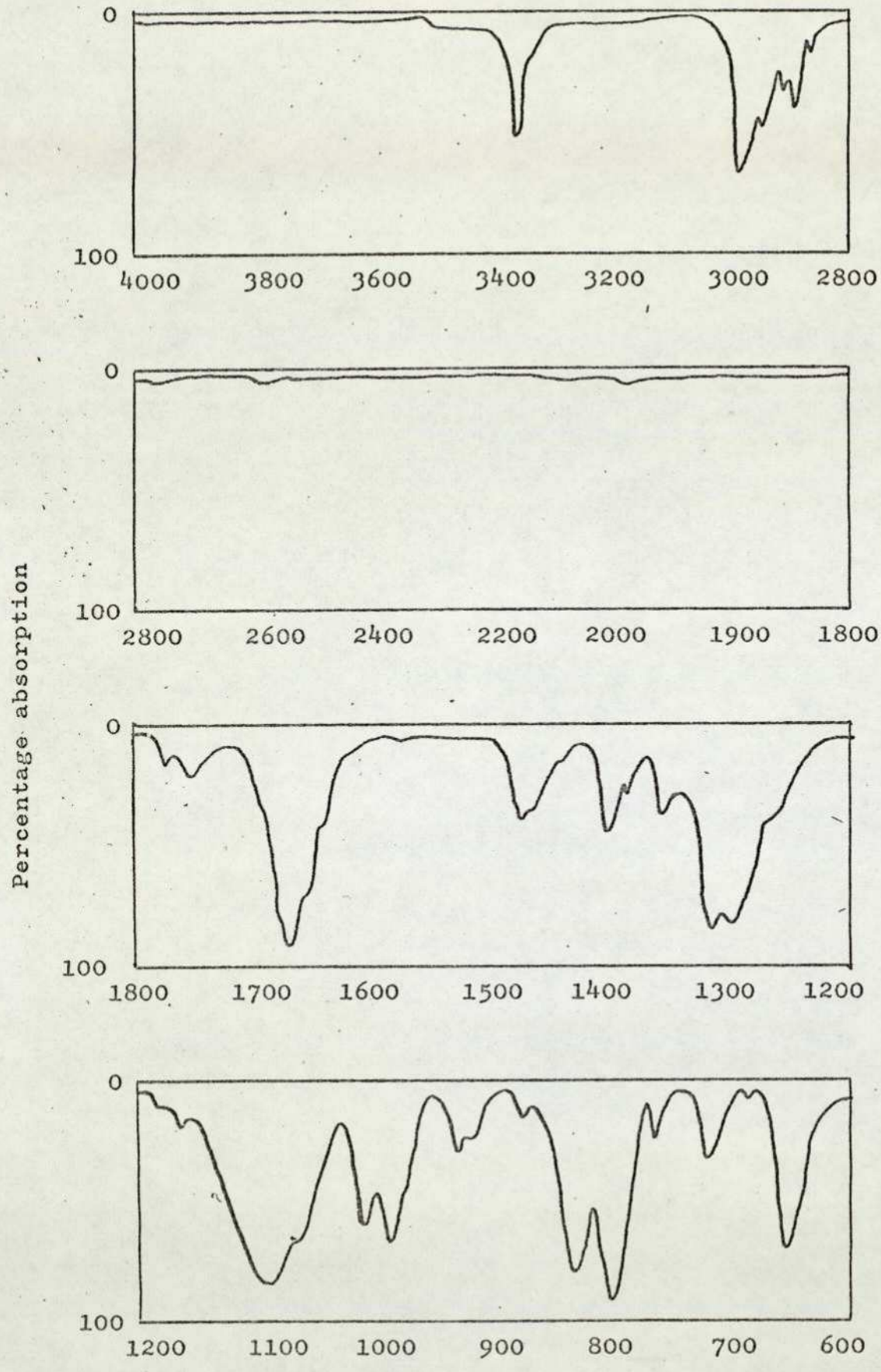


Fig. 27 Liquid phase infrared spectrum of n-propyl trichloro-acetimidate in the region 4000-600cm^{-1}

Table 46

Assignment of the infrared spectrum of n-propyl trichloroacetimidate.

Liquid	Gas	Solution	Assignment
3348s	3372m	3351m	νNH
2973vs	2981s	2972s	ν_{as}CH of propoxy CH_3
2941s		2941m	ν_{as}CH of propoxy CH_2
2928s.sh		2928m.sh	combination band 1265+1663=2928
2895m	2896m	2897m	ν_{s}CH of propoxy CH_2
2883m		2883m	ν_{s}CH of propoxy CH_3
2858w		2858w.sh	combination band 1391+1468=2859
2743vw			combination band 1083+1663=2745
2683vw			combination band 1670+1000=2670
2593vw			combination band 1670+925=2595
2150vw			overtone 2x1082=2164
2002vw			overtone 2x1000=2000
1767m			combination band 827+933=1760
1745m	1769m	1745mw	C=O impurity
1670vs.sh	1670vs		
1663vs	1664s.sh	1663vs	νC=N + overtones
1652vs.sh	1653m.sh	1652sh	
1475m.sh		1475m.sh	combination band
1468m	1460m	1468m	scissoring CH_2
1440m		1438w	$b_{as}CH_3$
1391s	1395m	1391m	$b_{s}CH_3$
1348m		1348m	ωCH$_2$
1321vsh			combination band
1309vs	1297vs	1308vs	skeletal mode A
1294vs.sh		1293vs.sh	βNH
1265m.sh			combination band 827+433=1260
1172w.sh		1172w.sh	combination band
1158w		1156w	rCH$_3$
1082vs	1085vs	1082vs	skeletal mode B

Table 46 cont.

Liquid	Gas	Solution	Assignment
1059ssh			combination band 711+358=1069
1000s	1003m.sh	995s	skeletal mode C
982s	983m	979s	ν_{as}C-C of propoxy
933m	932w	934m	combination band 287+645=932
925m		925m.sh	ν_{as}C-C of propoxy group
914m.sh		914m.sh	combination band 482+433=915
882w.sh			combination band 482+393=875
867w			ν_{s}C-C of propoxy group?
827vs	832m		skeletal mode D
798vs	806s		$\nu_{as}CCl_3$
759m			
711m	713mw		
679w			bending (O-C=N)
645vs	651m		$\nu_{s}CCl_3$
611vw			
493w			
482w			
433w			
393w			
358w			
326w			
287w			δ(O-C=N)
271w			
215w			rCCl_3

D. Methyl Trichloroacetimidate Deuterate

Methyl trichloroacetimidate deuterate $Cl_3C(C{=}ND)OCH_3$ was prepared to determine the modes associated with the C=N-H grouping. The presence of an imino impurity was manifested by a weak peak at 3351 and a shoulder at 1673 on the ν C=N mode at 1656. The modes associated with the methoxy and trichloro methyl groupings as given in Table 47, show little variation in position from the parent imidate.

Table 47

Comparison of the modes associated with the methoxy and trichloro methyl groups in methyl trichloroacetimidate and the deuterate.

Assignment	Methyl trichloroacetimidate	Methyl trichloroacetimidate D
$\nu_{as}CH_3$	2952s	2955m
$\nu_{s}CH_3$	2848m	2845w
$b_{as}CH_3$	1463m	1458m
$b_{s}CH_3$	1439m	1437s
wCH_3	1193m	1192w
$\nu_{as}CCl_3$	798s	811vs
$\nu_{s}CCl_3$	652s	655s

The remaining fundamental modes above 600 may be affected in their position as a result of deuteration. These include

the ν C=N, νNH, βNH, γ NH and skeletal modes. It was anticipated that assignment of the deuterate would allow the in-plane nitrogen-hydrogen bending mode, βNH, to be indentified in the parent compound. To simplify the discussions surrounding the assignment of this mode, the other modes will be discussed first.

Table 48

The position of the ν C=N mode in various imidates.

Compound	Wavenumber position
Methyl trichloroacetimidate	1673
Methyl trichloroacetimidate deuterate	1656
Ethyl trichloroacetimidate	1664
n-Propyl trichloroacetimidate	1663
Methyl acetimidate	1660
N-Chloro methyl acetimidate	1619
Ethyl acetimidate	1655
N-Chloro ethyl acetimidate	1617
N-Hydroxy ethyl acetimidate	1663
Ethyl propionimidate	1650
N-Chloro ethyl propionimidate	1606

The ν C=N mode, which occured in methyl trichloroacetimidate at 1673 in the liquid phase, is shifted to 1656 in the deuterate. The shift of this mode was much greater than

anticipated and would suggest that the skeletal modes will also be affected if they contain components of the νC=N stretching mode. To discover if the effect on the νC=N mode was consistent with the data on the band in other imidates, it was decided to tabulate the position in a variety of imidates (Table 48). Benzimidates were excluded as the azomethine band is subject to known conjugation.

From Table 48, it is clear that the substitution of the imino hydrogen by chlorine results in a lowering of the wavenumber position of the νC=N mode, but that this is not purely a mass effect is clearly indicated by the fact that the νC=N mode occurs at a higher wavenumber position in the N-hydroxy compound than in the parent imidate. It would appear that the shift in the N-chloro derivatives is partly due to a mass effect and partly an electronic effect.

In methyl trichloroacetimidate, the νNH mode was found at 3346 in the liquid phase. The shifted band in the deuterate at 2476cm^{-1} is assigned to the νND mode, the isotopic ratio of 1.352 being close to the $1/\sqrt{2}$ relationship.

The four skeletal modes of the methyl trichloroacetimidate and methyl trichloroacetimidate deuterate spectra are assigned to bands as follows:-

Compound	Skeletal mode A	B	C	D
Methyl trichloroacetimidate	1314	1083	1009	827
Methyl trichloroacetimidate deuterate	1283	1085	1026	852

The effect of deuteration is to considerably alter the position of three of the bands, the fourth band, mode B, which is thought to be basically a ν_{as}COC mode is virtually unaltered. This latter observation is consistent with the mode being associated with the ether linkage, rather than involving the azomethine grouping. It is therefore surprising that mode D which is tentatively assigned to the corresponding ν_{s}COC mode is raised considerably in its position and it can only be suggested that the mixing with the ν_{s}C-C=N is greater in this case. Impurities in the spectrum of the deuterate due to isotopic exchange were observed as shoulders at 1313 and 831 in the liquid phase and additionally at 1019 in the gas phase. As these are all strong bands in the parent compound, the deuterate was relatively pure.

The remaining bands at 1348, 1159,1055, 923, 755, 714, 685 and 617 are unassigned. The band at 923 is probably an overtone corresponding to the band at 906 in the parent compound. If the band is, as suggested in the assignment of the methyl trichloroacetimidate, a combination band involving the torsional mode and the $\nu_{as}CCl_3$ mode it might be expected to occur at a slightly higher wavenumber position as the $\nu_{as}CCl_3$ mode occurs at a higher wavenumber position in the deuterate. The bands at 714 and 685 are assigned by comparison with methyl trichloroacetimidate to an overtone and a b(O-C=N) mode. This latter assignment is rather unsatisfactory as it does not appear to have been shifted on deuteration.

The new band at 617 would appear too intense to be attributable to an overtone and it is suggested that this is the γND, the out-of-plane deformation mode, the imino analogue of which is probably submerged below the $\nu_{as}CCl_3$ mode (Ratio1.29) and this may in part account for the shift of the $\nu_{as}CCl_3$ mode in the deuterate.

The assignment of the corresponding in plane mode, βNH, for which the compound was originally prepared is not simplified. The three remaining unassigned bands at 1348, 1159 and 1055 are all weak bands. If assignment of the βND mode is made to the band at 1348, the βNH mode would probably be a shoulder on the νC=N band in methyl trichloroacetimidate. The band at 1159 is extremely weak and is most probably a combination band. The remaining band at 1055 would suggest assignment of the βNH mode to the shoulder at 1295 (ratio 1.24) on the skeletal mode at 1314. This assignment would appear to be in agreement with the corresponding assignment of Miyazawa et al[147] of N-methyl acetamide to a band at 1299, on the basis of a normal coordinate treatment.

Complete assignment of methyl trichloroacetimidate deuterate is given in Table 49 and the liquid phase spectrum is shown diagramatically in range 4000-600 in Fig.27.

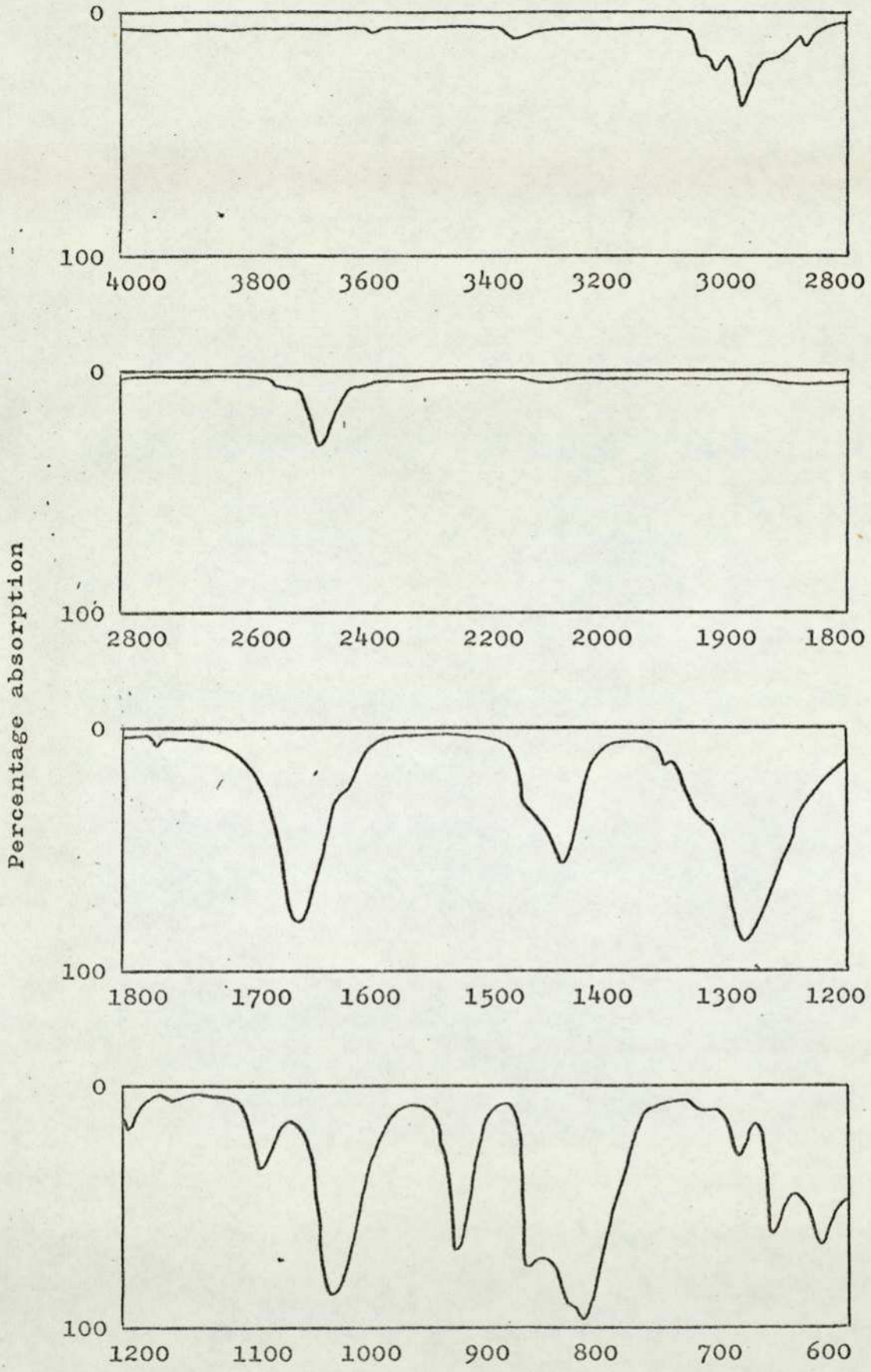


Fig. 27a Liquid phase infrared spectrum of methyl trichloro-acetimidate deuterate in the region 4000-600cm^{-1}

Table 49

Assignment of the spectrum of methyl trichloroacetimidate deuterate.

Liquid	Gas	Assignment
3351w	3375w	impurity νNH
3033w	3036w	combination band $\nu_s CH_3$ + $rCCl_3$
3001w	3033w	combination band
	2968m.sh	$\nu_{as} CH_3$
2955m	2964m	$\nu_{as} CH_3$
	2958m.sh	$\nu_{as} CH_3$
2906w	2923w	overtone 2x1458=2916
2845w		$\nu_s CH_3$
2581vw		overtone 2x1283=2566
2501vw		combination band 1656+852=2508
2476m	2494w	νND
1771w	1789vw	νC=O impurity
	1708mw	overtone 2x852=1704
	1686s.sh	
	1678s.sh	
1673s.sh	1674vs.sh	νC=N-H impurity
1656vs	1665vs	νC=N-D
1636s.sh		combination band 1026+617=1643
1617m.sh		overtone 2x811=1622
	1466w	$b_{as} CH_3$
1458m	1460w	$b_{as} CH_3$

Table 49 cont.

Liquid	Gas	Assignment
1439s.sh	1442m	$b_s CH_3$ + overtone
1437s	1435m.sh	
1348w		combination band 655+685=1340
1313m.sh		NH impurity
1283vs	1286vs	skeletal mode A
	1238m	overtone 2x617=1234
1192w	1198w	ωCH_3
1159vw		combination band
1085m	1090sm	skeletal mode B
1055w.sh		βND
1026±1.5vs	1033vs	skeletal mode C
	1019s.sh	NH impurity
923m	925m	combination band ($\nu_{as} CCl_3$ + torsional)
852s	853s	skeletal mode D
831vs.sh	828vs	NH impurity
811vs	807sh	$\nu_{as} CCl_3$
755w,sh		combination band
714w	713w	CCl_3 group overtone
685m	685w.sh	bending (O-C=N)
655s	658m	$\nu_s CCl_3$
617s	621ms	γNH

E. Methyl Benzimidate

The spectrum of methyl benzimidate does not appear to have been previously assigned. Hadzi and Prevorsek[88] investigated the spectrum of methyl benzimidate as a preliminary to their study of the O-derivatives of hydroxamic acids. The spectrum is presented diagramatically and strong bands at 1639, assigned to the νC=N mode and at 1320-1340 are described. The latter band is thought to be due to the stretching of the carbon-oxygen bond which had acquired some double bond character from the adjacent azomethine. The νNH mode appeared at 3311 in the pure liquid and 3356 in carbon tetrachloride solution.

Methyl benzimidate possesses a peak at 3336 in the νNH region (pure liquid) which compares with a band at 3336 in ethyl benzimidate.

Only one extremely weak peak was observed above 3400. This could be due to aqueous impurity but as it did not increase in intensity when the sample was exposed to moisture, it is attributed to an overtone band.

The region 3200-3400 is characterised by a peak at 3336 which is asymmetric towards the lower wavenumber side, there being a measurable shoulder at 3298. The shoulder is virtually absent in non-polar solvents such as cyclohexane where the main band is shifted to higher wavenumbers. As discussed in Chapter 3.B, this side band is thought to be a combination tone. Further evidence for this assignment was provided

during the measurement of the vapour spectrum. Attempts to obtain the spectrum at temperatures approaching 100°C were accompanied by condensation of the benzimidate on the window of the heated cell. At this temperature the profile of the νNH band remained unaltered. This would not be expected if two conformations were present, as the position of the equilibrium is likely to be temperature dependent. It was not found possible to obtain an accurate, complete vapour spectrum, but the vapour value of the νNH mode is given in Table 13.

Table 50

The aromatic νCH region of various benzimidates.

Methyl benzimidate	Ethyl benzimidate	N-chloro ethyl benzimidate	Assignment
3086	3092	3090	aromatic νCH
3059	3066	3069	aromatic νCH
	3042	3042	overtone
3025	3030	3031	aromatic νCH
3012			overtone

Assignment of the bands in the region 3000-3100 to the specific νCH modes of the aromatic system has not been attempted. It is well established[194] that aromatic systems, in general, exhibit three bands in the region of 3038, whilst in mono substituted, aromatic systems, as in the present case, the characteristic triplet occurs about 3055 in carbon tetra-

chloride. Comparison is drawn, Table 50, between observed positions of peaks in the region 3000-3100 in ethyl benzimidate, methyl benzimidate and N-chloro ethyl benzimidate.

As in the case of methyl trichloroacetimidate, the $\nu_{as}CH_3$ and $\nu_{s}CH_3$ bands of the methoxy group at 2950 and 2849, are little affected in their wavenumber positions in comparison with the corresponding bands at 2957 and 2846 in methyl acetate.

All the peaks in the region 2800-1750 are assigned to combination bands. However, the band at 2227 in the liquid phase would appear to be of some interest. It was initially suggested that this band may be due to a nitrile impurity, as a band occurs at 2222 in benzonitrile[195] and could be shifted to 2227 by the presence of the imidate which is present in solvent proportions. The peak, however, does not increase in intensity on standing, neither is its presence removed on fractionation. Consequently it is assigned to a combination band, possibly 1449+782. The four weak peaks in the region 2000-1700 are consistent with the combination bands observed in mono-substituted benzenes.

In the region below 1700 assignment of the fundamental frequencies is attempted, but overtone bands are not generally discussed.

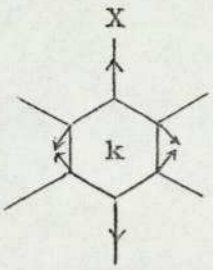
The νC=N mode is assigned to the very strong band at 1636 in the liquid spectrum. The position of this band was consistent with the findings of Melandez,[91] who found that conjugation with a benzene ring lowered the position of the νC=N

vibration by 20-30 wavenumbers as shown by the figures in Table 51.

Table 51

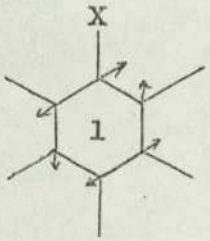
The position of the νC=N mode in various imidates.

Compound	Position(cm^{-1})	Reference
Methyl acetimidate	1660	100
Methyl trichloroacetimidate	1673	
Ethyl acetimidate	1655	
Ethyl caprioimidate	1653	37
Methyl benzimidate	1636	

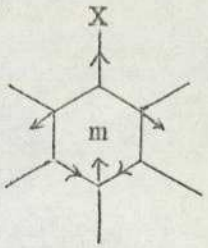


The peak at 1602 is assigned to the A_1 νC-C mode (k) of the benzene ring. The diagrams and nomenclature in this section will be those given by Whiffen and Randle.[196,197] A value of 1606 ± 7 is quoted for this vibration.

The doublet at 1581, 1577 is interesting because of its relatively large intensity compared with the 1602 band and also because of the small separation of the peaks which would seem to rule out Fermi resonance. The only fundamental band predicted in this region is the B_1 C-C mode (1) illustrated. The stronger of the peaks at 1581 would seem to correspond more closely to the quoted value[196] of



1588±9. Randle and Whiffen suggest that this band should be of low intensity, however, Bellamy[191] notes that the intensity of the band is enhancedif a carbonyl, or any unsaturated group is directly attached to the ring, and suggests that this band is indicative of conjugation with the ring, as one would indeed expect in this case.



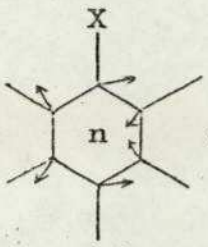
Assignment of the $A_1\nu C\text{-}C$ mode (m) is made to the band at 1493, the only band in the region 1470-1570, being positionally in agreement with data tabulated (Table 52).

Table 52

Wavenumber positions of the $A_1\nu C\text{-}C$ mode (m) in various mono substituted benzenes.

Mono substituents	Wavenumber position	Reference
Many	1499±7	196
Hydrogen	1479	198
Nitrile	1486	195
Iodine	1473	199
Bromine	1473	199
Chlorine	1477	199
Fluorine	1499	200
Fluorine	1492	199

The skeletal C-C frequency in the region of 1450, the



$B_1\nu$C-C mode (n) which was originally suggested by Lecomte et al,[201] is assigned to the strong band at 1449 by comparison with the data of Table 53.

Table 53

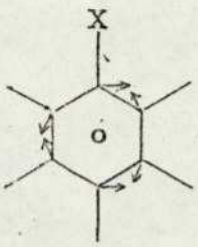
The position of the $B_1\nu$C-C mode (n) in various monosubstituted benzenes.

Substituents	Position	Reference
Various substituents	1451 ± 12	196
Nitrile	1445	195
Chloro	1445	199
Fluoro	1460	200
Iodo	1435	199
Bromo	1445	199

In methyl trichloroacetimidate and methyl acetimidate the $b_{as}CH_3$ mode was assigned to bands at 1463 and 1460 respectively while the corresponding symmetric bands were found at 1439 and 1446. With reference to these assignments the peaks at 1459 and 1439 are assigned to the antisymmetric and symmetric modes of the methoxy group. These modes are affected little by the nature of the rest of the molecule.

Two peaks occur in the region 1300-1359, the 1313 band occuring as a weak shoulder on the very strong 1343 peak. The latter peak is thought to be one of the skeletal modes, mode A,

which is shifted to a high wavenumber position, relative to the trichloroacetimidates, by conjugation with the benzene ring. Assignment of the 1313 peak to the $B_1\nu$C-C mode (o), is made



with reference to Table 54. The position of this mode is rather lower than had been anticipated as the other νC-C modes have born close agreement to values obtained by Green for benzonitrile.[195]

Table 54

The position of the $B_1\nu$C-C mode (o) in various monosubstituted benzenes.

Substituents	Wavenumber position	Reference
Various substituents	1324 ± 10	196
Fluorine	1324	199
Chlorine	1326	199
Bromine	1323	199
Iodine	1321	199
Nitrile	1335	195
Hydrogen	1309	198

The assignment is prefered to the 1343 band, as Randle and Whiffen describe it as being generally a weak band and quote certain authors as assigning it to a combination tone of bands at approximately 618 and 697. In this case bands have been observed at 695 and 613. The in-plane deformation

band, βNH, is again tentatively assigned to a band at 1295.

The B_1βCH mode (e) of the benzene ring, is assigned to the weak band at 1240, on the basis of data in Table 55.

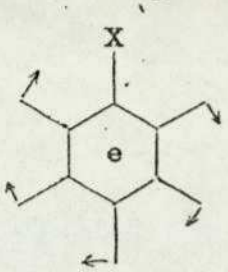


Table 55

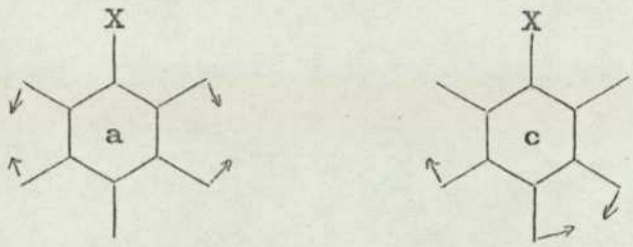
The position of the B_1βCH mode (e) in various monosubstituted benzenes.

Substituents	Wavenumber position	Reference
Fluorine	1282	199
Chlorine	1271	199
Bromine	1264	199
Iodine	1261	199
Nitrile	1282	195
Many	1240 ± 8	196

Randle and Whiffen quote the mode as being strongly substituent dependent and their value of 1240 is derived only from papers where Raman and infrared data were given.

The band at 1191 is assigned to the wagging motion of the methoxy group, and bears good agreement with methyl acetate ($1196 cm^{-1}$) and methyl trichloroacetimidate ($1193 cm^{-1}$).

The A_1βCH mode (a) of the benzene ring appears as a shoulder at 1183 on the CH_3 mode and the B_1βCH mode (c) as a medium intensity peak at 1165. These assignments appear to require



little explanation as they are consistent with the tabulated data[196] and are of the expected intensity.

Assignments of the B_1βCH mode (d), the A_1βCH mode (b) and the A_1 ring mode (p) are made on the basis of the data in Table 56.

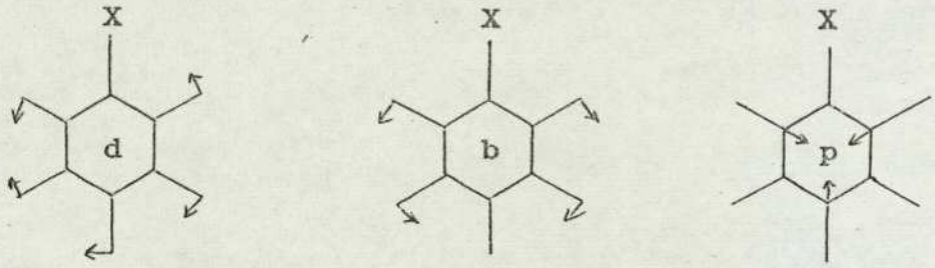


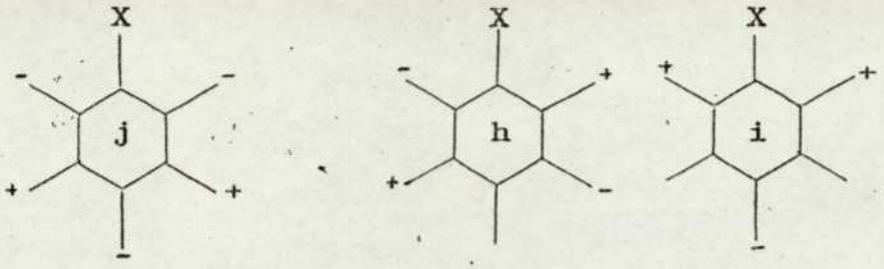
Table 56

The position of the benzene modes in the region 1000-1080 in various monosubstituted benzenes.

Compound	B_1βCH(d)	A_1βCH(b)	A_1ring(p)	Reference
Many mono benzenes	$1072^{\pm}7$	$1029^{\pm}5$	$1001^{\pm}4$	196
Fluorobenzene	1066	1020		199
Chlorobenzene	1068	1026	1003	199
Benzonitrile	1072	1026	1001	195
Ethyl benzimidate	1077	1028	1002	

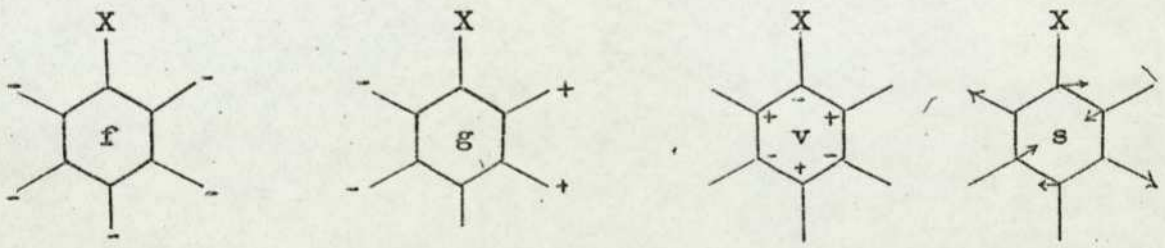
It is thought, however, that the enhanced intensity of the 1077 band in particular, indicates the presence of skeletal

mode B, whilst skeletal mode C may be masked by the A_1bCH mode (b).



The $A_2\gamma$CH mode (h) and the $B_2\gamma$CH mode (j) reported by Randle and Whiffen[196] at 982±6 and 962±6 are generally of low intensity. The $B_2\gamma$CH mode (i) is thought to be the weak band at 927. Whiffen and Randle suggest that this mode is of greater intensity than modes j and h, and the position agrees moderately well with the suggested region of 908±10.

Four of the remaining bands in the region 900-600 are also assigned to benzene modes, those at 823 ($A_2\gamma$CH mode (g)), 782($B_2\gamma$CHmode (f)), 695($B_2\phi$C-C mode(v)), and an in plane ring mode at 613($B_1\alpha$(C-C-C) mode (s)), on the basis of the data in Table 57.



The bending mode of the heavy atom skeleton O-C=N is difficult to assign on account of the number of bands in the region 600-700, however, the medium peak at 674 would seem to bear closest agreement with the peak which occurs at 682 in methyl

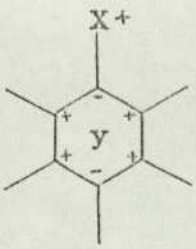
trichloroacetimidate.

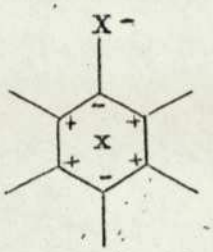
Table 57

Assignments of the Whiffen modes f, g, v and s in various monosubstituted benzenes.

Substituents	f	g	v	s	Reference
Many	751±5vvs	837±10w	697±11vs	620±4w	196
Fluorine	752		682	615	199
Chlorine	740	830	682	612	199
Bromine	735	832	681	615	199
Iodine	730	835	684	613	199
Nitrile	758	844	687	624	195

As with the other imidates complete assignment below 600 is not undertaken. The band at 125 is most probably a torsional mode, and that at 299, a mode associated with the bending of the O-C=N skeleton which occurs in methyl trichloroacetimidate at 288. A survey of some of the literature available on the low wavenumber modes associated with the benzene skeleton,[197,202-205] has shown that the position of the modes are extremely substituent dependent, often covering a range of 100-150 wavenumbers. Only two modes would seem to warrant consideration, the Whiffen mode (y) which Brown et al[202] suggest as occuring close to 490 in benzenes in which the mono-substituent next to the ring is a carbon





atom, and the B_1 vibration (x) which occurs at or below 240. The complete assignment is given in Table 58. and the spectrum shown diagramatically in Fig. 28.

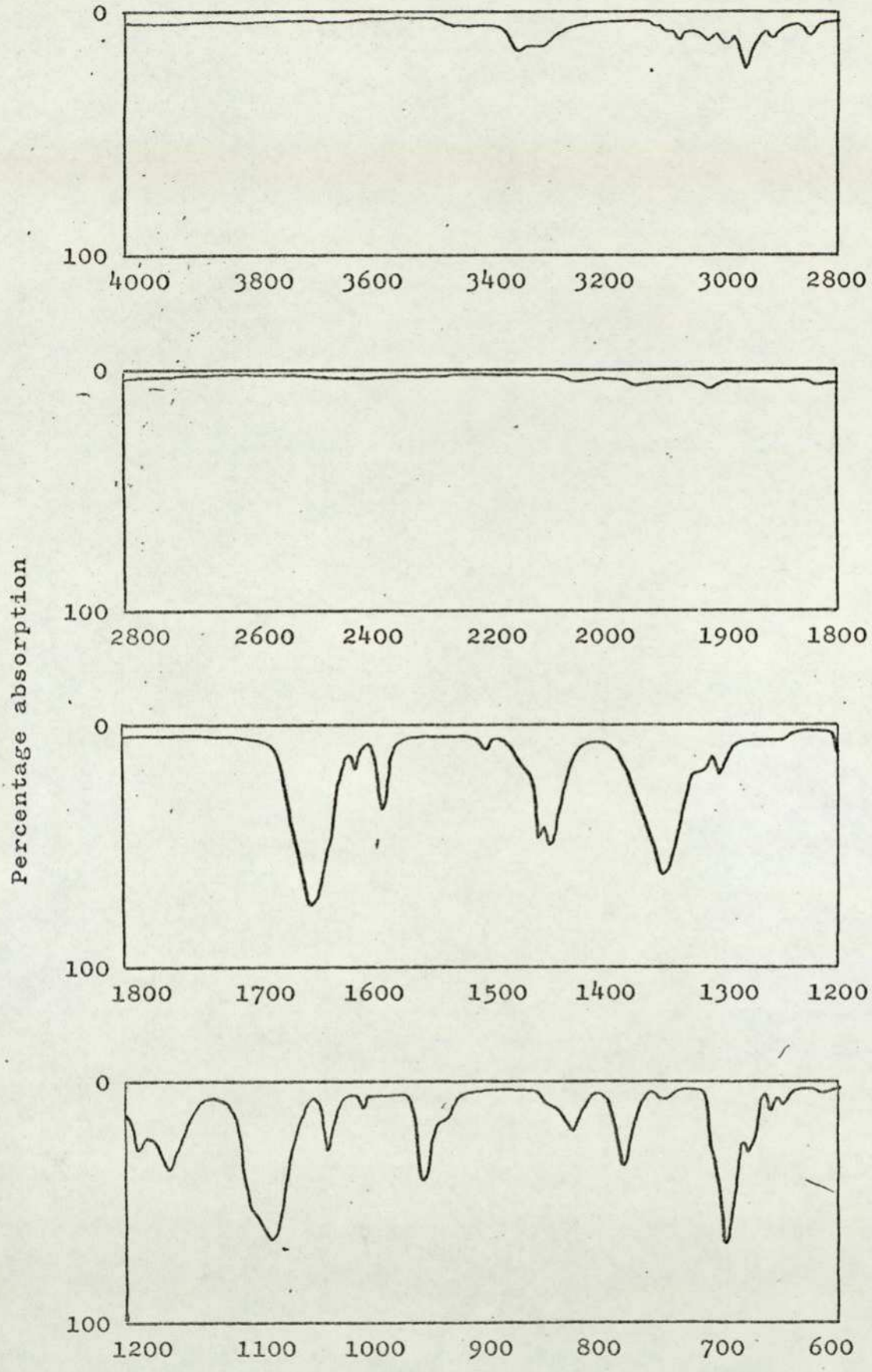


Fig. 28 Liquid phase spectrum of methyl benzimidate in the region 4000-600cm^{-1}

Table 58

Assignment of the spectrum of methyl benzimidate.

Liquid	Solution	Raman[a]	Assignment
3660vw			combination band 648+3012=3660
3336w	3347w	3336(00)	νNH
3298w.sh			overtone of νC=N?
3155vw			overtone 2x1581=3162
3086vw	3090w		aromatic νCH
3059w	3063w	3056(3b)	aromatic νCH
3025w	3028w		aromatic νCH
3012w	3016w		combination band
2982w	2986w		combination band 1343+1636=2979
2950m	2946m	2942(1)	$\nu_{as}CH_3$
2903vw	2903w		combination band $b_sCH_3+b_{as}CH_3$=2898
2849vw	2848w		ν_sCH_3
2648vw			combination band 1191+1449=2640
2630vw			combination band 1191+1437=2628
2597vw			combination band 1165+1437=2602
2502vw			combination band 1165+1343=2508
2440vw			combination band 1002+1439=2441
2381vw			overtone 2x1191=2382
2227vw			combination band 1449+782=2229 or C N impurity.
2139vw			combination band 1449+695=2142
2016vw			combination band 1343+674=1969
1962vw			combination band 674+1295=1969
1894vw			overtone 2x947=1894
1813vw			combination band 1449+365=1814
1775vw			combination band 967+823=1770
1654w.sh	1654w.sh		combination band 1313+340=1653
1649m.sh	1649m.sh		combination band 1002+648=1650
1636vs	1636vs	1653(2)	conjugated νC=N
1621m.sh	1620m.sh		combination band 927+695=1622

Table 58 cont.

Liquid	Solution	Raman[a]	Assignment
1616m.sh	1617 m.sh		combination band 947+667=1614
1602w	1604 w	1602(5b)	$A_1\nu$C-C mode (k)
1581s	1582 w		$B_1\nu$C-C mode (l)
1577s.sh	1577 w.sh		combination band 1028+547=1575
1493w	1494 w		$A_1\nu$C-C mode (m)
1459m.sh	1459 m.sh		$b_{as}CH_3$
1449s	1449 s		$B_1\nu$C-C mode (n)
1439vs	1440 vs		b_sCH_3
1437vs	1437 vs	1428(2b)	combination band 782+656=1438
1419vw.sh			combination band 340+1077=1457
1343vs	1344 vs		skeletal mode A
1313m.sh	1313 m.sh		$B_1\nu$C-C mode (o)
1295m	1295 m	1283(1)	βNH
1240vw			$B_1\beta$CH mode (e)
1191m	1194 sm	1190(5b)	ωCH_3
1184m.sh	1183 m.sh		$A_1\beta$CH mode (a)
1165m	1162 sm	1159(1)	$B_1\beta$CH mode (c)
1077vs	1074*	1092(0)	skeletal mode B+$B_1\beta$CH mode (d)
1028m	1030 m	1026(2)	skeletal mode C+$A_1\beta$CH mode (b)
1002vw		999(8)	A_1 ring mode (p)
947s	947 s		?
927w	921 w		$B_2\gamma$CH mode (i)
823w	819*	823(3)	$A_2\gamma$CH mode (g) + skeletal mode D
782s	779*		$B_2\gamma$CH mode (f)
758vw	754*	755(2)	combination band 613+137=750
695vs	693*		$B_2\delta$C-C mode (v)
674m	674*		bending (O-C=N)
667w.sh			difference band 1343-674=669
663vw.sh			combination band 365+299=664
656w			difference band 782-125=657
648w	648*		difference band 782-137=645

Table 58 cont.

Liquid	Solution	Raman[a]	Assignment
613vw		615(3)	$B_2\phi$ (C-C-C) mode (s)
547w			
500w		475(1)	B_2(skeletal) mode (y)
365m		369($\frac{1}{2}$)	
342m		324(0)	
299w.sh		283(0)	O-C=N skeletal bending mode
222w		242(3)	B_2(skeletal) mode (x)
173w			
137w			
125w			torsional mode

Solution values refer to 1% solution in carbon tetrachloride except those marked * which apply to cyclohexane solution.

[a] Ref. 92

F. Ethyl Benzimidate

Assignment of the spectrum of ethyl benzimidate has been made by direct comparison with the assignment of methyl benzimidate and N-chloro ethyl benzimidate for the benzene modes (Table 59), and ethyl trichloroacetimidate and N-chloro ethyl benzimidate for the ethyl modes (Table 60).

The ethyl group modes generally show good positional agreement with ethyl trichloroacetimidate. The scissoring deformation of the ethoxy methylene group is probably obscured by the strong $B_1 \nu$(C-C) benzene mode, The band at 873 provides the only major assignment problem. In methyl benzimidate there was no peak in the region 825-925. The unassigned strong peak at 947 would appear too high for assignment of skeletal mode D, and this was eventually assigned to the 823 band. In ethyl benzimidate, however, there is a strong band at 873 which corresponds to a band at 869 in N-chloro benzimidate. This is assumed to be the skeletal mode D, as the only other vibration which could be introduced on the substitution of an ethyl grouping for a methyl grouping, is a νC-C mode, and the band at 869 would seem too strong for such a band.

The benzene modes as given in Table 59 show good agreement with the modes in methyl benzimidate. The $B_2 \delta$CH mode (f) was again identified with a band close to 780. This is at a slightly high wavenumber position than the value presented by

Whiffen and Randle[196] and is slightly outside the region 770-730 proposed by Colthup,[206] who investigated a greater volume of data than Whiffen. Bellamy,[207] however, could only find a weak band at 806 in benzoic acid. The general strength and positional agreement of the band at 783 in ethyl benzimidate with the band at 782 im methyl benzimidate supports the assignment of the $B_2 \gamma$CH mode (f).

The bending (O-C=N) mode which has been observed in the region 650-725 in the imidates studied is assigned to the band at 655, as the band at 675 is more readily explained as an overtone.

The liquid phase infrared spectrum is shown in the region 4000-600 in Fig. 29 and the spectrum is assigned in Table 61.

Table 59

Comparison of the wavenumber position of modes in methyl benzimidate, ethyl benzimidate and N-chloro ethyl benzimidate.

Vibration	Methyl benzimidate	Ethyl benzimidate	N-chloro ethyl benzimidate
free νNH	3336w	3337mb	
overtone of νC=N	3298w.sh	3298m.sh	
aromatic νCH	3086vw	3092w	3090w.sh
	3059w	3066m	3069w.sh
	3025w	3030mw	3031w.sh
νC=N	1636vs	1634vs	1612s
$A_1 \nu$C-C mode(k)	1602w	1604m.sh	1594vs
$B_1 \nu$C-C mode(1)	1581s	1580s	1579s
$A_1 \nu$C-C mode(m)	1493w	1494w	1493s

Table 59 cont.

Vibration	Methyl benzimidate	Ethyl benzimidate	N-chloro ethyl benzimidate
$B_1\nu$C-C mode(n)	1449s	1450s	1448s
skeletal mode A	1343vs	1329vs	1306vs,1288vs
$B_1\nu$C-C mode(o)	1313m.sh	1315s.sh	1306vs
βNH	1295m	1297m	
B_1βCH mode(e)	1240vw	1242vw	
A_1βCH mode(a)	1184m.sh	1185m.sh	1173m
B_1βCH mode(c)	1165m	1169ms	1158m.sh
skeletal mode B	1077vs	1075vs	1110s,1094m
B_1βCH mode(d)			1074m
skeletal mode C	1028m	1016m	1017s
A_1βCH mode(b)		1030s	1030s
A_1 ring mode(p)	1002vw	1001mw	1001m
$B_2\delta$CH mode(i)	927w	926w	924w
skeletal mode D	823m	873m	869s
$A_2\gamma$CH mode(g)		827m	
$B_2\gamma$CH mode(f)	782s	783s	769s
$B_2\phi$(C-C) mode(v)	695vs	695s.sh	697vs
b(O-C=N)	674m	655mw	630m
skeletal O-C=N	299w.sh	284w	303w.sh
torsional mode	125w	110w	

Table 60

Comparison of the wavenumber position of the ethoxy modes in ethyl trichloroacetimidate, ethyl benzimidate and N-chloro ethyl benzimidate.

Vibration	Ethyl trichloro-acetimidate	Ethyl benzimidate	N-chloro ethyl benzimidate
ν_{as}CH of ethoxy methyl group	2985m	2989m	2988m
ν_{as}CH of methylene group	2961m.sh		2962w.sh
overtone of ethoxy system	2940mw	2941m	2940w
ν_{s}CH of methylene group	2906w	2903m	2903w
ν_{s}CH of ethoxy methyl group	2873w	2875w.sh	2872w.sh
ethyl group bending mode	1477mw	1479m	1475m
scissoring CH_2	1464mw		1466m.sh
$b_{as}CH_3$	1445mw	1438mw	1448s
$b_{s}CH_3$	1394mw	1399s	1394m
ωCH_2	1369m	1372s	1369s
ωCH_3	1174mw	1169ms*	1173m*
rCH_3	1116m	1114m.sh	1127s.sh

* Assignable to other modes.

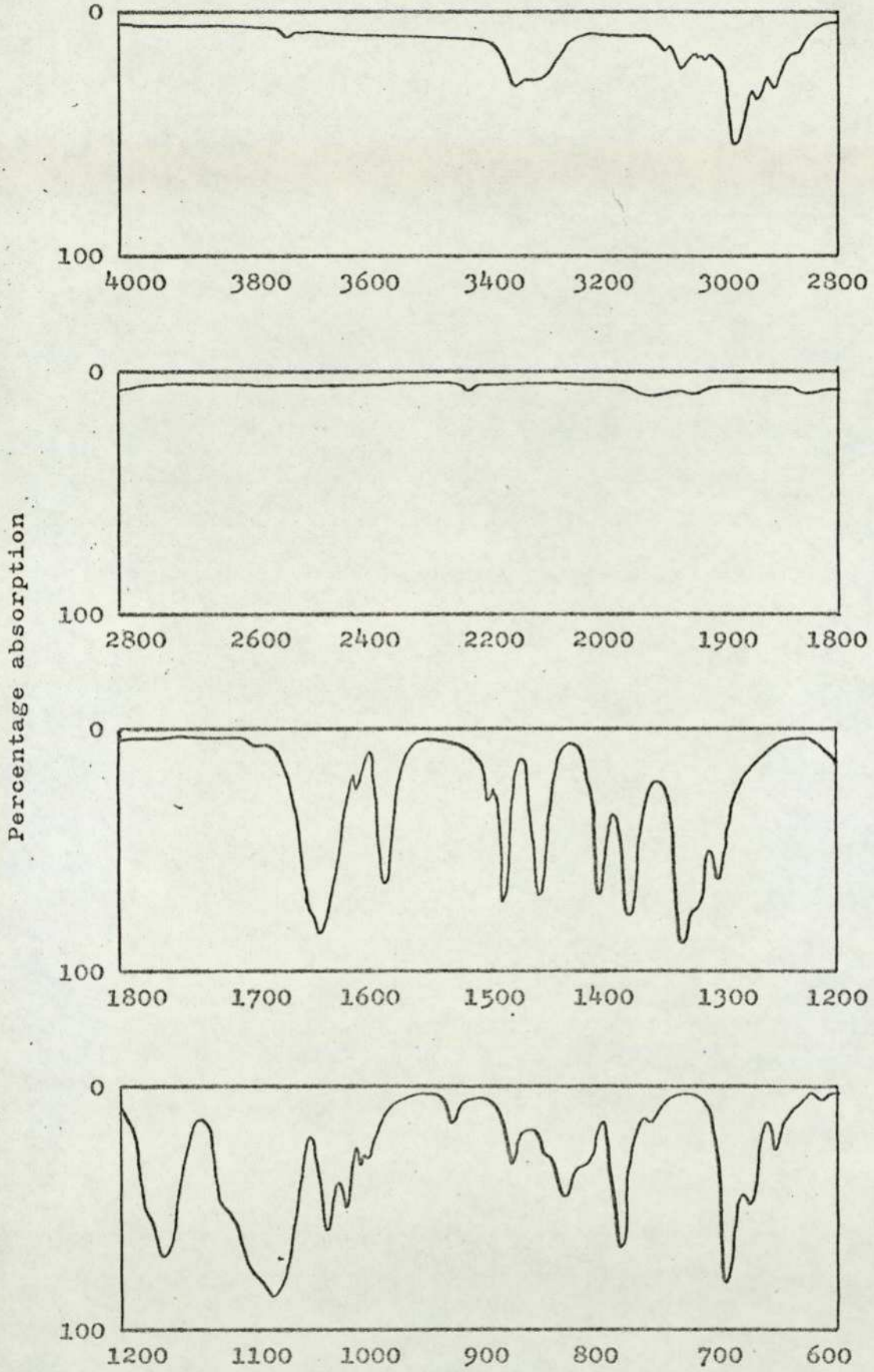


Fig. 29 Liquid phase infrared spectrum of ethyl benzimidate in the region 4000-600cm^{-1}

Table 61

Assignment of the spectrum of ethyl benzimidate.

Liquid	Gas	Raman[a]	Assignment
3590vw			νOH impurity or combination band
3337m	3363w	3333(00)	free νNH
3298m.sh			overtone of νC=N 2x1634=3268
3110vw.sh			combination band 1634+1479=3113
3092w			aromatic νCH
3066w	3075m		aromatic νCH
3042mw.sh	3043w		combination band 1604+1438=3042
3030mw			aromatic νCH
2989m	2990m	2975(00)	ν_{as}CH of ethoxy methyl
2941m	2945m	2928(0)	ν_{as}CH or ethoxy group overtone
2903m	2911w		ν_{s}CH of ethoxy methylene
2875w.sh			ν_{s}CH of ethoxy methyl
2792vw			overtone 2x1399=2798
2761vw			combination band 1315+1450=2765
2734vw			combination band 1399+1329=2728
2630vw			overtone 2x1315=2630
2602vw			combination band 1604+1001=2605
2581vw			combination band 1580+1001=2581
2487vw			combination band 1185+1297=2482
2409vw			combination band 1297+1114=2411
2343-58vw			overtone 2x1169=2338
2231vw			νC≡N impurity or overtone
2200vw			combination band 1016+1185=2201
2159vw			overtone 2x1075=2150
1961w			combination band 655+1315=1970
1904w			combination band 1016+783=1899
1814vw			combination band 994+827=1821
1771vw			combination band 1016+758=1774

Table 61 cont.

Liquid	Gas	Raman[a]	Assignment
1714w.sh	1742w		νC=O impurity
1656m.sh	1656sh		overtone 2x827=1654
1638vs.sh 1634vs	1644s	$1648^{+}8\frac{1}{2}(3)$	νC=N
1624vs.sh			combination band 758+873=1631
1618s.sh			combination band 1001+617=1618
1604m.sh		1598(3b)	A_1 ν C-C mode (k)
1580s	1580w		$B_1\nu$C-C mode (l)
1577s.sh			combination band 655+926=1581
1571m.sh			combination band 1372+198=1570
1494w			$A_1\nu$C-C mode (m)
1479m			ethyl group bending mode
1450s	1451m	1444(2)	$B_1\nu$C-C mode (n)
1438mw			$b_{as}CH_2$
1399s	1398m		b_sCH_3
1372s	1377s		ωCH_2
1329vs	1331vs	1333(0)	skeletal mode A
1315s.sh			$B_1\nu$C-C mode (o)
1297m	1276m		βNH
1242vw		1260(1)	$B_1\beta$CH mode (e)
1185m.sh		1195(3b)	$A_1\beta$CH mode (a)
1169ms	1160m	1155(1)	$B_1\beta$CH mode (c) + ωCH_3
1114m.sh			$rCCH_3$
1093vs.sh		1099(1)	combination band 400+695=1095
1075vs			skeletal mode B
1030s		1027(3)	$A_1\beta$CH mode (b)
1016m			skeletal mode C
1001mw		998(5)	A_1 ring mode (p)
994w.sh			$B_2\gamma$CH mode (j)
926w			$B_2\gamma$CH mode (i)
873m	869w	870(2)	skeletal mode D
827m	829mw		$A_2\gamma$CH mode (g)

Table 61 cont.

Liquid	Gas	Raman[a]	Assignment
811m.sh	808w		combination band 617+198=815
783s	781w	754(1)	B_2 γCH mode (f)
695vs	693s		B_2 δC-C mode (v)
	688s.sh		+ overtone
675mw			overtone 2x339=678
655mw			bending (O-C=N)
617vw		618(2)	B_1 α(C-C-C) mode (s)
546w			
		514(0)	
		474($\frac{1}{2}$)	B_2 skeletal mode (y)
400w			
339w		342($\frac{1}{2}$)	
284w		253(3)	O-C=N skeletal bending mode
198w			
173w			
110w			torsional mode

[a]Reference 92

G. Ethyl Phenyl Acetimidate

As with ethyl benzimidate the assignment of ethyl phenyl acetimidate is made chiefly by comparison with data already used in the earlier assignments. In the phenyl acetimidate system, Fig. 30, there is the added complication of the methylene group interposed between the azomethine group and the benzene ring.

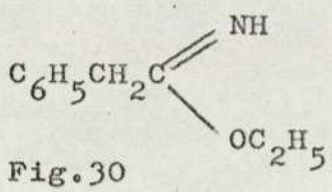


Fig.30

The assignment will be discussed mainly where interesting wavenumber shifts, intensity changes or particularly good agreement has been found between ethyl phenyl acetimidate and ethyl benzimidate. Data on the spectrum of methyl phenyl acetimidate will also be discussed, but this imidate has not been included in the assignment or experimental sections, because all the prepared samples of this imidate contained an estimated 5% of carbonyl impurity, which could have been due to the N-methyl phenyl acetamide, as the C H N analysis was close to the theoretical value.

Table 62

Comparison of aromatic νCH modes in various imidates.

Assignment	Ethyl benzimidate	Ethyl phenyl acetimidate	Methyl phenyl acetimidate
aromatic νCH	3092	3091	3088
aromatic νCH	3066	3067	3065
overtone	3042		
aromatic νCH	3030	3033	3032

The νCH modes associated with the aromatic system are remarkably constant in position in the three imidates (Table 62), and this substantiates the assignment of the 3042 band in ethyl benzimidate to an overtone mode.

The ν CH modes associated with the ethoxy grouping are complicated in ethyl phenyl acetimidate by the presence of the phenyl acetimino methylene group. From the spectra of methyl and ethyl acetates, [148,149] it is known that the spectrum observed is mainly characteristic of the ester grouping and contains only a minor contribution from the acid methyl grouping. The general position of the peaks at 2982, 2904, and 2874 in the aliphatic νCH region of ethyl phenyl acetimidate, agrees closely with band positions in ethyl trichloroacetimidate, ethyl benzimidate and N-chloro ethyl benzimidate (Table 60). From the assignment of ethyl acetate, [149] the ν_{as}CH mode of the methylene group is expected at 2960 and an overtone mode, characteristic of the ethoxy group at 2940. In the ethyl imidates studied, the 2960 peak is generally weaker then the 2940 peak and in ethyl benzimidate it was absent. In ethyl phenyl acetimidate, the appearance of a peak at 2930 may be due to an overtone, but it may be that the ν_sCH mode of the methylene group occurs at a lower wavenumber position than the assignment by Nolin and Jones suggests, but a normal coordinate treatment would be needed to establish the assignment.

The position of the νC=N mode is also of interest. This occurs in the phenyl acetimidates as a very strong band at

1643-49 in ethyl phenyl acetimidate and 1650 in methyl phenyl acetimidate. In the benzimidates this band shifts to 1634 in ethyl benzimidate and 1636 in methyl benzimidate, clearly demonstrating the effect of conjugation on the position of the νC=N mode. This conjugation also manifests itself in the intensity of the $B_1\nu$C-C mode (1). In the phenyl acetimidates this is a weak mode at 1586 in the ethyl and 1585 in the methyl ester, whereas in the benzimidates, it occurs at 1581 (methyl benzimidate), at 1580 (ethyl benzimidate) and 1579 (N-chloro ethyl benzimidate). Bellamy[191] presents evidence to show that the intensity of this band is enhanced by conjugation to an adjacent double or triple bonded group.

The in-plane (β) and out-of-plane (γ) deformation modes of the imino group are assigned to the bands at 1275 and 794 respectively. The latter assignment agrees with the assumption made in the spectrum of methyl trichloroacetimidate deuterate, that the γNH mode is masked by the strong $\nu_{as}CCl_3$ absorption which occurs at 798 in methyl trichloroacetimidate.

The liquid phase infrared spectrum is shown in the region 4000-600 in Fig.31 and the spectrum is assigned in Table 63.

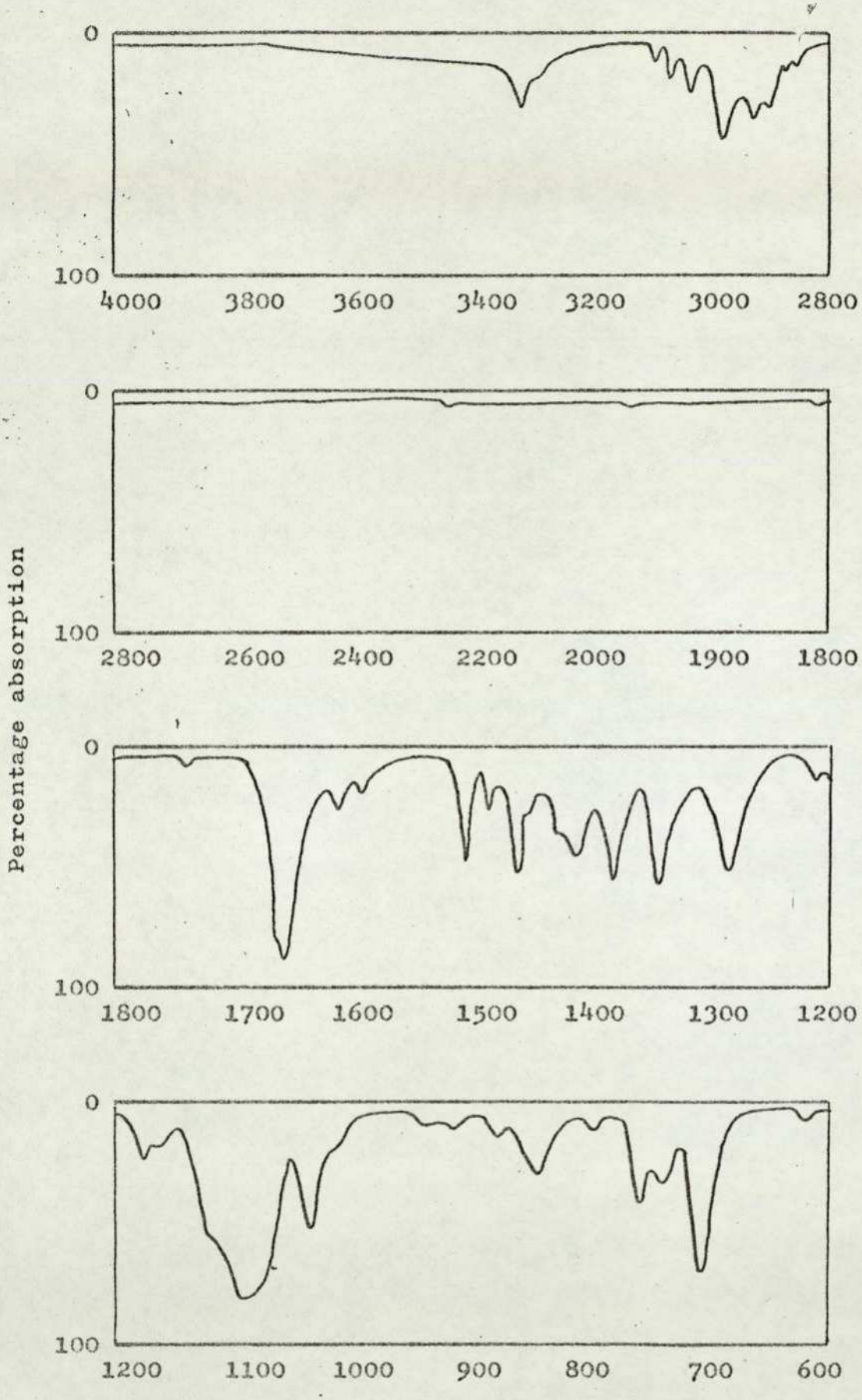


Fig. 31 Liquid phase infrared spectrum of ethyl phenyl acetimidate in the region 4000-600cm^{-1}

Table 63

Assignment of the infrared spectrum of ethyl phenyl acetimidate

Liquid	Carbon tetrachloride solution	Assignment
3611vw		combination band 2982+620=3602
3586vw		combination band 3067+519=3586 or ν OH impurity
3323w	3327.5w	νNH
3280w.sh		overtone 2x1646=3292
3091w	3092w	aromatic ν CH
3067w	3070w	aromatic ν CH
3033w	3035w	aromatic ν CH
2982m	2983m	ν_{as}CH of ethoxy methyl group
2930w	2931w	ν_{as}CH of methylene group
2904w.sh	2904w	ν_{s}CH of methylene group
2874w.sh	2873w.sh	ν_{s}CH of ethoxy methyl group
2853w.sh		combination band 1404+1455=2859
2828vw		combination band 1374+1455=2829
2737vw		combination band 1646+1091=2737
2631vw		combination band 1172+1455=2627
2586vw		combination band 1480+1115=2595
2339vw		combination band 1003+1541=2344
2253w		combination band 1646+612=2258
1955w		combination band 1115+841=1956
1809w		combination band 1115+704=1819
1736w		νC=O impurity
1655vs	1655vs.sh	νC=N region
	1650vs	
1643-49vs	1647vs.sh	
1635sh		combination band 929+704=1633
1603w	1604w	$A_1\nu$C-C mode (k)
1586w		$B_1\nu$C-C mode (l)
1498m		$A_1\nu$C-C mode (m)

Table 63 cont.

Liquid	Carbon tetrachloride solution	Assignment
1480mw		ethoxy group bending mode
1455m	1455 m	scissoring CH_2+$B_1\nu$C-C mode (n)
1421m.sh	1423 m	combination band 585+841=1426
1404m	1403 m	$b_s CH_3$
1374s	1373 s	ωCH_2
1341s	1342 s	skeletal mode A
1275m		in-plane deformation βNH
1204w		combination band
1172w		ωCH_3 + $A_1\beta$CH mode (a)
1156w		$B_1\beta$CH mode (e)
1115m.sh		rCH_3
1091vs	1083 s	skeletal mode B
1030m	1032 sm	skeletal mode C
1003w.sh		A_1 ring mode (p)
929w		overtone
911w		$B_2\gamma$CH mode (i)
875w		overtone
851w.sh		$A_2\gamma$CH mode (g)
841wm		skeletal mode D
794w		out-of-plane deformation NH
757m		$B_2\gamma$CH mode (f)
704s		$B_2\phi$C-C mode (v)
620w		Bα(C-C-C) mode (s)
612w		
585w		
545w		
519w		
479wm		
462w		

Table 63 cont.

Liquid	Carbon tetrachloride solution	Assignment
408w		
347w		
328w		
241w		
236w		
142w		

H. Ethyl Propionimidate

In the infrared spectrum of ethyl propionimidate, Fig32, certain peaks (Table 64) may be assigned to modes associated with the ester grouping. Here recourse is again made to data on ethyl acetate,[149] data for N-chloro ethyl propionimidate is also included in the table for future reference.

Table 64

Ethoxy group modes of ethyl propionimidate and N-chloro propionimidate.

Assignment	Ethyl acetate[a]	Ethyl propionimidate	N-chloro ethyl propionimidate
ν_{as}CH of methyl group	2982	2979	2985
ν_{as}CH of methylene	2962		
overtone of ethoxy group	2939	2944	2944
ν_{s}CH of methylene	2906	2904	2904
ν_{s}CH of ethoxy methyl	2873	2875*	2872
bCH mode of methylene	1475	1481	1478
scissoring CH_2	1464	1465	1464
b_{as}CH of ethoxy methyl	1446	1446	1446
b_{s}CH of ethoxy methyl	1393		1397
ωCH_2 of ethyl	1359		
ethoxy mode	784	795	797

[a] Reference 149 * CCl_4 solution

As with ethyl benzimidate and ethyl phenylacetimidate, no band in the region of 2960 was observed in ethyl propionimidate or N-chloro ethyl propionimidate. This is taken as indicative that the peak at 2944 in ethyl propionimidate is more likely the ν_{as}CHmode of the ethoxy methylene group. The band at 2934 in ethyl propionimidate may be an overtone but could possibly be the ν_{as}CH mode of the methylene group adjacent to the azomethine group.

In methyl acetate modes were observed at 1430 and 1373 corresponding to the antisymmetric and symmetric bending modes of the CH_3CO group. In ethyl propionimidate bands at 1430 and 1372 may be associated with the b_{as}CH modes of the methylene group of the $CH_3CH_2C{=}N$ structural unit.

One component of the doublet at 1338 and 1348 may be the wagging CH_2 vibration of the ethoxy methylene group. This in ethyl acetate was displaced to 1359 by interaction with the 1377 band, and a similar displacement to 1338 or 1348 may occur in ethyl propionimidate.

Four skeletal modes, at 1278, 1089, 1032 and 838 are recognised. It is interesting that there is no corresponding band to the 1278 band in ethyl acetimidate[49] and this is thought to be indicative of the mode being basically a ν_{as}[(C-C)=N] mode, which is only infrared active if the attached groupings on the azomethine are of sufficiently large mass. This hypothesis is amply supported by the activity of this mode in N-chloro methyl acetimidate.

Of the remaining bands, a torsional mode is recognised at 142 and as with the other imidates studied a band at 290 is thought to be a skeletal mode associated with the O-C=N group.

The β(NH) vibration is probably submerged beneath the strong 1278 skeletal mode and the γNH may be the weak band at 795. This, however, may be assigned to an ethoxy mode. Other bands are assigned to combination tones with the exception of the 883 band which may be associated with stretching of the carbon-carbon bond in the ethyl group adjacent to the azomethine group.

Complete assignment of the infrared spectrum is given in Table 65, together with the Raman values of Kohlraush and Seka.[92]

Table 65

Assignment of the spectrum of ethyl propionimidate.

Liquid	Raman[a]	Gas	Solution	Assignment
3584w.sh		3660w		νOH impurity
3327m±	3330(3)	3358w	3341w	υNH
2979vs	2975(7)	2989vs	2981s	ν_{as}CH of ethoxy methyl
2944s		2948vs.sh	2943m	ν_{as}CH of ethoxy methylene
2934m.sh	2934(10b)		2932m.sh	ν_{as}CH of CH_2-C=N
2904m			2904mw	ν_sCH of ethoxy CH_2
2887m.sh	2887(3)	2891s	2885m.sh	overtone 2x1446=2892
			2875vsh	ν_sCH of ethoxy methyl
	2837(1?)			
2741vw	2741(1b)			combination band 1650+1089=2739
2531vw				combination band 1073+1465=2538

Table 65 cont.

Liquid	Raman[a]	Gas	Solution	Assignment
2500vw				combination band 1032+1465=2497
2462vw				combination band 1377+1089=2466
2100vw				combination band 1073+1032=2105
1947w				combination band 1089+858=1947
1927w.sh				combination band 1089+838=1927
1737mw		1753m	1739w	νC=O
1655vs.sh			1655vs.sh	combination band 1465+180=1645
1650vs	1652(5)	1658vs	1650vs	νC=N
1636m.sh			1636s.sh	combination band 838+795=1633
1481m			1480mw	bCH of ethoxy methylene
1465s		1464m	1464m	scissoring CH_2
1457m.sh	1457(3)		1457m.sh	combination band 1278+180=1458
1446m			1445mw	b_{as}CH of ethoxy methyl
1430m	1433(2)		1430m	b_{as}CH of $CH_2C{=}N$
1406m		1409m.sh	1407m	combination band 838+578=1416
1377s	1392(1)		1377s	b_sCH of $CH_2C{=}N$
1348s.sh		1345s	1348m	combination band 554+795=1349 + b_sCH of $CH_2C{=}N$
1338s		1339s.sh	1337sm	
1278s		1274s	1277s	skeletal mode A
1248m.sh	1254(1)			combination band 453+795=1248
1174mw		1186m		combination band 1032+142=1174
		1140m.sh		

Table 65 cont.

Liquid	Raman[a]	Gas	Solution	Assignment
	1116(4)			
1089vs			1089vs	skeletal mode B
1073vs.sh	1079(3)	1085vs	1073vs.sh	+ combination band
				795+290=1085
1032sm	1029(0)		1031s	skeletal mode C
991w				
883mw	890(00)			ν C-C of acid ethyl
858m.sh				group
838m	853(4)	837m	834*m	skeletal mode D
795w.sh				γNH or ethoxy mode
578w	578(2)			
554w				
453w	454($\frac{1}{2}$)			
	374(4)			
290w	297(0)			
180w				
142w				torsional mode

Solution values apply to carbon tetrachloride solution, hexane values marked *

$\pm$ Band asymmetric on lower wavenumber side.

[a]Reference 92.

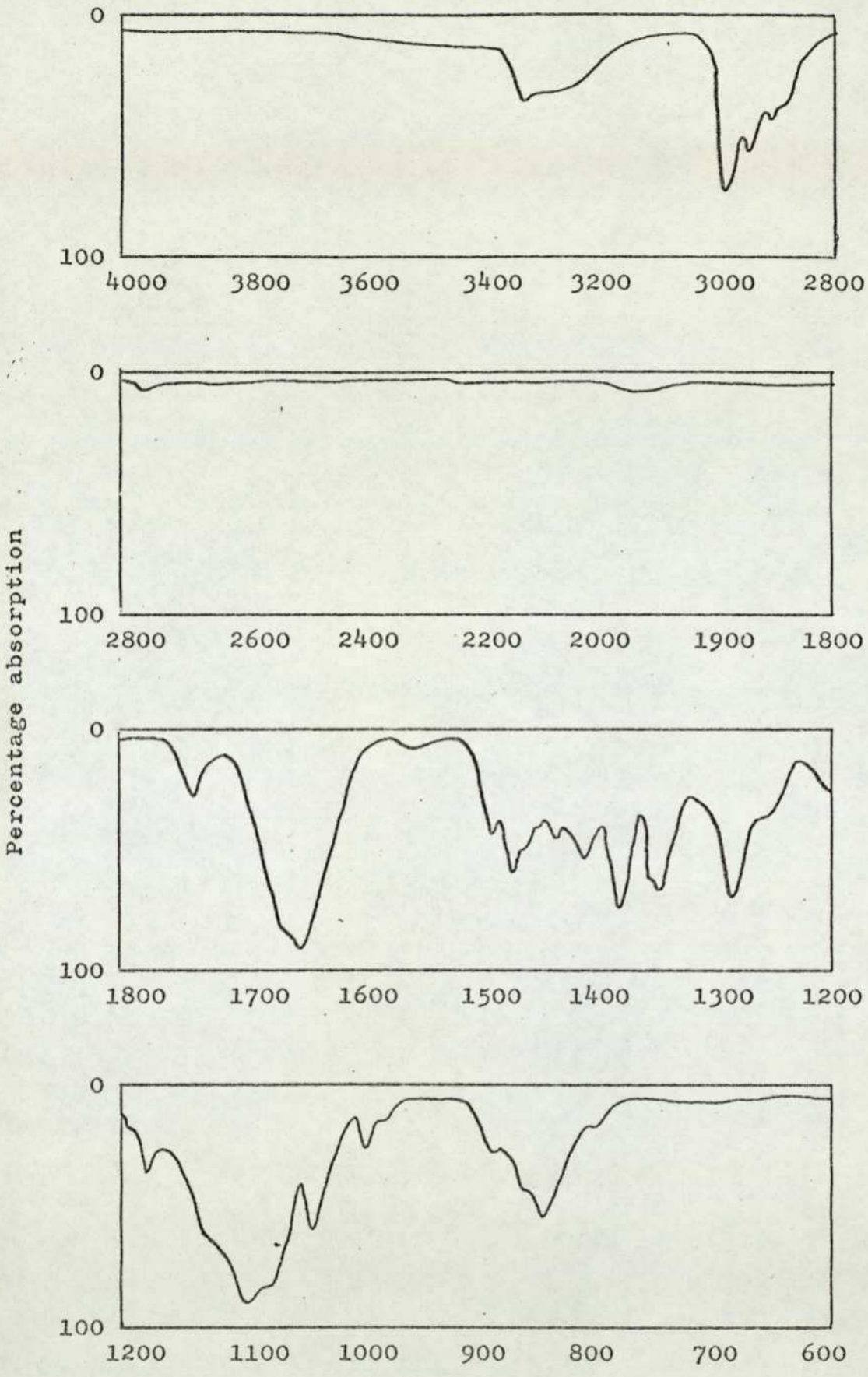


Fig. 32 Liquid phase infrared spectrum of ethyl propionimidate in the region 4000-600cm^{-1}

I. N-Chloro Methyl Acetimidate

Only one N-chloro substituted imidate, N-chloro ethyl acetimidate appears to have been previously prepared and assigned.[49] A literature survey revealed very few papers on the νNCl mode which is the principal feature of the spectrum.

The spectrum, Fig.33 shows no evidence of the parent compound, there being no measureable imino group absorption in the infrared or N.M.R. spectrum. In the νCH region, good agreement is found in Table 66 between the νCH modes of the methyl group with methyl acetimidate,[49] however, the overtones of N-chloro methyl acetimidate show interesting agreement with the overtone modes of methyl trichloroacetimidate.

Table 66

The aliphatic carbon hydrogen stretching region of various imidates.

Assignment	Methyl acetimidate	N-chloro methyl acetimidate	Methyl trichloroacetimidate
overtone	3005	3022	3025
overtone	2978	2994	2999
$\nu_{as}CH_3$	2948	2951	2952
overtone	2902	2906	2905
$\nu_{s}CH_3$	2853	2852	2848

The combination band at 2900-2905 is most probably a

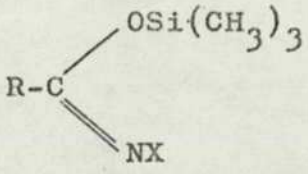
combination tone of the $b_s CH_3$ and $b_{as} CH_3$ modes which occur in all the compounds in Table 66.

The presence of a carbonyl impurity at 1746 was detected as a weak band only in the liquid phase spectrum and its presence was confirmed by the shift and increased intensity of the band in the vapour phase.

The ν C=N mode is clearly the very strong band at 1619, and agrees positionally with the band at 1617 in ethyl N-chloro acetimidate.[49]

The position of this band represents a shift of approximately 40 wavenumbers from the νC=N band at 1660 in methyl acetimidate.[100] The position of the ν C=N in N-chloro imidates is interesting when compared with the position of the corresponding band in Imidoyl chlorides. As discussed in chapter 1.D, the imidoyl chlorides have the general formula, R-CCl=NR' and so the chloro substituent on the azomethine group is situated on the carbon in these compounds. In the imidoyl chlorides, Bosshard and Zolinger,[82] found the ν C=N absorption at 1689 (R=H, R'=CH_3) and 1672 (R=C_6H_5, R'=C_6H_5) and the spectral data presented by Ulrich[73] shows that the ν C=N mode in imidoyl chlorides generally occurs higher than in the N-chloro imidates. N-chloro chlorothioformimodoyl chloride, CIS-C(-Cl)=NCl, was the only N-chloro system, outside the imidates and imidoyl chlorides, in which reliable data for the azomethine grouping was found. Here the νC=N band was quoted at 1604 in the Raman and 1603,[208] or 1604[209] in the infrared. The only paper with

data on the $\nu C{=}N$ of N-halogen derivatives of imidates, specifically the silyl esters, is due to Birkofer and Dickopp.[210] They measured the $\nu C{=}N$ of the three imidates, given in Table 67.



imidate

silyl ester

Table 67

The $\nu(C{=}N)$ absorption in some imidate silyl esters.

Substituent X	Substituent R	Wavenumber position
Cl	CH_3	1609
Br	CH_3	1608
Cl	C_6H_5	1600

Positionally these results bear the closest agreement with the present work. As with the study of the skeletal modes, the actual ester grouping little affects the position of the band.

Although it is dangerous to draw inferences on a limited amount of data, a comparison of the band position of the $\nu C{=}N$ mode in the N-chloro imidates and the imidoyl chlorides would appear to suggest that the effect of the chloro grouping on the position of the $\nu C{=}N$ mode is mainly an electronic effect. In N-hydroxy ethyl acetimidate the $\nu C{=}N$ band is found at 1663cm^{-1}

and would be expected at a lower wavenumber position if the band was mass sensitive.

Four in-plane CH bending modes associated with the methoxy and $CH_3C{=}N$ groupings were identified, by comparison with methyl acetate and methyl acetimidate, Table 68.

Table 68

In-plane bending modes of the carbon-hydrogen groupings in N-chloro methyl acetimidate.

Mode	N-chloro methyl acetimidate	Methyl acetimidate[b]	Methyl acetate[a]
$b_{as}(OCH_3)$	1459	1460	1456
$b_s(OCH_3)$	1445	1446	1436
$b_{as}(CCH_3)$	1374	1380	1369
$b_s(CCH_3)$	1331	1341	

[a]Ref. 148 [b]Ref. 100

The latter assignment is suggested, as the band at 1341, would appear to be too strong for the βNH mode suggested by Prichard and Orville-Thomas[100] and would appear to correspond to that at 1331 in the N-chloro derivative.

Assignment of four skeletal modes to bands at 1293, 1072, 1049 and 876, agrees well with the position of bands at 1299, 1094, 1049 and 860 in N-chloro ethyl acetimidate. In N-chloro ethyl acetimidate[100] a fifth band at 948 was assigned as a possible skeletal mode but as no band was observed in this

region in N-chloro methyl acetimidate, this band may, despite its intensity, be a combination band.

The rocking and wagging modes of the methoxy group are assigned to the peaks at 1190 and 1157 with reference to Table 38.

The N-chloro band at 732 varies little in its position from the ethyl ester at 729. Prichard[49] could only find one compound in which the νNCl mode was assigned; this was at 703 in the N-chloromonoimine of benzoquinone,[211] the band being assigned mainly on its strength and its position relative to the known position of the νCCl mode.

In this work there is the additional evidence of the solvent effects on the N-chloro band (Chapter 3.B). A literature survey revealed only four references and these were generally unsatisfactory for comparison purposes. Moore and Badgers work on chloro substituted ammonia,[212] in which bands were assigned at 686 (NH_2Cl), 687 and 666($NHCl_2$) and 652(NCl_3) to the νNCl mode are vapour phase values. Heasely et al[213] studied N-halo alkylamines, from which they concluded that absorption in the region 500-670 is characteristic of the N-chloro absorption. The choice of carbon tetrachloride for a solvent is inexcusable and no assignment is made. Petterson et al[215] give the νNCl modes of five compounds, trichloroisocyanic acid, 800, p-dichloro sulphamyl benzoic acid, 782, NN-dichloro benzene sulphonamide, 771, NN-dichloro-p-toluene sulphonamide, 762 and dichloroisocyanuric acid, 790, but here

the measurements are solid phase (nujol mulls). Moll,[214] studied N-chloro secondary amines, where the νNCl mode was identified by the appearence of new bands at or above 600.

The chief barrier to any comparison between the published νNCl values and the present study is that the nitrogen is trigonally hybridised in the imidates and the resulting proximity of the azomethine bond must place the N-chloro grouping in a unique environment.

The remaining bands above 700 are assigned to combination tones. Below 700 only two possible assignments were recognised, to the bands at 640 and 303 which may be due to (O-C=N) deformation modes.

Complete assignment of the infrared spectrum of N-chloro methyl acetimidate is presented in Table 69, and the liquid phase spectrum shown diagrammatically in Fig.33.

Table 69

Assignment of the infrared spectrum of N-chloro methyl acetimidat

Liquid	Solution	Gas	Assignment
3320vw			overtone 2x1619=3238
3022mw	3022m	3020m	combination tone ν_sCH + 170=3022
2994m	2992m	2996m	combination band 1619+1374=2993
2951m	2950m	2954m	$\nu_{as}CH_3$ of methoxy group
2906w.sh	2906w.sh		combination band $b_sCH_3+b_{as}CH_3$=2904
2852w	2851w	2863w	ν_sCH_3 of methoxy group
2806vw			combination band 1190+1619=2809
2778vw			combination band 1331+1445=2776
2731vw			combination band 1445+1293=2738
2578vw			overtone 2x1293=2558

Table 69 cont.

Liquid	Solution	Gas	Assignment
2492vw			combination band 1049+1445=2494
2382vw			overtone 2x1190=2380
2252vw			combination band 1374+876=2250
2160vw			overtone 2x1072=2154
2021vw			combination band 978+1049=2027
1922vw			combination band 876+1049=1925
		1776w.sh	νC=O
1746w	1747w	1758m	νC=O
		1628vs	νC=N in gas phase
1624vs.sh		1624vs.sh	combination band 1072+553=1625
1619vs	1621vs		νC=N in liquid phase
	1617vs.sh	1617s.sh	combination band 1445+170=1615
1459s.sh	1458sh	1459m.sh	$b_{as}CH_3$ of methoxy
1445s	1444s	1449m	b_sCH_3 of methoxy
		1437m.sh	b_sCH_3 of methoxy
1374vs	1374vs	1374m	$b_{as}CH_3$ of C-CH_3
1331m.sh	1331w.sh		b_sCH_3 of C-CH_3
1293vs	1291vs	1290vs	skeletal mode A
1190w	1190w		rCH_3
1157w	1157w		ωCH_3
1072m.sh	1072m.sh		skeletal mode B
1049s	1050s	1054m	skeletal mode C
978m	974mw	970w	combination band
876s	876s	872m	skeletal mode D
		740m.sh	combination band 435+303=738
732ms		727m	νNCl
712w.sh			combination band 170+553=723
640w			bending (O-C=N)
607w			Overtone 2x303=606
553m			
458w			
435w			
303w			δ(O-C=N)
170w			

Solution values apply to a 1% solution in carbon tetrachloride.

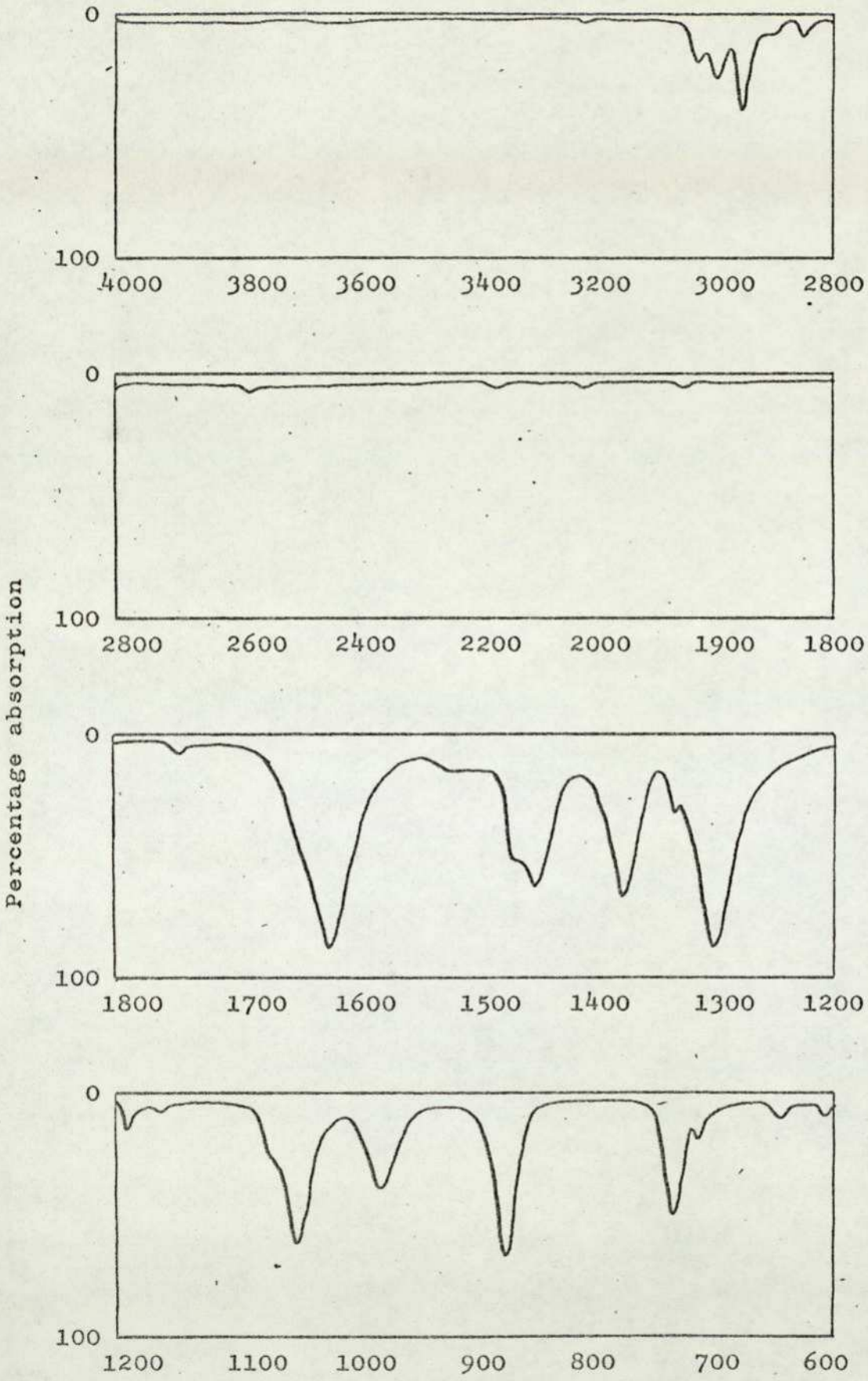


Fig. 33 Liquid phase infrared spectrum of N-chloro methyl acetimidate in the region 4000-600cm^{-1}

J. N-Chloro Ethyl Benzimidate

The modes associated with three structural features, the N-chloro group, the ethyl group and the benzene ring have all been previously discussed. The skeletal stretching modes and the modes associated with the benzene ring are included in Table 59, together with the corresponding data for methyl benzimidate and ethyl benzimidate. The modes associated with the benzene ring are little affected by the introduction of the N-chloro substituent. The skeletal modes are less easily and satisfactoraly assigned by comparison. Two bands at 1306 and 1288 occur in the region where skeletal mode A is normally observed and likewise two bands at 1110 and 1094 where one would expect skeletal mode B. In each case it was found difficult to make the assignment. For band B in particular the greater intensity of the band at 1110 would favour assignment to the mode, but the weaker band at 1094 shows closer positional agreement with the mode in other imidates, Table 24. For mode A the two bands are both strong bands and both occur in the region accepted for this mode.

The modes associated with the ethoxy group are given in Table 60. together with the corresponding bands in ethyl trichloroacetimidate and ethyl benzimidate. The agreement is so clearly apparent that no further discussion will be presented.

The remaining interest is associated with the $\nu C{=}N$ and νNCl modes. The former mode is assigned to a very strong band

at 1612. To ascertain the effect of the dual substitution of a benzene ring and an N-chloro atom on the azomethine grouping, reference was made to Table 70 in which the groupings R_1, R_2 and X refer to the structure $R_1C(=NX)OR_2$.

Table 70

The effect of substitution on the position of the $\nu C=N$ mode.

Substituent			$\nu C=N$	Reference
R_1	X	R_2		
CH_3	Cl	$Si(CH_3)_3$	1609	210
CH_3	Br	$Si(CH_3)_3$	1608	210
C_6H_5	Cl	$Si(CH_3)_3$	1600	210
CH_3	H	C_2H_5	1655	49
CH_3	Cl	C_2H_5	1617	49
C_6H_5	H	C_2H_5	1634	
C_6H_5	Cl	C_2H_5	1612	

Whilst the introduction of an N-chloro atom or an aromatic substituent, both produce a shift in the $\nu C=N$ mode to lower wavenumbers, the presence of both groupings fails to produce an additive effect. Although the $\nu C=N$ mode of N-chloro ethyl benzimidate is lower than in ethyl benzimidate or N-chloro ethyl acetimidate the band however is only five wavenumbers lower than in N-chloro ethyl acetimidate. This observation compares with the silyl esters in which the comparable shift is nine wavenumbers. It can only be concluded that the presence

of the N-chloro atom reduces the degree of conjugation of the azomethine group with the benzene ring.

The νNCl mode has not been assigned. In N-chloro methyl acetimidate the mode was observed as a strong band at 732. In N-chloro ethyl benzimidate an out of plane γCH deformation which occurs at 697 would appear to mask the presence of this mode. A solvent effect study on this band revealed the presence of a shoulder at 706 on the main peak, but as this band did not appear to move with the polarity of the solvent, assignment of the νNCl remains speculative.

Assignment of the liquid phase spectrum of N-chloro ethyl benzimidate in the region 4000-250 and the spectrum shown diagramatically in Fig. 34, no gas phase spectrum was run.

Table 71

Assignment of the infrared spectrum of N-chloro ethyl benzimidate

Liquid	Solution	Assignment
3090vw.sh	3090vw.sh	aromatic νCH
3069w		aromatic νCH
3042w.sh	3042w.sh	combination band
3031w.sh	3031w	aromatic νCH
2988m	2987m	ν_{as}CH of methyl
2962w.sh	2961w.sh	ν_{as}CH of methylene
2940w	2941w.sh	ethoxy group overtone
2903w	2905w	ν_{s}CH of methylene
2872w.sh	2875w.sh	ν_{s}CH of methyl
2729vw		combination band 1140+1594=2734
2673vw		combination band 1369+1306=2675

Table 71 cont.

Liquid	Solution	Assignment
2503vw		combination band 1394+1110=2504
2411vw		combination band 1394+1017=2411
2343vw		overtone 2x1173=2346
2322vw		combination band 1030+1288=2318
2262vw		combination band 1493+769=2262
2231vw		combination band 1306+924=2230
1961vw		combination band 1094+869=1963
1897w		combination band 1030+869=1899
1812w		combination band 1110+697=1807
1765vw		combination band 1001+769=1770
1719w	1724w	νCO impurity
1619s.sh	1619s.sh	combination band 1001+614=1615
1612s	1614s	νC=N
1594vs	1593vs	$A_1\nu$C-C mode (k)
1579s		$B_1\nu$C-C mode (l)
1559m.sh		combination band 869+697=1566
1493s		$A_1\nu$C-C mode (m)
1475m	1477m	C_2H_5 group bending mode
1466m.sh	1466m.sh	scissoring CH_2 of methylene
1448s	1448s	$b_{as}CH_3$ of ethoxy + $B_1\nu$C-C mode (n)
1394m	1394w	b_sCH_3 of ethoxy group
1369s	1369s	ωCH_2
1318s.sh	1317s.sh	$B_1\nu$C-C mode (o)
1306vs 1288vs	1305vs 1286vs	skeletal mode A. See text
1173m	1175w	$A_1\beta$CH mode (a) + $\omega(CH_3)$
1158m.sh	1159m.sh	$B_1\beta$CH mode (a)
1140	1140s	combination band 697+453=1150
1127s.sh	1127m.sh	rCH_3
1110s 1094m	1111m) 1093m)	skeletal mode B. See text
1074m	1072m	$B_1\beta$CH mode (d)
1030s	1031s	$A_1\beta$CH mode (b)

Table 71 cont.

Liquid	Solution	Assignment
1017s		skeletal mode C
1001m		A_1 ring mode (p)
924w	923w	B_2 γCH mode (i)
869s		skeletal mode D
794w		ethoxy group mode
769s	768*	B_2 γCH mode (f)
759m.sh	756*	
	707*	B_2 ρC-C mode (v) + υNCl
697vs	694*	
630m	633*	bending (O-C=N)
614vw		B_1 α(C-C-C) mode
589m		
544w		
453w		
431m		
419w.sh		
320m		
303w.sh		δ(O-C=N)

Solution values apply to 1% solutions in carbon tetrachloride with the exception of those marked * which apply to cyclohexane.

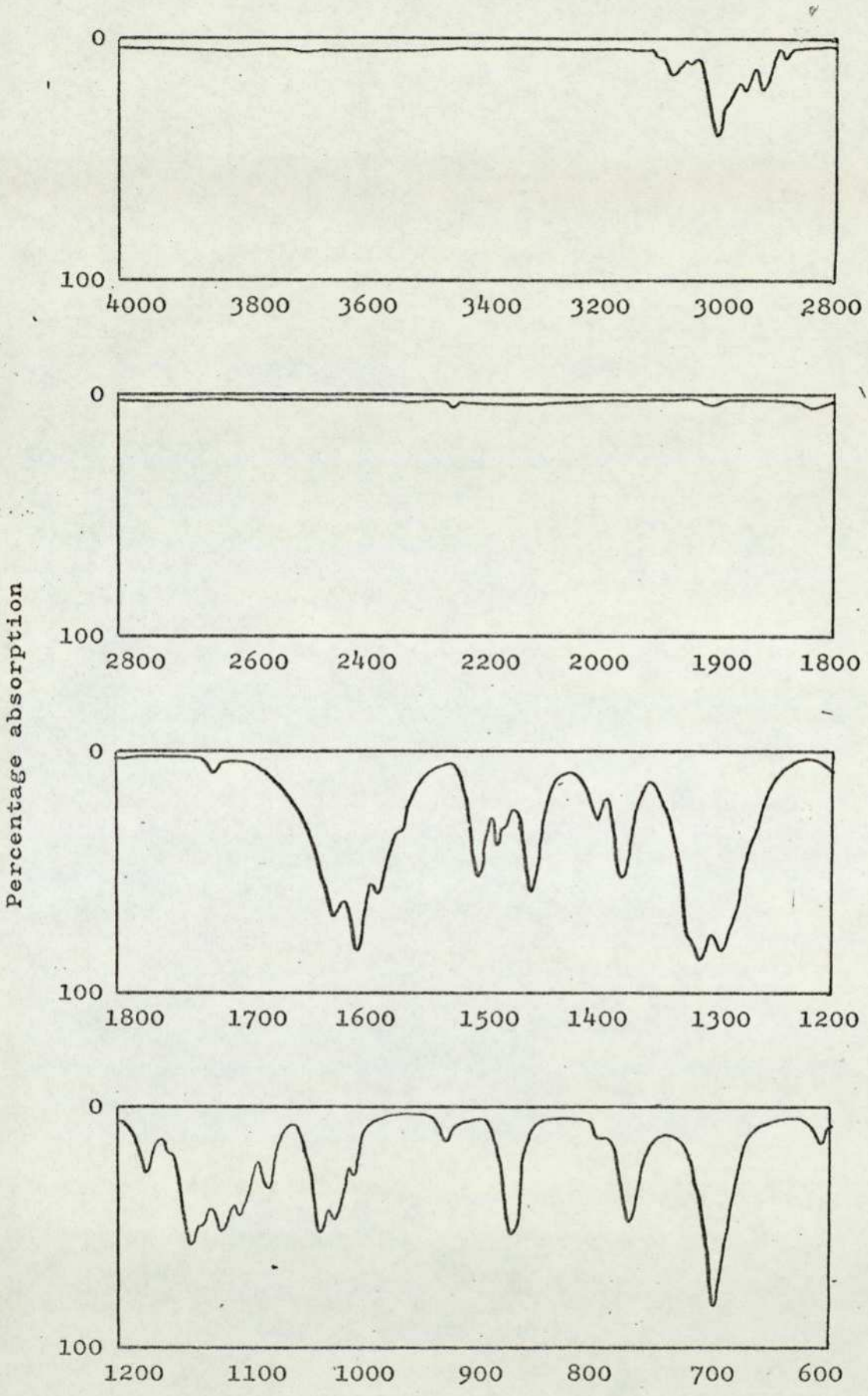


Fig. 34 Liquid phase infrared spectrum of N-chloro ethyl benzimidate in the region 4000-600cm^{-1}

K. N-Chloro Ethyl Propionimidate

No strong bands were observed in the region 3000-4000 wavenumbers and the absence of a peak in the region of 1650 would seem to confirm the absence of the parent imidate. A weak carbonyl impurity was observed at 1740 in the liquid phase. This band was shifted to higher wavenumbers and increased in intensity in the gas phase, but the other bands in the spectrum were little affected positionally on the change of state.

The ethoxy group vibrations have been recognised by comparison with ethyl propionimidate and ethyl acetimidate. The assignment of the data, Table 64, closely follows the original assignments of Nolin and Jones[149] with the exception of the band at 2944 which would appear to be the $\nu_{as}CH$ mode of the methylene group rather than the ethoxy group overtone mode suggested.

Two bands at 1379 and 1331 are assigned to the b_sCH and $b_{as}CH$ modes of the $CH_2C{=}N$ grouping as discussed in the assignment of ethyl propionimidate. The νNCl mode occurs at 729, this corresponding with the value of 732 for N-chloro methyl acetimidate.[49] The mode is even weaker than in N-chloro methyl acetimidate, but the reason for the comparitive weakness is not understood.

The remaining modes are assigned in Table 72 and the liquid phase infrared spectrum depicted in the range 4000-600, Fig. 35.

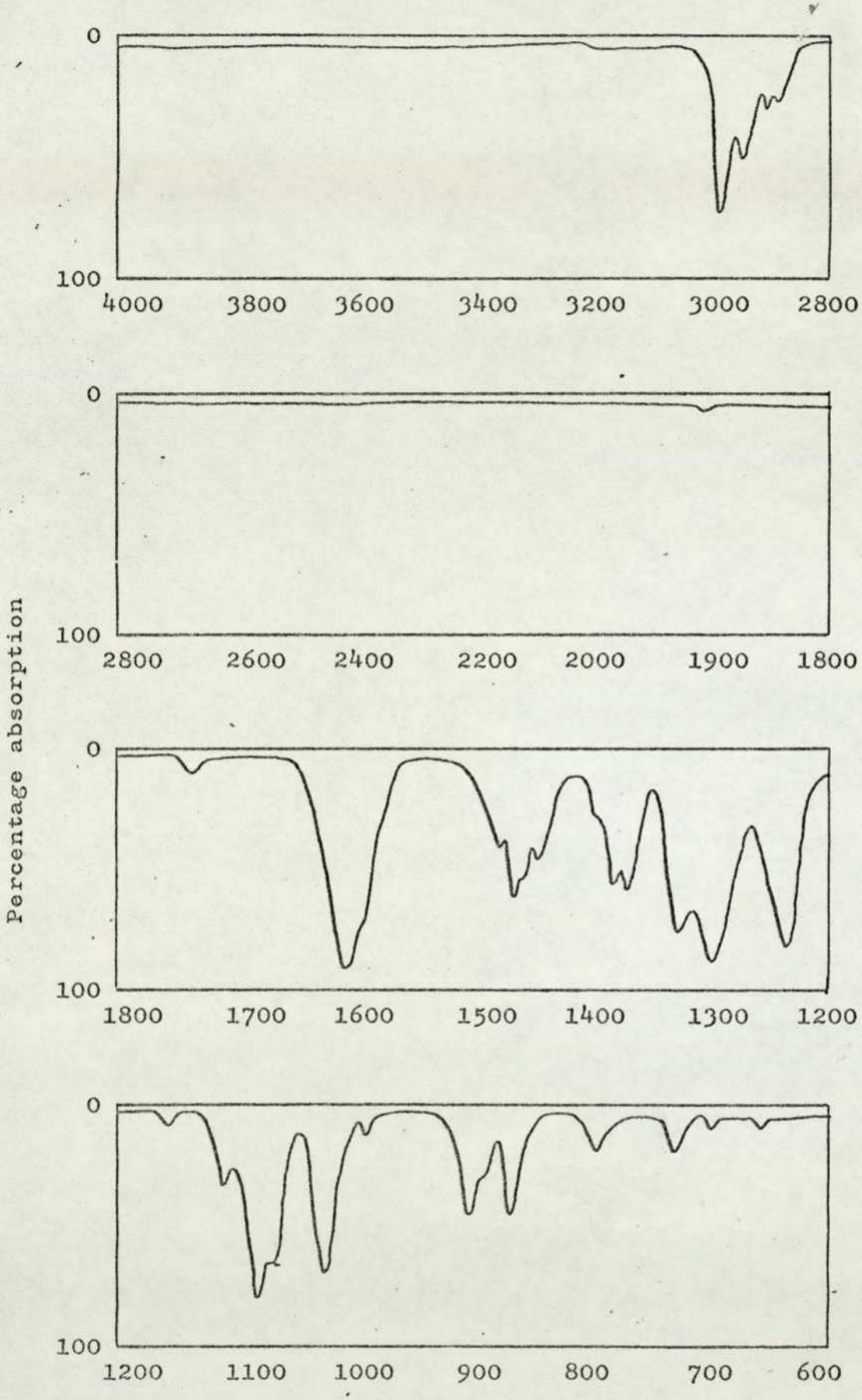


Fig. 35 Liquid phase infrared spectrum of N-chloro ethyl propionimidate in the region 4000-600cm^{-1}

Table 72

Assignment of the spectrum of N-chloro ethyl propionimidate

Liquid	Gas	Solution	Assignment
2985s	2991m	2986m	ν_{as}CH of ethoxy methyl group
2944m	2952mw	2944W	ν_{as}CH of ethoxy methylene group
2904m	2904mw	2905W	ν_{s}CH of ethoxy methylene group
2884m.sh		2884W	ethoxy overtone mode
2872w.sh		2873W	ν_{s}CH of ethoxy methyl group
2785vw			combination band 1397+1379=2776
2750vw			combination band 1379+1368=2747
2732vw			combination band 1606+1118=2724
2692vw			combination band 1085+1606=2691
2665vw			overtone 2x1331=2662
2598vw			combination band 1606+998=2604
2530vw			combination band 1444+1085=2529
2506vw			combination band 1478+1028=2506
2458vw			combination band 1464+998=2462
2421vw			combination band 1397+1028=2425
2380vw			combination band 1478+907=2385
2315vw			combination band 869+1444=2313
2266vw			combination band 797+1464=2261
2197vw			combination band 869+1331=2200
2168vw			overtone 2x1085=2170
2097vw			combination band 700+1397=2097
2023vw			combination band 1297+729=2026
1956vw			combination band 1297+663=1960
1895vw			combination band 1232+663=1895
1768vw			combination band
1740w	1754w		νC=O impurity
1618m.sh	1617m	1618*	combination band 700+907=1607
1606vs		1608*	νC=N
1478m		1478W	bCH of ethoxy CH_2
1464m	1467w	1464m	scissoring CH_2

Table 72 cont.

Liquid	Gas	Solution	Assignment
1457m.sh		1457w.sh	overtone 2x729=1458
1444m		1444w	$b_{as}CH_3$ of ethoxy
1397w			b_sCH_3 of ethoxy
1379m	1377wm	1379w	$b_{as}CH$ of $CH_2C{=}N$
1368m		1369w	combination band 663+700=1363
1331s	1333mw	1332m	b_sCH of $CH_2C{=}N$
1297vs		1297vs	skeletal mode A
1232s	1233mw	1230m	combination band
1168w			combination band
1158w			ω CH_3
1118m.sh		1113w	combination band
1085vs	1082m	1085ms	skeletal mode B
1071s.sh		1071m.sh	combination band
1028s	1029mw	1028m	skeletal mode C
998w.sh			νC-C
907m	903w	907w	combination band
869m	872w	869w	skeletal mode D
797m	795vw		ethoxy group mode
729w			νNCl
700w			
663w			bending (O-C=N)

Solution values apply to 1% solutions in carbon tetrachloride, except those marked * which apply to hexane.

CHAPTER 5

The Spectra and Structure of Imidates-

Conclusion

The infrared spectra of imidates are characterised by the appearance of four absorptions in the region 1350-800cm^{-1}, due to stretching of the heavy atom skeleton. They are described in the following paragraphs as modes A, B, C and D.

Mode A

This is principally a $\nu[(C-C) = N]$ vibration with a ν_sC-O-C contribution. The mode is mass sensitive to the substituent on C_1, being inactive in ethyl acetimidate and methyl acetimidate.

Normal range:- 1330-1280cm^{-1}vs

Mode B

This is principally a ν_{as}C-O-C vibration, coupled with a ν(C=N) vibration. The wavenumber position of the band is little affected by the substituent on C_1 or N, and the ν C=N coupled vibration causes the band to occur at a higher wavenumber position relative to the ν_{as}C-O-C mode of methyl acetate.

Normal range:- 1100-1075cm^{-1}s

Mode C

This is a $\nu[(C-C) - X]$ vibration, where X is the substituent on C_1. The band is sensitive to the mass of the substituent on C_1, and the mass and electronic nature of the substituent on the nitrogen.

Normal range:- Acetimidates 1060-1045cm^{-1}vs

Other imidates 1030-1000cm^{-1}vs,s

Mode D

This is a ν_sC-O-C vibration associated with a ν[(C-C)=N] vibration.

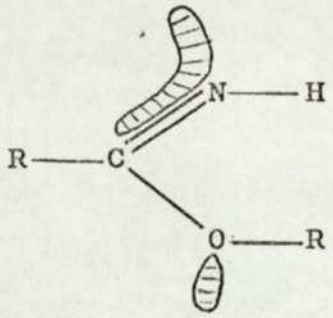
Normal range:- 880-810cm^{-1} variable

Two additional vibrations, possibly associated with the in-plane and out-of-plane deformation modes of the O-C=N grouping were recognised at 630-710cm^{-1} and 305-285cm^{-1} respectively.

The νNCl mode of aliphatic imidates was found at approximately 730cm^{-1}, the infrared solvent study of this mode showed a variation with solvent polarity. The remaining work was concentrated on ascertaining the way in which the imino hydrogen was bonded in the various imidates on the evidence of infrared solution, liquid and vapour measurements, dipole moment and N.M.R. studies.

In the aliphatic imidates, that is the acetimidates and propionimidates, the relatively large shift in the position of the ν(NH) from the gas phase to the liquid phase in the infrared spectrum, the broadness of the band in the liquid phase, and the shift to higher wavenumbers of the mode in the majority of solvents studied, suggested an intermolecularly bonded species. This is consistent with the lack of a site for intramolecular bonding within the imidate.

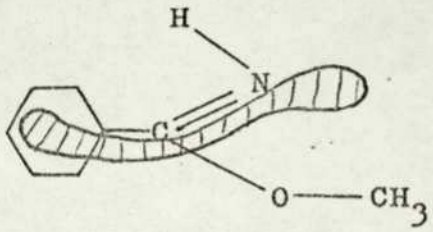
The infrared solvent shifts on the imino group in imidates are uniformly less than the corresponding solvent shift on the ν(NH) mode of pyrrole. This is thought to be due to the difference in hybridisation (sp^2 in the case of the imino nitrogen in the imidates and sp^3 in pyrrole), allowing conjugation of the lone pair of electrons on the nitrogen with the azomethine group in the imidates, resulting in electronic shielding of the imino grouping from solvent attack.



For the aliphatic imidates no structure has been accepted as the preferred orientation. The vectorial calculations by the present and previous authors, being so much at variance the findings for the dipole moment studies have been ignored. There would appear to be no steric hinderance to any orientation of the imino or alkoxy groupings.

In the benzimidates the dipole moment studies favour either a cis trans' or trans cis' structure (see section 3.E.). The smaller shift in the infrared from the gas to liquid phases suggests intramolecular bonding or steric hinderance. In the N.M.R. spectrum the imino absorption is shifted upfield by non polar solvents and downfield by polar solvents. The

shift, however, is relatively small, but noticeably larger than in methyl trichloroacetimidate . In the N.M.R. spectra of the liquid imidates, the imino absorption occurs at low fields. This is consistent with the group being affected by the ring current induced in the benzene ring. These data are thought to be consistent with the cis trans' structure illustrated:-

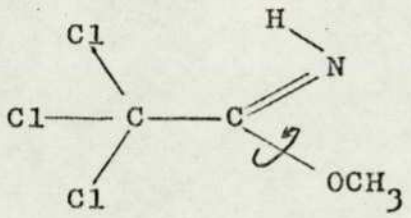


cis trans' methyl benzimidate

The imino group is hindered both sterically and electronically by the presence of the benzene ring, this reducing drastically the degree of intermolecular bonding in the liquid phase.

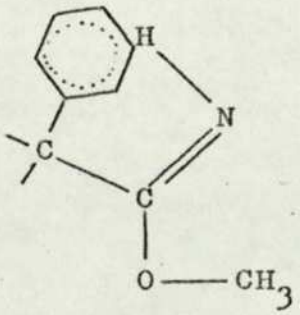
In the trichloroacetimidate, the small shift from the vapour phase value to the liquid phase value in the infrared, the small shift and relatively high wavenumber position of the ν(NH) in the liquid phase in comparison to the position of the band in the solvents studied in the infrared studies, the low field position of the imino absorption in the N.M.R. spectrum relative to the aliphatic imidates, and the insensitiveness of the imino grouping to the effect of solvents in the N.M.R. would all appear consistent with an intramolecularly bonded system.

The dipole moment studies show that the three structures in which the imino group is cis to the trichloromethyl grouping are all favorable and thus the cis free' structure has been accepted for these imidates.



cis free' methyl trichloroacetimidate

Less data is available on the remaining class of imidates, the phenyl acetimidates. The uniformly low infrared solvent shifts and small shift from the vapour phase to the liquid phase in the infrared wavenumber position, are indicative of an intramolecularly bonded species, and the most favorable structure would appear to be:-



The shoulders on the νNH mode in the infrared spectra of the benzimidates and phenylacetimidates are believed to be due to a ν(C=N) group overtone.

CHAPTER 6

Computer Correlation of Infra-red Solvent Effect Shifts

A. THEORETICAL INTRODUCTION

The vibrational spectrum of a compound in the vapour state differs from that obtained in solution. Hallam[217] itemised the differences as follows:-

1) In solution the rotational structure of the bands disappears or is replaced by a very simple contour e.g. CH_3X molecules.
2) The band positions obtained do not correspond with the pure vibrational frequencies of the molecule in the vapour state.
3) The band half width may be greatly increased in solution.
4) The band intensities may be altered, sometimes by a factor of ten or more.

Many attempts have been made to relate the experimentally observed shift in the wavenumber position of a band in going from the vapour phase into solution with the physical properties of the solvents used.

The earliest attempts were generally based on the Onsager model of an oscilating point dipole in a cavity in a medium of continuous dielectric. Kirkwood,[218] and Bauer and Magat[219] independently deduced a mathematical relationship, whereby the frequency of oscillation is modified by the field acting, as described by the equation:-

$$\frac{\Delta\nu}{\nu} = \frac{c(\varepsilon-1)}{2\varepsilon+1}$$

where $\Delta\nu$ is the difference between the wavenumber position of a band in the vapour phase and in solution, ν is the wavenumber position in the vapour phase and ε is the dielectric permittivity of the solvent.

The final equation does not include any terms dependent on the size of the solute molecule, nevertheless, because of its simplicity the Kirkwood, Bauer, Magat (KBM) relationship has been rigorously tested experimentally[117,120,220,221] by plotting $\Delta\nu/\nu$ against $\varepsilon-1/2\varepsilon+1$.

Despite its inherent weakness, the relationship appears to hold reasonably well for nonpolar solvents. With polar solvents the relationship breaks down and few if any of the points lie on the line and there appears to be no systematic shift of points to one side of the line. The obvious conclusion from these plots is that the relationship will only hold where there is no possibility of hydrogen bonding. However, doubts are raised against the validity of the KBM relationship even for nonpolar solvents. The shifts observed in nonpolar solvents are small compared with those in polar solvents and any scale used to include all the points will tend to hide the variance of the nonpolar points from the line.

Josien[222] investigated the use of n^2 (where n is the refractive index) in place of the dielectric permittivity in the KBM relationship for solvent shifts on the νNH band of pyrrole. Again better agreement was obtained for nonpolar

solvents, but the agreement was generally poor. Unfortunately the refractive indices used were determined in the visible region, and were not infra-red determined values at the wavelength being investigated. While the discrepancy between visible and infra-red determined values is generally small, the error may be serious (as much as 25%) in the region of a solvent absorption.[223] Even allowing for the inaccuracy in the refractive index data used, the spread of points is too great for this to be an acceptable improvement, and a basic weakness in the theory was again indicated.

Pullin[224,225,226] tried to relate the dielectric nature of the medium to the solvent shifts observed. As a starting point[225] the work required to bring a non polarizable point dipole of moment, μ, from infinity to the centre of a spherical cavity inside a dielectric, was considered as being given by[227] :-

$$W = \tfrac{1}{2}\mu R$$

where R is the reaction field of the dipole given by $f.\mu$ where

$$f = \frac{2(\varepsilon-2)}{(2\varepsilon+1)} \times \frac{1}{a^3}$$

ε is the dielectric permittivity of the medium and a, the cavity radius.

For a diatomic molecule[225] it was assumed that the vapour phase dipole moment $\mu(x)$ was given by:-

$$\mu(x) = \mu_0 + M'x + M''x$$

where x is an extension of the vapour phase equilibrium internuclear separation.

The vapour phase potential energy factor for the molecule was assumed to be:-

$$V(x) = \tfrac{1}{2}kx^2 - bx^3 + Cx^4$$

In solution the potential energy of the molecule will be given by:-

$$Vs = V(x) + W = V(x) + \tfrac{1}{2}\mu R$$

or as $$R = f.\ \mu(x)$$

$$Vs = V(x) + \tfrac{1}{2}f.\ \mu^2(x)$$

Expanding, this becomes:-

$$Vs = V(x) + \tfrac{1}{2}f.\ \mu_0^2 + f.\ \mu_0 M'x + \tfrac{1}{2}f.M'^2x^2 - f.\ \mu_0 M''x^2 - f.\ M'M''x^3 - \tfrac{1}{2}f.\ M''^2x^4 \quad \ldots\ldots\ldots (1)$$

This expression was then further expanded,[225] allowance being made in calculating f. for the difference in dielectric permittivity for static and oscillating fields and used to predict wavenumber shifts for the carbonyl stretching mode of acetone. The treatment will not be pursued further, as the basic agreement between theoretically predicted, and practically observed values was poor, the observed values generally being about twice the calculated values. The treatment appears to have inherent in it an error associated with the exclusion of

intermolecular forces, in this case due to the acceptance of a non-polarizable point dipole as the model.

Subsequently, Pullin[224] reexamined equation (1) and decided that, of the terms additional to V(x) on the right hand side of the equation only $-f.\mu_0 M'x$, $-\frac{1}{2}f.M'^2x^2$ and $-f\mu_0 M''x^2$ were of sufficient magnitude to materially affect the value of the relative shift $(\Delta\nu/\nu)$.

The first of these three terms describes the change in the equilibrium bond length in solution, and, if the molecule is mechanically anharmonic, the resultant frequency shift. This was designated the distortion term. The other terms are quadratic in x and will cause the value of d^2Vs/dx^2 to differ from $d^2V(x)/dx^2$. The second term, the intensity term, operates to decrease the wavenumber position in solution, proportionately with the band intensity. The third term, the overtone effect, operates similarly to the intensity term, but here the frequency shift may be in either direction.

Dielectric theory[226] predicts that the distortion effect should depend on the dielectric permittivity of the medium. The distortion effect, which will always lower wavenumber positions relative to the vapour phase, should be proportional to the band intensity and to n^2, where n is the solvent refractive index, at the frequency of vibration. The overtone effect is also thought to depend on n^2, but its magnitude and sign are not clearly known, and this was considered in his later paper.[226] The fact that the intensity term also depends

on n^2 suggests that the theory will only account for bulk solvent effects.

Now if $\Delta\nu' = \nu^0 - \nu_s$

where ν^0 is the frequency such that $\varepsilon = n^2 = 1$ and ν_s = the frequency in solution, it follows that:-

$$\Delta\nu' = k'(\text{intensity effect}) + k''(\text{distortion effect})$$

$$\Delta\nu' = A^i . f(n^2, V) + A^d . f(\nu, V)$$

where V is the volume of the cavity.

While this is relatively correct for nonpolar solvents, for polar solvents, ε may be considerably greater than n^2 and the distortion effect will be smaller than predicted, due to dielectric saturation and to the short range nature of dipolar forces. The equation may be modified to give

$$\Delta\nu' = B . f(n^2, V) + C\left[f(\varepsilon, V) - f(n^2, V)\right] \qquad \ldots . (2)$$

At this point the author had reached the limit of useful theoretical deduction, and the nature of the term, which was a function of n and V was investigated empirically. The functions tested were:-

$$\frac{n^2-1}{2n^2+1} \quad , \quad \frac{(n^2-1)}{(2n^2+1).V} \quad , \quad \frac{n^2-1}{(2n^2+1).\bar{V}} \quad , \quad \frac{n^2-1}{(2n^2+1).V^*}$$

where V, $\bar{V}$, and V^* were respectively the solvent molar volume, the arithmetic mean molar volume of the solute and solvent, and the corresponding geometric mean. The latter three

approximations were equally as good, but it was eventually decided to use the mean molar solvent radius R as defined by $V = 4\pi R^3/3$, and plots of the wavenumber shifts were made against the function:-

$$\left\{\frac{(n^2-1)}{(2n^2+1)} \cdot \frac{1}{R}\right\} + b\left\{\left[\frac{(\varepsilon-1)}{(2\varepsilon+2)} \cdot \frac{1}{R}\right] - \left[\frac{(n^2-1)}{(2n^2+1)} \cdot \frac{1}{R}\right]\right\} \quad \ldots\ldots (3)$$

Plots were made for the $1720cm^{-1}$ and $1220cm^{-1}$ bands of acetone for 1% solutions, using values of b between 0 and 0.1. The plots obtained[226] showed less deviations from the least squares curve than the previous KBM plots, while the value of b did not appear to be of great significance.

The importance of Pullin's final equation is the inclusion of a cavity radius term, although solvent-solute interactions are still excluded. It is possible that equation (3) may be reduced to a simple function of $\frac{n^2-1}{(2n^2+1)} \cdot \frac{1}{R}$, but this is debatable as the overall agreement for any of the chosen values of b is poor.

Another theoretical study of the problem at this time used the Hamiltonian H, leading to the vibrational energy levels of a gaseous diatomic molecule, in the form[228] :-

$$H = H_0 + H_a = -hcB_e\frac{d^2}{d\xi^2} + \frac{hc\omega_e^2}{4B_e}\left\{\xi^2 + \frac{A\xi^3}{\omega_e} + \frac{B\xi^4}{\omega_e} + \ldots\right\}$$

and $$H_0 = -hcB_e\frac{d^2}{d\xi^2} + \frac{hc\omega_e^2\xi^2}{4B_e}$$

where H_0 is the harmonic oscillator Hamiltonian, H_a is the anharmonic oscillator Hamiltonian, $\frac{hc\omega_e^2}{2B_e r_e^2}$ is the force constant, and $\xi = \frac{r-r_e}{r_e}$, a dimentionless parameter proportional to the displacement from the equilibrium internuclear distance, r_e. The constants r_e, ω_e, B_e, $\mathcal{A}$, $\mathcal{B}$ can be obtained by comparing the observed energies with those obtained by treating the anharmonic Hamiltonian H_a, as a small perturbation to H_0.[228]

In solution the frequency arising from a transition between energy levels W_{sn} and W_{sm} will be given by:-

$$\omega_{m,n} = \frac{W_{sn} - W_{sm}}{hc}$$

If W_{gn} and W_{gm} are the corresponding energy levels in the gas phase, the relative frequency shift will be given by:-

$$\frac{\Delta\omega_{mn}}{\omega_{m,n}} = \frac{(W_{sn} - W_{sm}) - (W_{gn} - W_{gn})}{W_{sn} - W_{sm}}$$

For a fixed configuration of solvent molecules, the interaction potential U of the system is expandable as a power series in ξ

$$U = U_e + U'\xi + \tfrac{1}{2}U''\xi^2 + \ldots$$

The total Hamiltonian becomes $H_0 + H_a + U$, and if

$H_0 + U - U_e$ is treated as a small perturbent to H_0, it can be shown that[229] :-

$$W_{sn} = W_{gn} + U_e + (n+\tfrac{1}{2})\frac{B_e}{\omega_e}\left\{U'' - \frac{3\mathcal{A}U'}{\omega_e}\right\} - \frac{B_e}{\omega_e}\cdot\frac{(U')^2}{hc\omega_e}$$

and hence that $$\frac{\Delta\omega_{m,n}}{\omega_{m,n}} = \frac{B_e}{hc\omega_e^2}\left\{\bar{U}'' - \frac{3\mathcal{A}U'}{\omega_e}\right\} \quad \ldots\ldots (4)$$

where $\bar{U}$ signifies the mean value over all solvent configurations.

From equation (4) it follows that the shift for the ith overtone should be (i+1) times that of the fundamental as $\Delta\omega_{m,n}/\omega_{m,n}$ is independent of m and n, while the shift for different isotropic species will be of the same order since B_e/ω_e^2 and $\mathcal{A}/\omega_e$ should be little changed. These two predictions were shown to be in agreement respectively with the data of West and Edwards[230] for hydrogen chloride and Hornig and Hielbert[231] for hydrogen chloride and deuterium chloride.

If it is now assumed that the field F, acting on the infra-red active molecule, due to the charge distribution in a nonpolar environment is proportional to its dipole moment μ, then $F = g\mu$, where for the Onsager model[229] :-

$$g = \frac{2(\varepsilon-1)}{(2\varepsilon+1).a^3}$$

where a is the cavity radius in the dielectric. For nonpolar solvents it is possible to write equation (4) in terms of a

power series, which is then simplified to give an extended form of the KBM relationship.

$$\frac{\Delta\nu}{\nu} = C_0 + C_1\left\{\frac{\varepsilon-1}{2\varepsilon+1}\right\} + C_2\left\{\frac{\varepsilon-1}{2\varepsilon+1}\right\}^2 \qquad \ldots\ldots(5)$$

or approximating further:-

$$\frac{\Delta\nu}{\nu} = C_0 + C_1\frac{(\varepsilon-1)}{(2\varepsilon+1)} \qquad \ldots\ldots(6)$$

For a polar environment, $F = g_\varepsilon \mu_\varepsilon + g_n \Delta_\mu$ where μ_ε is the equilibrium dipole moment of the absorber and Δ_μ the oscillating dipole moment resulting from the molecular vibrations.

For the Onsager model:-

$$g_\varepsilon = \frac{2(\varepsilon-1)}{(2\varepsilon+1).a^3} \qquad \text{and} \qquad g_n = \frac{2(n^2-1)}{(2n^2+1).a^3}$$

Hence for polar solvents

$$\frac{\Delta\nu}{\nu} = C_0 + C_1\frac{(\varepsilon-1)}{2\varepsilon+1} + C_2\frac{(\varepsilon-1)^2}{(2\varepsilon+1)^2} + C_3\frac{(n^2+1)}{(2n^2+1)} + C_4\frac{(\varepsilon-1)(n^2-1)}{(2\varepsilon+1)(2n^2+1)}$$

which is approximated[229] to

$$\frac{\Delta\nu}{\nu} = C_0 + C_1\frac{(\varepsilon-1)}{(2\varepsilon+1)} + C_2\frac{(n^2-1)}{(2n^2+1)} \qquad \ldots\ldots(7)$$

The original Buckingham equation (4) proved satisfactory

for the data of West and Edwards[230] and Hornig and Hielbert[231] which were specifically for diatomic molecules. The simplified equations, (5), (6), and (7) have this inherent disadvantage when considering polyatomic systems, and again they do not account for specific interactions. This has since been highlighted by the work of Caldow and Thompson[232] and Horak and Moravec.[233,234]

Horak and Moravec concluded, from work on phenols[233] and acid dimers,[234] that the Buckingham equation could only be used to cover molecules which did not form strong complexes in polar solvents, for example, carbonyl solutes with very low basicity of the carbonyl grouping, and is generally less satisfactory for polar solutes.

Caldow and Thompson[232] in a study of the solvent shifts of N,N-dimethyl acetamide, N-acetyl pyrrolidine, acetone and hydrogen cyanide derived constants to fit the data. They showed that the Buckingham equations alone would give poor agreement with experimental data, but that this could be improved by including a term to allow for solute-solvent interactions. The inductive power σ^* of the residue R in a solvent RH was considered as being proportional to the interaction of the solvent with a carbonyl group and as a result they included a term $C_4\sigma^*$ on the right hand side of the Buckingham equation.

The relative importance of the four terms in the Buckingham equation, as indicated by the results of Caldow

and Thompson[232] is as follows:-

1) The constant term C_1. This was always the largest term, and, in the case of N,N-dimethyl acetamide, N-acetyl pyrrolidine and acetone, this term constituted some 70 to 90% of the shift observed in cyclohexane solution. The pattern for the νCH mode of hydrogen cyanide appears anomalous in comparison with the other solutes, the value of C_1 being larger than the shift observed in nonpolar solvents and the sign of the $C_4\sigma^*$ term is negative to overcome this effect, but the solute dipole is of opposite polarity. The large value of the constant term suggests that part of the effect observed may be the same regardless of the solvent. This could be associated with the shift observed with the change in state and for this reason, rather than study the shifts relative to the vapour phase value of the solute, the shift investigated later in this work will be relative to the value in a nonpolar solvent. The highest wavenumber position in any of the nonpolar solvents will be chosen as a standard in order that the observed shifts will all be in one direction.

2) The interaction term, $C_4\sigma^*$, shows the most marked variation of all four terms, and hence is mainly responsible for the agreement of the calculated results with the experimental values. This once again points to the weakness of all the preceeding theories, including the original Buckingham equation, in that interaction effects were not considered. These would appear to be equal or greater in magnitude to

bulk solvent effects for the solvents and solutes studied.

3) The term $C_2(\varepsilon-1)/(2\varepsilon+1)$ is generally much larger than the term $C_3(n^2-1)/(2n^2-1)$ and the ratio of these terms is fairly constant. The highest value obtained for the C_3 term in the solvents and solutes studied was $3.3cm^{-1}$, this being in a total shift of $24cm^{-1}$, while for N-acetyl pyrrolidine and hydrogen cyanide all the values lay in the range 0 to $2cm^{-1}$. If the findings of Josien and Fuson[222] are reconsidered where the function $(n^2-1)/(2n^2+1)$ was found to be equally as good as the function $(\varepsilon-1)/(2\varepsilon+1)$ for a KBM plot, it would be reasonable to approximate the modified Buckingham equation to the form:-

$$\frac{\Delta\nu}{\nu} = K_1 + K_2\sigma^* + K_3\frac{(\varepsilon-1)}{(2\varepsilon+1)}$$

In this form the calculation of the constants should be simplified and the error introduced by the removal of the refractive index term should be largely overcome by an increase in the value of K_3 relative to C_2.

The form of the equation is now basically:-

$$\frac{\Delta\nu}{\nu} = \text{constant} + f(\text{bulk solvent properties}) + f(\text{solvent-solute interaction effects})$$

In this form the equation appears to define adequately the factors which induce a solvent shift. The problem now lies in deciding:-

1) Whether the modified Buckingham equation is based on the relevent bulk solvent properties;

2) Whether the Taft factor is an adequate method of

describing intermolecular effects;

3) Whether the constants bear any theoretical relationship to the solute under investigation.

If suppositions (1) and (2) above hold, and the Buckingham equation as modified by Caldow and Thompson describes accurately the factors causing a solvent shift, the equation still suffers the disadvantage of having four constants, all of which have to be empirically derived.

Another approach to the presentation of solvent shift data is designated the BHW (Bellamy, Hallam and Williams) plot. Bellamy et al[235] arrived at this approach partially as a result of the unsatisfactory nature of the KBM approach as shown by its use by earlier workers.[117,220,236] In this type of approach the relative frequency shifts for two solutes in a variety of solvents were plotted directly against each other. It is suggested that, if the shift relied solely on some bulk property of the solvent, such as the dielectric permittivity, a simple linear relationship would hold and a slope of 45^{o} would be obtained. If the properties of the solute are involved, the slope would differ from 45^{o} and if solvent-solute interactions are important and different in the two cases, a marked departure from linearity would be expected.

As the charge on the free end of the solute dipole being examined is of great importance in determining the order of associations between solvent and solute, it is necessary to plot against a grouping of similar dipole. For an XH shift

the νNH mode of pyrrole has generally been used as the standard, as extensive data is already available for this solute.

For X=O dipoles Bellamy and Williams[237] used data for the C=O stretching mode of acetophenone as the standard, and showed that νS=O and νP=O vibrations followed a similar pattern of behaviour to that observed for carbonyl shifts. The failure of lines to pass through the origin is explained[235] in that the factors which operate to produce a frequency shift on passing from one solvent to another will not necessarily be the same as those which determine the effect of a change of phase and any marked differences between two solutes in this latter respect will lead to a sideways displacement of the resulting line. This would again appear to suggest that the measurement of shifts relative to a standard nonpolar solvent would offer a direct comparison of solvent effects alone. Attempts to relate the slopes, or S values, obtained for BHW plots to bond polarity have failed except where a closely related series has been investigated; some correlation with the pK_a values of solutes has been noted,[235] some variance being expected as the pK_a values are measured in water.

The plots obtained for νXH vibrations,[235] generally show little spread from the best line, and generally there is no discontinuity, but the slope is seldom 45°. The continuity of the line suggests that there is a regular change in the interacting powers of solvents and to quote Bellamy et al[235] "that the solvent effects are purely local in character, and

that the overall dielectric constant of the medium plays little or no part in determining the size of the frequency shifts in solution".

Le Fevre[239] calculated the wavenumber position of a stretching mode in solution, ν_{xy}, from the empirically derived equation:-

$$\nu_{xy} = \left(\frac{9273}{r^2_{xy}}\right)\left(\frac{b^s_L}{m}\right)^{1/3} - 254$$

where m is the reduced mass, b^s_L is the longitudinal polarizability of xy, and r is the xy bond distance.

Armstrong et al[240] had previously shown that the effect of a change of state on the apparent molecular polarizability can be predicted from an equation of the type:-

$$\frac{b^s_L}{b^v_L} = \left\{\frac{(n_1^2-1)}{(n_1^2+2)} \times 0.333\right\} - k_1 \quad \ldots\ldots (8)$$

where the polarizabilities b^s_L and b^v_L apply to the molecule in solution and in the vapour phase, k_1 is an anisotropy factor for the molecule and n_1 is the refractive index of the solvent. Modifications of equation (8) are also included where $(n^2-1)/(n^2+2)$ is replaced by $(\varepsilon-1)/(\varepsilon+2)$ and $(\varepsilon-1)/(2\varepsilon+1)$.

The study represents a radical approach to the problem of solvent shifts but the results are generally less impressive, as although the calculated shifts generally parallel the

observed values, the scaling varies greatly with the value of r chosen. The authors accept a correlation involving $(\varepsilon-1)/(2\varepsilon+1)$ as being the best fit, as the algebraic sum of the differences between observed and calculated wavenumber positions is the lowest in this case. Statistically it is the sum of the squares of these differences which is significant.

Cunliffe-Jones[238] has discussed the significance of long range and short range effects with regard to four nonpolar solutes in what is principally a qualitative approach. This approach is based on Coulson's assertion[241] that the fluctuating electrostatic field of a solute molecule will be greatly screened by the first layers of electronic charge it meets. If this is accepted one would expect the field of the solute molecule to be damped by the most polarizable parts of neighbouring solvent atoms and as a result long range dielectric effects would be of minor importance.

Cunliffe-Jones studied the four compounds, carbon tetrachloride, carbon tetrabromide, carbon dioxide, and carbon disulphide, which were described as nonpolar solutes, for which strong specific interactions were not expected. It should be observed that solutes such as carbon tetrachloride are known to form interactions, as instanced by the shifts obtained when using carbon tetrachloride as a solvent in solvent effect studies. It is also postulated[238] that if long range forces predominated a uniform increase would be observed in the shift with a function of the solvent refractive index, and that there

would be no radical differences in the behaviour of nonpolar solutes of differing geometry. If, however, the shifts arise mainly from short range interactions some differences might be expected. These interactions will probably include coulombic, inductive and dispersive forces. Coulombic forces result from the attraction between unlike charges or repulsion between like charges as given by Coulomb's Law.

Inductive forces result from the attraction of a charge to an opposite charge induced in another molecule. Positive nuclei and negative electrons undergo oscillations with respect to each other and as a result of the displacement of positive and negative charges, every molecule behaves as an oscillating dipole.

Inductive and dispersive contributions to the shift will increase with solvent atom polarizability. Cunliffe-Jones felt that in view of the anisotropy of polarizability of most solvents, the behaviour should be less regular than expected from the reaction field model. For linear solutes a large departure might be expected due to the alignment of solute and solvent polar bonds in temporary attractive complexes, and as such steric considerations will be important.

The results obtained were discussed with reference to the shape of the molecules. It is chosen at this stage to ignore the data presented for carbon tetrachloride in the paper, as the ν_{as}CCl band is in Fermi resonance, and rather to consider only the results for carbon tetrabromide. For

this solute the following arguments for favouring a short range interaction theory are presented:-

1) the inability of the KBM plot to adequately define the data.

2) the polar solvents such as acetonitrile and acetone give the smallest shifts to a lower wavenumber position, attributed to their low polarizability. This is substantiated by the observation that methyl sulphoxide, the most polar of the solvents studied, did not give the smallest shift, this solvent having a higher refractive index and presumably higher average peripheral polarizability than acetonitrile or acetone.

3) A large variation in band half width, without a change in the overall intensity was observed. This is explained by Cunliffe-Jones on the basis of the anisotropy of the solvent. The half band widths are smallest in hydrocarbon solutes where the immediate environment is reasonably uniform and largest in solvents such as acetonitrile and dioxan where there are large differences in the effects of the different groups, as suggested by the wavenumber position measurements. The separate contribution of short range interactions in different parts of the solvent molecule can be used to explain the doublet observed for the ν_{as}CBr mode in solution in an aliphatic ether. The higher band which is only slightly perturbed is assigned to

interactions involving the oxygen and the lower band, where the shift is comparable to that observed in aliphatic hydrocarbons, to alkyl interactions.

For the linear nonpolar solute, carbon disulphide, the shifts observed in acetone and acetonitrile are larger than those observed in aliphatic hydrocarbons and the shift is as great as for the highly polarizable s-tetrabromoethane. This is explained, if we accept short range interactions as being a function of the alignment of the solvent dipole with the solute molecule, or, in the case of benzene, with the π electron cloud. Anomalous behaviour for carbon dioxide may be due to the retention of rotational energy by this solute in solution.

Horrocks and Mann[242] developed the work of Benson and Drickamer[243] and Wiederkehr and Drickamer[244] whose approach led to an expression of the form:-

$$\nu_g - \nu = (8\pi^2 c^2 m_r \nu)^{-1} \left\{ \frac{3k_a}{k_H} \left[\frac{\partial E_{12}}{\partial r_1} \right] + \left[\frac{\partial^2 E_{12}}{\partial r_1^2} \right] \right\}$$

where ν and ν_g are frequencies in the condensed and gas phases, m_r is the reduced mass, k_H and k_a are harmonic and first anharmonic force constants, E_{12} is the interaction energy between the solute bond and its surroundings in solution and r_1 is the solute bond distance.

The interaction energy E_{12} can be split into component energies corresponding to the energies of dipolar orientation,

dispersion, dipole-induced dipole interactions and intermolecular repulsion. The authors qualitatively considered the first derivatives of the energy terms to explain the effect of solvents on the νN≡C mode of isonitriles. The theory can be criticised in that the authors could only base conclusions as to the relative importance and sign of the four energy terms on the basis of results obtained and it is difficult to visualise the extension to real systems on account of the complexity of the treatment and the number of unknowns which can only, at the present state of knowledge, allow qualitative use of the equation.

B. MULTIPLE CORRELATION

a) Relevance

The attempts at explaining solvent effects on infra-red spectra, that have been discussed in the previous section, have treated solvent effects from two basic standpoints. The first would appear to be the theoretical standpoint of workers such as Kirkwood, Bauer and Buckingham. The second group, which includes Cunliffe-Jones and Bellamy et al have sought evidence from a qualitative treatment, in certain cases, as for example the work of Horrocks and Mann,[242] because the complexity of the mathematical model allowed only a qualitative treatment. It was from amongst this latter group, namely from the work of Bellamy et al,[235] that impetus for the present study came.

The relative frequency plots, BHW plots of X=O dipoles using the C=O vibration of acetophenone and of the XH dipoles using the NH vibration of pyrrole, clearly demonstrated, from the linearity of the plots obtained, that although the effect of solvents on solute dipoles is not theoretically understood, each solvent has a consistent action on a particular type of dipole. Thus, for example, with the C=O vibrations one would expect the wavenumber positions to be higher in n-hexane than in carbon tetrachloride and the wavenumber position in carbon tetrachloride higher than in bromoform. The problem therefore appeared to lie not in the fact that workers were

trying to find a relationship where no relationship existed, but rather that the theories so far evolved were inadequate. It would appear that all the theories suffer from the necessity to define a model of the solvent-solute system. Taking the Onsager model as an example, the acceptance of a point dipole at the centre of a cavity when studying the shift of the $\nu C{=}O$ vibration of acetophenone, must introduce an inaccuracy due to the anisotropy of the molecule. The acceptance of a dielectric continuum would appear to rule out short range interactions.

In the present study the data obtained for the solvent shifts on a particular solute have been treated empirically. Solvent parameters such as dielectric permittivity, molar polarisation, and refractive index, used singly or in combination, may be related, using suitable constants, to the solvent shifts observed. The mathematical treatment is by a process known as multiple correlation, but before discussing this in detail the work of Allerhand and Schleyer will be mentioned.

These authors present a completely empirical approach to solvent effects.[245] It must be emphasised that this approach differs from the present work in that the authors were not attempting to correlate any existing solvent parameters, rather they attempted to establish an empirical scale of solvent polarity. As such an empirical equation was defined as follows:-

$$\frac{\nu^0 - \nu^s}{\nu^0} = aG$$

where ν^0 is the wavenumber position in the vapour, ν^s is the wavenumber position in solution, a is a function of the particular vibration in a particular solute and G is a function of the solvent only. Taking the value of G for dichloromethane as 100 to fix the scale, the authors calculated values of G for a number of solvents, which provided the best fit for data on the νC=O vibrations of dimethyl formamide and benzophenone and the νS=O vibration of dimethyl sulphoxide. By rearranging the equation in the form $\nu^s = \nu^0 - aG\nu^0$, it can be seen that by plotting ν^s against G, ν^0 can be obtained as the intercept at G=0, and a from the slope $(-a\nu^0)$. The value of a obtained is usually of the order 1.0 to 4.0×10^{-4}. The authors note that the value of a is an indication of the sensitivity of a particular dipole in the solute to solvent systems and hence may be related to the polarity of the vibration. They also present plots of the wavenumber position of a band in various solvents against the G values of the solvents which, as with the BHW plots, are sufficiently linear to suggest that solvent effects are similar in like systems. A preliminary study of the nature of solvent effects on various solutes[246], has confirmed this trend for carbonyl stretching vibrations.

The method of multiple correlation, the mathematical significance of which is described in Section 6B. (b), is a statistical method for deriving the relationship between

dependent and independent variables. In chemistry the technique has been used mainly in conjunction with kinetic data.

Koppel' and Palm[247] fitted data to an equation of the type, $\log k = a + b\,(\varepsilon-1)/(2\varepsilon+1)$, calculated the correlation coefficient and later[248] extended the data to two and three factor equations. Multiple correlation coefficients were calculated but the approach differs from the present study in that data are fitted to equations which have already been theoretically established.

Malinowski et al[249,250] applied the mathematical technique of factor analysis to N.M.R. proton shift data. By this method the shift is described in terms of linear factors which reproduce the original data. An attempt is then made to rotate the empirically derived factors mathematically into physically significant parameters. The present technique has been preferred as the relationship between the observed shift and the physical parameter involved is derived directly.

Chapman et al[251] deduced that for many solvents the reaction of diazodiphenylmethane with benzoic acid may be correlated with the dielectric permittivity, ε , of the solvent using the relationship, $\log k = 0.98 - \{2.60/(0.916+0.084\varepsilon)\}$ but the effect of specific interactions was often discernable.

The authors attempted to correlate the results for the rate constant in a series of alcohols as solvents, using L (the solubility of hydrogen chloride in the solvent), σ^* the Taft factor of R-O of the alcohol ROH, and E_s the steric

parameter of the same grouping. Two equations were deduced:-

$$\log k = 5.30 - 5.58L - 0.30E_s$$

$$\log k = 0.36 + 2.9\sigma^* - 0.03E_s$$

The multiple correlation coefficients were 0.976 and 0.998 respectively. The results, however, are less impressive in that the correlations apply to six solvents only, all of these being alcohols, data for benzyl alcohol and methyl propan-1-ol being excluded, as these would have introduced a marked decrease in the multiple correlation coefficient. This work and later work by the same authors,[252] suffer from the narrow range of solvents and solvent parameters investigated. Good correlation would be expected if the solvents were members of a homologous series, and the number of solvents treated would appear to be too small for any conclusion to be drawn.

The most comprehensive study of the use of multiple correlation,[253] has appeared since the present work was initiated. These authors have attempted to correlate ultra-violet, N.M.R. and infra-red spectra data, and kinetic data. The correlations use different statistical parameters to the present work as criteria for data assessment. The physical parameters correlated include several derived from ultra-violet data, for example the E_T value. With infra-red and N.M.R. data only moderate or poor agreement was obtained. This is undoubtedly due to the exclusion of such parameters as the KBM function

and Taft factor which have already been shown to be of significance when assessing infra-red solvent shifts.

From the statistical arguments given in Section 6B. (b) it was considered necessary to correlate as much data as possible for a particular vibration, in various solutes and solvent systems. In this way it was hoped to exclude chance correlations when assessing the significance of the correlations obtained. Five modes were considered when deciding which mode to use throughout the correlations, the νOH of alcohols and phenols, the νNH mode of amides, imides and pyrroles, the νC$\equiv$N mode of nitriles, the νC=O mode of ketones, aldehydes and esters, and the νC-X mode of halogenated hydrocarbons.

The large shifts observed for the νOH and νNH modes suggested solvent-solute interactions as a possible origin. Considering the νOH vibration of a solvent ROH, it was anticipated that interaction would occur between the hydroxyl hydrogen and an electronegative atom on the solvent.

If chloroform is taken as an example, the polarity of the chlorine atom will depend on the attached grouping, R, in this case CCl_2H, the effect of which could be explained by an inductive factor such as the Taft factor σ^*. Problems arise when solvents are considered in which interaction can occur with an oxygen atom e.g. dioxan or acetone. Here, in addition to considering the effect of the residue R, account must also be taken of the change of reaction centre from a halogen to oxygen.

On this basis it was decided to study either the $\nu C{\equiv}N$, $\nu C{=}O$ or $\nu C{-}X$ solute systems in which interaction would occur between the electronegative atom of the solute dipole and a hydrogen atom on the solvent. Whilst the $\nu C{\equiv}N$ system offered a vibration which would not be affected by the presence of solvent bands, the relatively small shifts observed in previous work,[221] and the difficulties of calibration in the region eventually led to rejection. Although the observed shifts for $\nu C{-}X$ dipoles[254] were generally larger, these vibrations fall in a region in which many of the readily available solvents absorb strongly.

On the basis of the relatively large shifts observed for the $\nu C{=}O$ band, the ease of calibration of the spectrum in the region, and the expansion of the wavenumber scale below $2{,}000cm^{-1}$ which allowed more accurate measurement, and the relatively small observed interference from overtone bands or solvent absorptions in the region, this was eventually chosen for correlation purposes.

b) Mathematical Meaning

The degree of relationship that exists between three or more variables is called multiple correlation. The fundamentals of multiple correlation are analogous to those involved in simple correlation, when only two variables are involved.

By plotting data for two variables, x against y, a

qualitative estimation of the relationship existing between the variables can be obtained visually. In the simplest case, where a straight line explains the relationship, the least square regression line of y on x is:-

$$y = a + bx$$

The term regression is used to describe the estimation of one variable (the dependent variable) from one or more related variables (the independent variables).

In fitting the best straight line to the data, this is taken to be that line which makes minimum the sum of squares of the deviations from the line of the measurements of y, the independent variable x being assumed to be free of error.

To test for the significance of an apparently linear relationship, the correlation coefficient r, as defined by equation (1) is used:-

$$r = \pm \sqrt{\frac{\text{explained variation}}{\text{total variation}}} = \pm \sqrt{\frac{\sum (y_{est} - \bar{y})^2}{\sum (y - \bar{y})^2}}$$

where $\bar{y}$ is the mean value of y, and y and y_{est} are respectively the observed and estimated values of y.

If the correlation coefficient has a value of ± 1, the data can be represented exactly by a straight line, +1 if the slope is positive and -1 if the slope is negative. If there is no relationship at all between the variables then r=0. Even when there is no genuine relationship between variables,

it is normal to obtain a non zero value for r, since accidents in sampling will generally lead to an apparent trend. Tables exist, however, from which it is possible to test if the observed value of r is significant. In these tables the value of r is read by entering into the tables, two degrees of freedom less than the number of pairs of observations (the two degrees of freedom being used in the fitting of the constants a and b). If the value of r exceeds that given in the table for the 5% level of significance then there is a 19:1 chance that the correlation is genuine which increases to 99:1 at the 1% level of significance.

For any line the standard deviation or residual variance σ_r of the scatter of points about y, measured in units parrallel to the y axis is given by equation (2):-

$$\sigma_r = \sqrt{1-r^2} = \sqrt{\frac{\sum(y-\bar{y})^2}{N-2}}$$

The residual variance is thus an estimate of the reliability of estimating y from a given value of x.

In practice it is often found that whilst two independent variables will not accurately correlate data alone, a marked improvement may be noticed when the variables are considered in combination. In these cases, it becomes necessary to isolate the effect of each independent variable from the effects of the other independent variables.

A regression line of the type:-

$$y = a + bx_1 + cx_2 + dx_3 \ldots\ldots\ldots + nx_m$$

may be indicated. Mathematically this equation means that, if all the independent variables, x_2 to x_n, are kept constant then the graph of y against x, will be a straight line, and similary a straight line would result from a plot of y against any of the other independent variables provided the remaining independent variables were kept constant. As such this is called a linear regression equation of y on x_1 to x_m.

As in the case of simple linear regression, it is necessary to define the goodness of fit. The quantity used is the coefficient of multiple correlation, or more correctly the coefficient of linear multiple correlation, R. This can be expanded in terms of the correlation coefficients r, relating y to x_1, x_2, . . . x_m; x_1 to x_2, x_3, . . . x_m and x_2 to x_3 . . . x_m etc.

The coefficient of multiple correlation takes a value between 0 and +1, the closer the value being to +1, the higher is the correlation. Although a multiple correlation coefficient of zero could be taken to indicate no linear relationship between variables, it is possible that a non-linear relationship may exist. A further correlation coefficient, the coefficient of partial correlation can also be mathematically defined to represent correlation between a dependent variable and one particular independent variable, when all the other variables are kept constant.

Mathematically, the calculation of the constants (regression coefficients), the standard deviations and multiple

correlation coefficients involves heavy arithmetic even for two or three independent variable cases,[255,256] but statistically this is the only sound way of assessing their several effects.

Recently the extension of multiple correlation treatments to a large number of dependent variables has been facilitated by the I.C.L. 1900 Series Statistical Analysis system (mark 2) in the form of the #XDS3 package. With this program it is possible to set out the necessary matrices for the calculation of the data by defining the size of the matrices, and the facilities for data presentation and print out.

A typical program, data excluded is given schematically in Appendix 3 (the actual field positions of the symbols is critical, and is rigidly defined in the manual). The cards JOB XDS3, 51022, J. C. HUGHES to the first * * * * * card, and the second * * * * * card, are to facilitate the processing of the program under the GEORGE system operable within the college.

The data cards are interposed before the END OF DATA card. In the format followed, the value for the observed shift (the dependent variable), is followed by the data for the solvent parameters (independent variables) in the order prescribed by the COL NAMES control block, continuing onto a second card, until all the independent variables pertinent to that solvent have been presented, and the operation repeated for all the solvents used in the study.

A TRANSFORMATIONS control block can be included immediately following the END OF DATA card. This allows mathematical manipulation of the independent variables, before the observation matrix is solved. This provision is explained more fully in section 6.C., study B.

In addition to the statistical parameters already discussed, such as the multiple correlation coefficient, the program in its print out facility provides data on other parameters as yet unmentioned. Of these factors, the T-statistic is probably the most important. The T-statistic, or 'Students' T-statistic, is an important parameter for evaluating the validity of a regression line. Mathematically it is calculated from the partial regression coefficient R, by the ratio:-

$$\text{T-statistic} = \frac{\text{regression coefficient}}{\text{standard deviation}} = \frac{R}{\sigma_r}$$

The variation in the regression coefficient necessary to explain 95% of the total shift is given by twice the standard deviation. Thus the value of the T-statistic increases with the correlating ability of the independent variable. Statistically a value of 3.0 is often quoted as being significant, this indicating that a 30% variation in the value of the independent variable parameter will account for 95% of the measured variation, whilst a value of 10.0 infers that only a 10% variation would be needed to account for 95% of the measured variation.

The error sum of squares, E.S.S., as presented in the

output from the program represents the quantity $\Sigma(y-y_{est})^2$ where y and y_{est} are the observed and estimated values of the shift respectively and in this case, the smaller the sum, the better the correlation.

The final print out under the RESIDUALS control block, (RESI), gives a list of the y values, the corresponding value of y_{est}, in addition to other statistical quantities which were not relevant to the present study.

The program could be used to correlate regression equations based on any number of parameters chosen from the group of independent variables. In the present work, this facility was limited to cover sets based on one to four independent variables, as it was found that, even in cases where three or four parameters were included, the T-statistic values were often below 3.0 and hence these correlations were unsatisfactory.

At this stage it has been felt necessary to mention one or two mathematical inexactnesses in the treatment and also some notes of caution to be considered when analyzing the results.

The mathematical inexactness results directly from the setting up of the regression equation. The equation chosen was:-

$$y = a + bx_1 + cx_2 + dx_3$$

The statistical treatment of the data to obtain the regression equation by the least squares method assumes that

the values of x_1 to x_n are free from error. This is not so in the present case as the need to extend the correlation to as many solvents as possible has necessitated the estimation of certain of the parameters for a particular solvent.

The solvent shifts treated in this study refer to the shift from the highest wavenumber position in solution, generally from n-hexane, n-heptane or n-pentane. This choice accepts that there is a constant shift from the vapour phase to the condensed phase, irrespective of the solvent involved. Transforming this idea into mathematical terms, the constant in the regression equation becomes zero. Thus the one factor equations referred to in sections 6.C. and 6.D. are strictly two factor equations, and thus when considering the significance of the correlation, one extra degree of freedom must be removed from the number of pairs of observations made, when entering the table.

The notes of caution refer to the actual relationships deduced. From a spectroscopic standpoint, it is known that the data for the shift y is probably accurate to $\pm 1 cm^{-1}$, and where small shifts are involved this becomes significant. There are three extremes which one could expect to encounter in the regression equations predicted in the present work:-

a) Random choice of parameters.

b) Consistent choice of particular parameters for all the equations involving the $\nu C{=}O$ vibration.

c) The favouring of particular regression equations for

particular types of carbonyl environment.

The first would occur if all the independent variables were equally as good or as bad in their correlating ability. The second could be expected to occur if the effect of solvents on the $\nu C{=}O$ mode was independent of the molecular environment of the carbonyl grouping. The third possibility may occur if, for example, the basicity of the carbonyl group is an important factor.

If either of the latter two possibilities is found, the study will be likely to produce useful results. The problem now lies with the possibility of chance correlations occuring. As will be shown later, the possibility is least likely with the one factor equations, but increases with the number of parameters correlated. To attempt to minimise the possibility of spurious correlations, the later study, Section 6.D., based on data measured by the author was designed to cover as large a number of solvents as possible, and additionally several solutes from a homologous series, for example, the ketones were included. In this way any genuinely useful correlation might be expected to be statistically favorable in the majority of cases.

The second note of caution must be associated with the significance of the relationship obtained. It is very easy to obtain spurious relationships which are statistically sound. For example one could relate the increase in crime to the annual increase in the consumption of Cornflakes to give

an approximately linear plot. In this case each of the variables is related to a particular independent variable, namely population.

Thus in the present study any relationship obtained may, or may not be of theoretical importance, and having obtained a relationship, the implications of the relationship will be considered, especially where certain of the independent variables are interrelated for example, the dipole moment to the dielectric permittivity or the KBM function to the refractive index.

In the following sections, equations are computed which relate wavenumber shifts to various solvent parameters. The units of the 'constants' in these equations are such as to preserve their dimensional exactness.

C. FEASIBILITY STUDY

To test the feasibility and usefulness of a multiple correlation approach to the data on solvent effects in the infrared, it was decided to use data already available in the literature as the basis of a preliminary study.

Whilst there were many papers available with data on solvent effects, few authors included sufficient solvents, in the opinion of the author, to allow a useful correlation study to be performed. For the program, study A, thirteen solutes were investigated, for which data for fifteen or more solvents were available.

The choice of solvent parameters was limited to nine physical properties for which data could be obtained for the majority of solvents. Although the program had facilities for the inclusion of missing values in the data, it was preferred to estimate those values which had not been measured for a particular solvent. The actual values of the solvent parameters used in the program are given in Appendix 4. As may be seen there are comparitively few cases in which extrapolation was necessary, and generally these were either on solvents which were seldom studied or for solvent parameters which showed low T-statistic values in the correlations.

Whilst the choice of solvent parameters for study A was limited to some extent by the availability of data, the theoretical basis on which the parameter was chosen will be discussed.

Parameters used in Study A

Dielectric Permittivity

The dielectric permittivity of a material is defined as the ratio of the electrical capacity of a condenser of which the substance in question forms the dielectric to the capacity when a vacuum separates the plates and as such is a measure of the polarisability of the solvent. In a study of the solvent effects on the νC-halogen mode, Hallam and Ray[254] found a common pattern of shifts, the mechanism of which was described as being primarily a function of the dielectric permittivity.

Molar Polarisation P_M

The molar polarisation was defined by Mossotti and Clausius as:-

$$P_M = \frac{(\varepsilon-1)}{(\varepsilon+2)} \cdot \frac{M}{d}$$

where M and d are the molecular weight and density of the material respectively. In an electric field a molecule will be polarised, i.e. there will be a redistribution of the electrical charges. This is then followed by an orientating effect if the molecule is polar. Le Fèvre[239] has suggested that the band position of a solute dipole may be related to the molecular polarisability of the solute, the effect of the polarisability of the solvent does not appear to have been previously investigated.

Molar Volume M_v

As discussed in section 6.A, the size of the solvent cavity may be expected to affect the field at the solute as there is a rapid decrease in electric intensity with distance. The molar volume may be related to the size of the cavity.

Dipole Moment μ

The dipole moment represents the distribution of electrical charge within a molecule. As the dipole moment represents the electrical anisotropy of a polar molecule, a relationship between the shift observed in solution and the dipole moment of the solvent may result if there is preferred orientation. As the dipole moment may be calculated from dielectric permittivity measurements a comparison of the correlating powers of the two terms was also sought. Lutskii and Vragova[257] have used an equation of the form $\Delta\nu = C_1 + C_2\mu_2$, where C_1 and C_2 are constants, to represent solvent shifts.

Refractive Index n

The refractive index of a medium is the ratio of the sines of the angles of incidence and refraction of light falling on the medium and is generally based on the sodium D line. It is possible that the refractive index will be related to the orientation of solvent molecules within the medium. As the refractive index depends on the wavelength of the incident light, the values used in the present study should

be determined in the infra-red region. It is well established [223] that a system will absorb energy from the radiating wave in the region of a vibrational transition. A region of anomalous dispersion occurs and the refractive index in the vicinity of the absorption band may vary. As there are few solvents for which the refractive index has been determined throughout the infra-red region, the values of the refractive indices (Appendix 4), are the normal values based on the sodium D line. As the basis of the choice of a solvent for solvent effect studies is that there is no appreciable absorption by the solvent in the region of the absorption being studied, the error which is introduced by using visible data is likely to be relatively small.

Josien et al[222,258] suggested that a KBM type plot was in better agreement with experimental data if the square of the refractive index was used in place of the dielectric permittivity in the $(\varepsilon-1)/(2\varepsilon+1)$ relationship. Later work by Horak et al[233] on phenols apparently supported this hypothesis as the constant in the refractive index term of the Buckingham equation was much larger than the corresponding dielectric term.

Standard Entropy S^{0}_{298}

The second law of thermodynamics takes many forms. In one of these forms, which states that all natural or spontaneous processes, that is processes which occur without

external aid, are thermodynamically irreversible in character, the need for a thermodynamic function to serve as a criteria of spontaneity is established.

The most important spontaneity function is the entropy, S, of the system. The relevance of the standard entropy to the present work is not from the use of entropy as a criteria of spontaneity but from its use to define the randomness of a system.

As spontaneous processes lead to increasing disorder, there will be a relationship between the entropy and the order of a system. Consideration of this phenomenon led Boltzmann to put forward the equation:-

$$S = k \ln W + \text{constant} \quad \ldots\ldots\ldots (1)$$

This relates the entropy of a system to its thermodynamic probability, W, where k is the Boltzmann constant, and where the thermodynamic probability of a system was defined as the ratio of the probability of the actual state to that in which there is complete order, for the energy and volume. Planck suggested that the constant in equation (1) should be zero. The equation is then consistent with the third law of thermodynamics, which states that the entropy of a perfect crystalline solid of a pure substance is zero at the absolute zero of temperature.

The standard entropy, S^{o}_{298}, the entropy of the solvent measured at 298K, has been used in the present study as it was hoped that this would place all the solvents on a similar

scale.

As a correlating factor it is suggested that the entropy will describe the order of the solvent about the solute. It is possible that solvent-solute interactions of the type normally associated with hydrogen bonding will confer order on the orientation of the solvent molecules and in this case entropy may be subject to correlation.

KBM Function

The use of the KBM function as a parameter for correlating solvent effects has been previously discussed in Section 6.A, The model used has often been criticised but the volume of papers which have investigated this factor, make its inclusion necessary in any comprehensive study of solvent parameters. The function itself has been used in two forms $(\varepsilon-1)/(2\varepsilon+1)$ and $(n^2-1)/(2n^2+1)$. In this study more interest was expressed in comparing this factor with other factors, and not with comparison of the two forms of the KBM function, a choice had to be made between the use of the refractive index or the dielectric permittivity. Although there is some evidence to suggest that the KBM function as calculated from the square of the refractive index may give better correlation, the lack of infra-red determined refractive indices led to the calculation of the KBM function from the dielectric permittivity.

δ Value

The solubility of a polymer in the solvent is of fundamental importance in the application and durability of polymer coatings. The unreliability of polarity and simple "like dissolves like" rules for the choice of suitable solvents, with special regard to the paint industry, led Burrell[259] to investigate a further solubility parameter, the δ value. This parameter may be conveniently calculated from:-

$$\delta = \left(\frac{\Delta E}{V}\right)^{\frac{1}{2}} = \left(\frac{\Delta H - RT}{V}\right)^{\frac{1}{2}}$$

where ΔH is the latent heat of vaporization of the solvent at temperature T (degrees Kelvin), R is the gas constant and V is the molar volume.

The original derivation belongs to Hildebrand[260] who assumed that the heat of mixing was dependent on $(\delta_1 - \delta_2)^2$, where δ_1 and δ_2 refer to the δ values of solvent and solute respectively. When the value of δ_1 approaches δ_2, the heat of mixing approaches zero and solution is assured by the increase of entropy in the system. Burrell[259] gives a table of molar attraction constants, G, which allow calculation of δ values for solvents for which ΔH values were unavailable from the equation $\delta = d\Sigma G/M$, where d is the density of solvent and M the molecular weight.

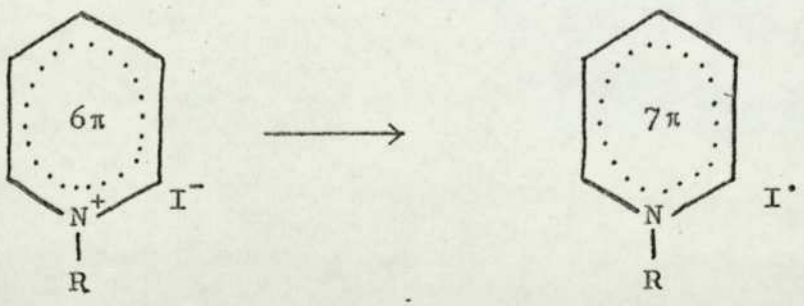
As the δ value involves both the latent heat of vaporization and molar volume of the solvent, it may express both cavity size and interaction effects.

$\underline{E_T}$ Value

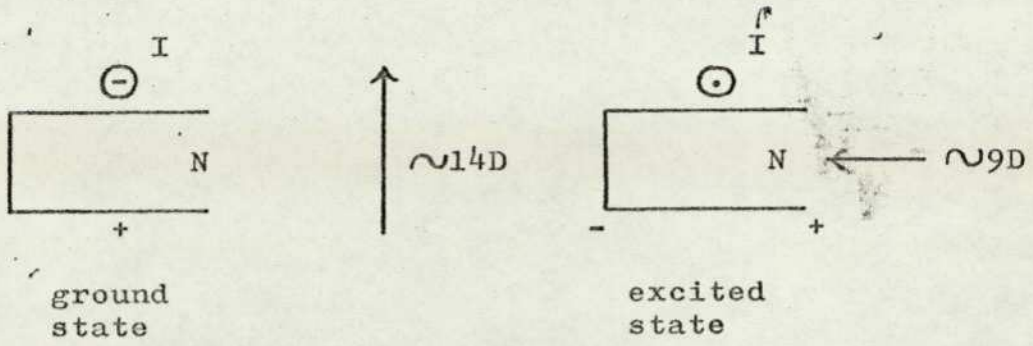
Recently a number of empirical solvent parameters have been derived from the changes that take place in the electronic spectra of various aromatic molecules in solution. These parameters include the Y values of Winstein and Grunwald,[261] the Ω values of Berson, Hamlet and Mueller,[262] the Z values of Kosower,[263] the X values of Gielen and Nasielski,[264] aand the S values of Brownstein.[265]

Whilst any of these parameters may have been chosen for correlation purposes in the present work, it was eventually decided to use the E_T values of Dimroth and Reichardt,[266-8] as these covered a greater range of solvents than any of the other parameters. The scale was based on the N-phenol betaines, where the displacement of the solvatochromic band was larger than for the earlier solutes investigated.

The theoretical importance of this group of parameters is more easily demonstrated for the 1-alkylpyridinium iodides. Here the charge transfer process responsible for the spectrum may be represented:-



It is believed that the ion pair ground state and the excited state are such that the molecular dipoles are perpendicular:-



In the ground state, highly polar solvent molecules will be orientated about the solute to give considerable stabilisation, but, since the time required for an electronic transition, is far too short for there to be reorganisation of the solvent molecules around the excited state, the excited state will have an inappropriately high energy. Diagrammatically this effect can be represented as follows (Fig. 36):-

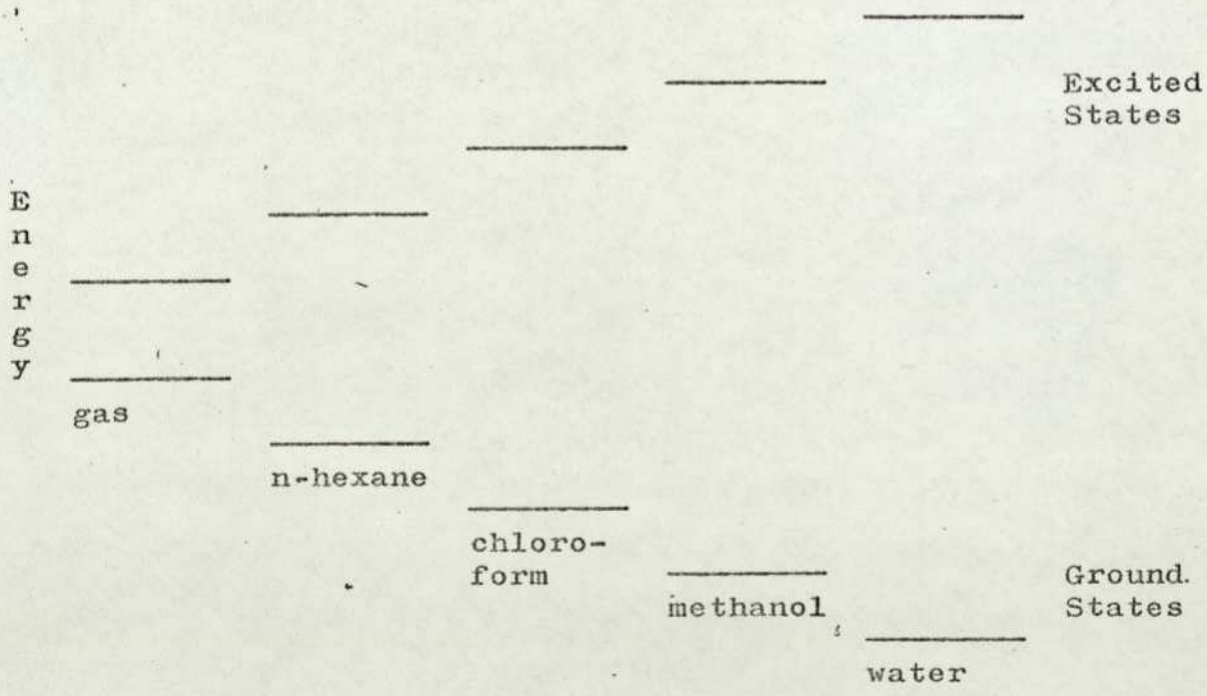


Fig. 36

Thus the E_T value will be a measure of the effect of solvent orientation on infra-red solute bands.

Appraisal of the Results of Study A

For this study equations involving one to four variables were deduced for each solute. The predicted equations involving one variable only are given in Table 73. The data for N,N-dimethyl formamide was treated twice because the original paper found a doublet in the $\nu C=O$ region of this solute in methanol and ethanol, and it was hoped to determine if one of the peaks was infact an overtone. On the basis of the results of study A, an Onsager approach would favour the assignment of the $\nu C=O$ band to the band shifted $39cm^{-1}$ by methanol from the peak position in n-hexane.

It is clear from the data in Table 73, that the KBM function is the best single parameter, of the parameters studied, for correlating solvent shifts, giving in eleven of the thirteen solutes, the best fit to the data. Taking the results for acetone as a typical example, the relatively high T-statistic and multiple correlation values must not be considered in isolation. The multiple correlation coefficient of 0.931 represents an overall error of approximately 7%. The actual error may be quite large in certain solvents, bromoform, hexane or ethyl ether being examples whilst for others, carbon disulphide, benzene and nitromethane, virtually 100%

agreement between observed and estimated shifts was obtained. Additionally the measurement accuracy in any particular determination is unlikely to be better than $\pm 1 cm^{-1}$. The program considers any variation from the measured value as an error and it is possible that inaccuracy in only one measurement may be sufficient to cause the program to accept a different parameter or set of parameters for correlation.

The plot of the observed data against the calculated data for acetone using the predicted 22.32KBM relationship is given in Fig. 37 and shows the generally poor linearity of the KBM type plot. In table 73, only two correlations, those for ethylene carbonate and N-acetyl tetrazole, were predicted, in which the KBM function was rejected as the most satisfactory single parameter. With ethylene carbonate the choice of the E_T parameter may indicate that the orientation of the solvent molecules round the large carbonate grouping is the important factor. Although high T-statistic and multiple correlation coefficients were obtained, this was the only system for which less than seventeen solvents were correlated.

Bellamy and Williams[237] studied a series of N-acetyl heterocyclics. In N-acetyl pyrrole resonance occurs, increasing the polarity of the carbonyl group:-

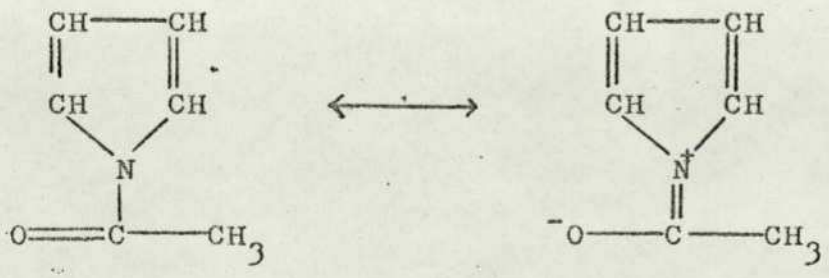


Table 73

The predicted one factor equations for the multiple regression analysis under study A.

Solute	N	Relationship	T	E.S.S.	M.C.
N,N-dimethyl formamide[af]	20	46.23KBM	12.96	617	0.948
N-acetyl pyrrole[d]	18	27.83KBM	11.15	222	0.938
Cyclohexanone[f]	20	36.72KBM	11.72	476	0.937
Acetone[cef]	21	22.32KBM	11.36	211	0.931
Benzophenone[f]	18	23.03KBM	10.49	172	0.931
N-acetyl iminazole	18	13.73KBM	10.38	62	0.929
N,N-dimethyl formamide[bf]	20	50.53KBM	10.69	1083	0.926
N-acetyl indole[d]	18	26.92KBM	9.92	262	0.923
N-acetyl pyrrolidine[d]	18	65.92KBM	9.79	1616	0.922
Acetophenone[f]	17	24.96KBM	9.47	207	0.921
Methyl acetate[f]	18	29.58KBM	8.53	428	0.900
Acetyl chloride[f]	17	13.15KBM	6.01	145	0.833
Ethylene carbonate[f]	15	$0.915E_T$	13.87	1281	0.966
N-acetyl tetrazole[d]	18	0.603n	2.47	39	0.514

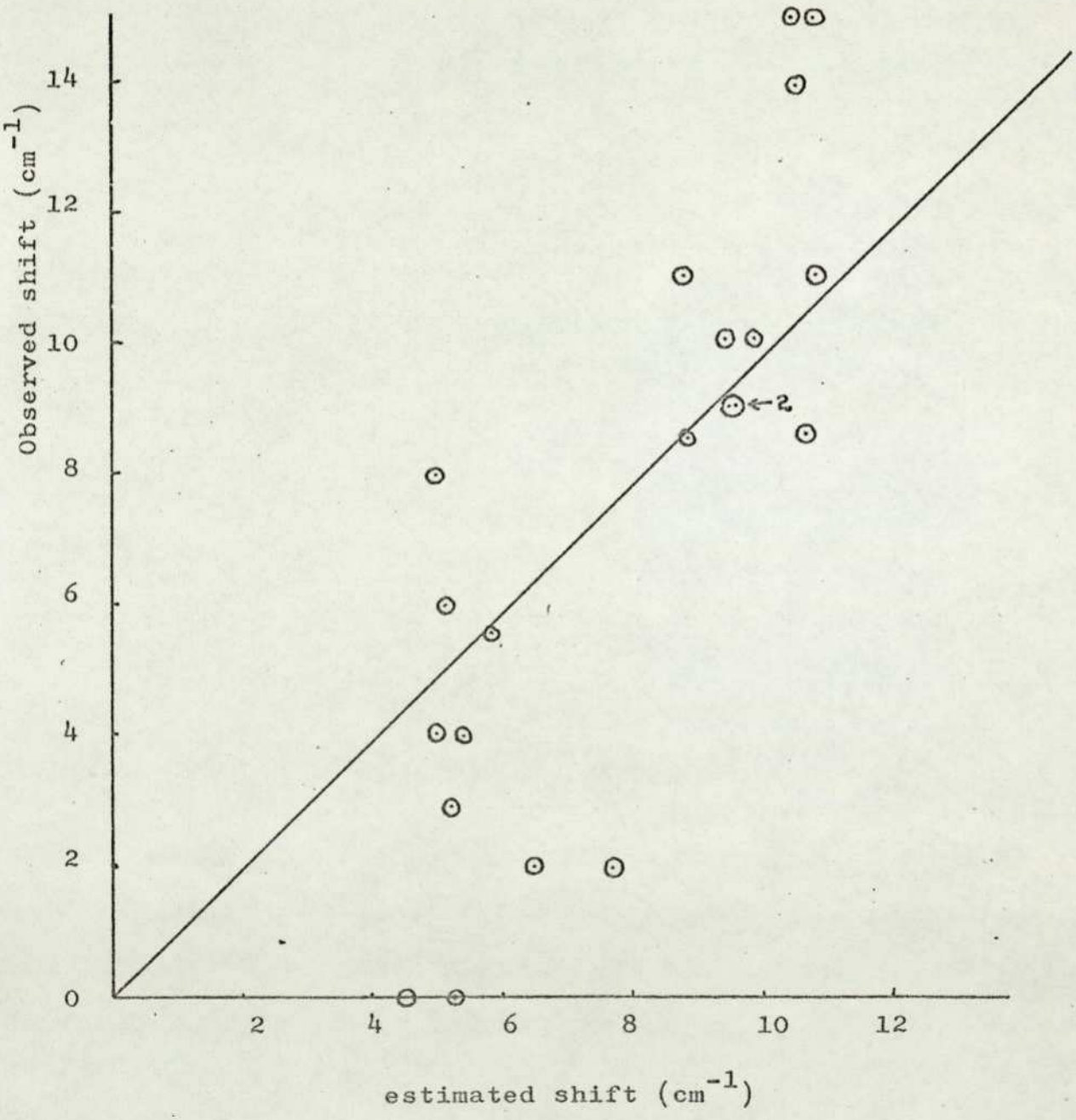
The data for N,N-dimethyl formamide was treated twice taking the solvent shift respectively from n-hexane as $39cm^{-1}$ in methanol and $39cm^{-1}$ in ethanol (a) and $27cm^{-1}$ in methanol and $28cm^{-1}$ in ethanol (b)

Solute data extracted from (c) Ref. 226, (d) Ref. 237 (e) Ref. 269, (f) Ref. 270.

M.C. Multiple correlation N Number of solvents T T-statistic E.S.S. Error sum of squares.

Fig. 37

A plot of the observed solvent shifts for acetone against the estimated shifts using the 22.32KBM relationship predicted in Study A.



As the resonance in the ring is increased by the introduction of succesive nitrogen atoms, the carbonyl group resonance decreases and with it the polarity of the carbonyl group. In N-acetyl tetrazole shifts to high wavenumber positions relative to n-hexane were observed which could be attributed to preferred association of the carbonyl group with the heterocyclic ring. As such the low multiple correlation coefficient and T-statistic values for this system were not unexpected.

The predicted, two parameter equations, Table 74, again show a remarkable consistency, this time in the choice of a relationship involving the E_T and molar volume (M_V) parameters, in eleven of the thirteen solutes studied. At first it may appear remarkable that the KBM function, which had high T-statistic values in the majority of the one parameter correlations, has been chosen in one case only for correlation. The choice of the E_T value would appear to suggest that the orientation of the solvent molecules may be an important factor and the negative contribution from the molar volume term would suggest that the distance of approach is also important. In this prelimary study the usefulness of this relationship will not be further discussed, rather it is felt necessary to point out that the T-statistic value for the molar volume term is relatively low, four of the twelve correlations presented involving T-statistic values below the value of three accepted in Section 6.B (b). Again using the data for acetone, Table 75, as an example, the improved agreement

between the estimated and observed values makes the two factor equation more acceptable, and the plot of the results, Fig. 38, shows a closer approach to linearity than the plot, Fig. 37, based on the KBM approach.

The extensions of the program to produce three and four parameter equations will only be briefly mentioned, as the inclusion of the extra parameters produced equations which showed little statistical improvement over the two parameter equations. The choice of the three parameters appeared to be more random than for either the one or two parameter cases and the T-statistic values of at least one of the chosen parameters was generally less than 3.0.

The data thus obtained from study A was sufficient to suggest that useful correlations could be drawn from the parameters already available.

Study B

This study was designed to investigate the TRANSFORMATION facility included in the XDS3 program. In the previous study a unit power relationship has been assumed for all the parameters investigated. There are many simple mathematical relationships, however, which are based on squared terms. Additionally the solvent effect observed may not be directly related to parameters x and y, but a relationship with xy or x/y may exist.

Before embarking on this second phase an appraisal of

Table 74

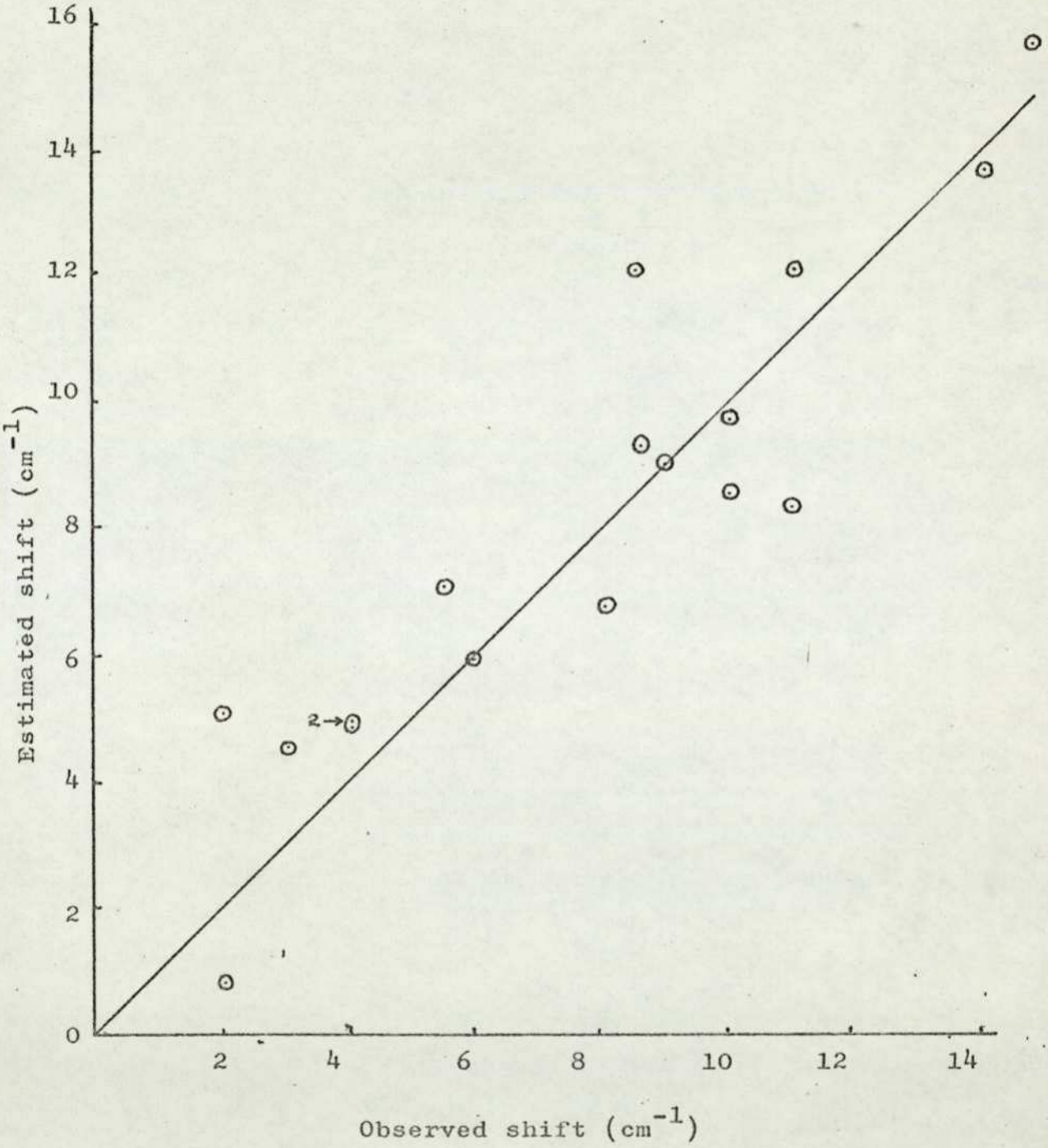
The predicted two factor equations for the multiple regression analysis, Study A

Solute	Relationship	T-statistic E_T	T-statistic M_V	E.S.S.	Mutiple correlation A	Mutiple correlation B
Ethylene carbonate	$1.25E_T - 0.152M_V$	8.00	2.31	909	0.976	0.966
N, N-dimethyl formamide[a]	$0.758E_T - 0.146M_V$	11.49	5.16	502	0.966	0.948
N,N-dimethyl formamide[b]	$0.633E_T - 0.105M_V$	10.76	4.17	401	0.966	0.926
Acetone	$0.326E_T - 0.584M_V$	10.03	4.24	130	0.958	0.931
N-acetyl pyrrole	$0.415E_T - 0.070M_V$	8.23	3.59	156	0.957	0.938
Cyclohexanone	$0.508E_T - 0.087M_V$	9.30	3.70	345	0.955	0.937
Acetophenone	$0.406E_T - 0.076M_V$	7.87	3.87	127	0.953	0.921
Benzophenone	$0.345E_T - 0.586M_V$	7.90	3.42	119	0.952	0.931
N-acetyl iminazole	$0.189E_T - 0.027M_V$	7.01	2.57	46	0.949	0.929
N-acetyl pyrrolidine	$1.041E_T - 0.194M_V$	7.81	3.69	1115	0.947	0.922
N-acetyl indole	$0.393E_T - 0.642M_V$	7.02	2.91	197	0.943	0.923
Methyl acetate	$0.454E_T - 0.080M_V$	6.45	2.88	312	0.928	0.900
Acetyl chloride	$6.15n - 0.051M_V$	4.33 (n)	2.36 (M_V)	113	0.873	0.833
N-acetyl tetrazole	$2.40n - 8.06KBM$	3.43 (n)	2.69 (KBM)	27	0.703	0.514

Data and superscripts as given in Table 73. The multiple correlation data refer to A, the two factor equations, and B, the one factor equations under study A.

Fig. 38

A plot of the observed solvent shifts for acetone against the estimated shifts using the $0.326E_T - 0.584M_V$ relationship predicted in Study A.



the results of study A was made from which it was decided to retain the E_T, molar volume, KBM function, refractive index and dielectric permittivity parameters for further correlation.

The TRANSFORMATIONS CONTROL block is interposed before the END OF DATA card. The transformations to be performed immediately follow this card, and the remaining cards which contain the matrix name, for example the POBS card, are now altered to the new matrix. Transformations performed were broadly of two types:-

1) If the original parameter on the data card is to be used, it must be transformed into itself. It is not sufficient to include the required variable in the list of independent variables on the card following the INDE control block. An example of this type is:-

KBMFUN = KBMFUN

2) True mathematical transformations. These can include any particular variable or combination of variables, as many times as required, for example the inclusion of the KBM function in the form given above does not preclude further mathematical variants.

The following transformations with their appended names were performed in study B, (the transformations are in the FORTRAN language and employ the six character name applied to the particular independent variable in the program).

$$\text{RADIUS} = (21\text{x}\text{MOLVOL}/88)^{0.3333}$$

KBMVOL = KBMFUN/MOLVOL

DILMOV = DILECT/MOLVOL

REFSQD = REFIND x REFIND

ETOVMV = EEETTT/MOLVOL

The first transformation, RADIUS, is the molecular radius as calculated from the molar volume of the solvent. In the two parameter equations derived in study A, the most common correlation linked the solvent shift with the E_T value and Molar volume, M_V of the solvent. If the solute molecule is approximately spherical it may be anticipated that a volume term may be important. If, instead, the effect of the solvent acts principally in one direction then a linear distance term, the molar radius, may provide better correlation.

Three parameters, the KBMVOL, DILMOV and ETOVMV, represent the mathematical division of the KBM function, the dielectric permittivity and the E_T values respectively, by the molar volume. Pullin,[226] attempted to correlate solvent effects with the KBM function divided by various molar volume and radii parameters. Improved correlation over the KBM function is claimed and this was tested statistically in the present study. The fifth parameter REFSQD, is the square of the refractive index. As discussed previously, the correlations observed in study A suffered from the exclusion of higher power terms. The transformation process represents a way of overcoming this problem. Obviously it is impracticable to study many higher power terms without any theoretical basis. In the present study, the author has limited the choice to the

square of the refractive index.

The predicted one parameter equations are given in Table 76. Again the KBM function is the most often correlated parameter, accounting for eight of the fourteen relationships predicted. The remaining six relationships involve the ETOVMV parameter (three), the REFSQD parameter (two), and the E_T parameter (one). In N-acetyl tetrazole, the use of the REFSQD parameter as a correlating agent was still insufficient to suggest any true statistical relationship (T statistic, 2.65; Multiple correlation coefficient, 0.541). In acetyl chloride the use of the REFSQD parameter appears of little significance. Acetyl chloride is a poor solute on account of its reactivity and the multiple correlation coefficient is only raised from 0.833 (KBM function, one factor equation Study A), to 0.837 in the present study.

The remaining three relationships involving the ETOVMV parameter are theoretically the most interesting. The multiple correlation coefficients for these solutes are in the range 0.93 to 0.95 and suggest that this combined parameter should be further investigated in the comprehensive study (Section 6.D). The inherent difficulties in the present empirical approach are demonstrated by the results for acetone. In study B, a relationship involving the ETOVMV parameter is prefered, but this preference is only based on an increase in the multiple correlation coefficient from 0.931 in study A to 0.932 in study B. Obviously this increase is not significant when the accuracy of the original data is considered and thus in many

cases there may be two parameters which would equally well correlate a particular set of data. In the present study, a particular relationship was only considered significant if it occurred in a large percentage of the cases studied. It is possible to find the best relationship between the solvent shift and a particular independent variable, for example the ETOVMV parameter, by reducing the number of independent variables to the one desired parameter. It was not, however, felt profitable to investigate the correlating ability of the ETOVMV parameter in this way as the relationship could be further explored (Section 6.D), and because the multiple correlation coefficients for the solutes studied did not exceed 0.950.

The results of the two factor analyses are given in Table 77. At a glance a correlation involving the E_T and molar radius parameters would appear to have replaced the E_T and molar volume relationship of study A. A closer examination of the data revealed that the improvement, as measured from the multiple correlation coefficient, is often minimal (acetone, 0.959 as against 0.958 and N-acetyl pyrrolidine 0.949 as against 0.947). However, there remains the possibility that the molar radius may correlate with the data better than the molar volume. For ethylene carbonate, the $37.51Rd-0.797M_V$ relationship is preferable (Error sum of squares, 882) to the $1.25E_T-0.152M_V$ relationship of study A (Error sum of squares, 909), although both have a multiple correlation coefficient of 0.976. This preference however,

Table 76

The predicted one parameter equations for the multiple regression analysis, study B.

Solute	Relationship	T statistic	E.S.S.	M.C.
N,N-dimethyl formamide[b]	46.23KBMFUN	12.96	617	0.948
N-acetyl pyrrole	27.83KBMFUN	11.15	222	0.938
Cyclohexanone	36.72KBMFUN	11.72	476	0.937
Benzophenone	23.03KBMFUN	10.49	172	0.931
N-acetyl iminazole	13.73KBMFUN	10.38	62	0.929
N-acetyl indole	26.92KBMFUN	9.92	262	0.923
N-acetyl pyrrolidine	65.92KBMFUN	9.79	1616	0.922
Methyl acetate	29.58KBMFUN	8.53	428	0.900
N,N-dimethyl formamide[a]	31.04ETOVMV	13.27	740	0.950
Acetone	13.76ETOVMV	11.50	207	0.932
Acetophenone	17.79ETOVMV	10.08	186	0.930
Acetyl chloride	2.067REFSQD	6.12	142	0.837
N-acetyl tetrazole	0.432REFSQD	2.65	38	0.541
Ethylene carbonate	$0.915E_T$	13.87	1281	0.966

References to the solute data, the number of solutes correlated and the meaning of the suffixes (a) and (b) and abbreviations are given in Table 73.

Table 77

The predicted two factor equations under the multiple regression analysis study B

Solute	Relationship	T-statistic		E.S.S.	M.C.
		E_T	R_d		
N,N-dimethyl formamide[a]	$1.050E_T - 8.87R_d$	10.45	6.14	402	0.973
N,N-dimethyl formamide[b]	$0.820E_T - 6.04R_d$	8.21	4.21	397	0.967
Acetone	$0.432E_T - 3.39R_d$	7.91	4.35	127	0.959
N-acetyl pyrrole	$0.581E_T - 4.56R_d$	6.47	3.77	149	0.959
Acetophenone	$0.604E_T - 5.13R_d$	6.52	4.21	116	0.957
Benzophenone	$0.478E_T - 3.72R_d$	5.96	3.45	118	0.953
N-acetyl pyrrolidine	$1.501E_T - 12.56R_d$	6.27	3.90	1058	0.949
N-acetyl indole	$0.544E_T - 4.14R_d$	5.34	3.02	192	0.945
		E_T	M_V		
Cyclohexanone	$0.508E_T - 0.087M_V$	9.30	3.70	345	0.955
Methyl acetate	$0.454E_T - 0.080M_V$	6.45	2.88	312	0.928
		R_d	M_V		
Ethylene carbonate	$37.51R_d - 0.797M_V$	8.15	5.63	882	0.976
		n^2	R_d		
Acetyl chloride	$7.05n^2 - 3.89R_d$	4.13	2.96	89	0.901
		n^2	KBM		
N-acetyl tetrazole	$1.64n^2 - 8.04KBM$	3.96	3.08	24	0.746

Data, superscripts and abbreviations are as given in Table 73.

does not preclude the use of an E_T , Molar volume relationship to describe the data.

The results for N-acetyl tetrazole still show the inability of the solvent parameters correlated to adequately express the effects in this system.

Study C

The results of the previous studies were sufficiently promising for the study to be extended (Section 6.D) to a wider range of solvents, however, before embarking on this study, the correlation with one further type of parameter was investigated. Caldow and Thompson[232] had previously shown that the Taft factor, σ^*, could be introduced into the Buckingham relationship to explain at least part of the observed variation. Correlation has also been noted between the wavenumber positions of carbonyl, amino, hydroxyl and nitrile stretching vibrations and various inductive factors,[271] the Taft factor providing the highest correlating ability of those studied. It was decided to investigate this parameter at this stage as there were fewer solvents for which the Taft values were available.

From the results of studies A and B, it was decided to include five parameters, the KBM function, the molar radius, the E_T value, the molar volume, and the E_T value/the molar radius for correlation together with the Taft factor, σ^*.

It is, however, realised that the exclusion of the other parameters used in studies A and B, does not necessarily exclude correlations involving these parameters and the Taft factor, but the poor correlating ability of the these parameters as instanced by the low T statistic values, suggests that they will largely be chance correlations. The results from the previous studies are now standards against which subsequent correlations can be judged. Before presenting these results, however, an appraisal of the various linear free energy relationship will be made.

Linear free energy relationships

These are empirical correlations relating the reactivities of organic compounds to the logarithms of rate or equilibrium constants. The Hammett equation[272] is concerned with the influence of meta or para substituents on the reactivity of aromatic compounds and takes the form:-

$$\log\frac{k}{k_0} = \sigma.p$$

where k and k_0 are the rate constants for the substituted and standard compounds respectively. Hammett chose the ionisation of benzoic acid in water at 298K, as a standard process for which p was defined as 1.00.

Later Taft[273] recognised the occurence of steric as well as polar effects in aliphatic systems and in ortho-substituted

aromatic systems. He proposed the following equation for evaluating the polar effect of a substituent, R, as manifested in the ester RCO_2R':

$$\sigma^* = \frac{\left\{\log(k/k_0)_B - \log(k/k_0)_A\right\}}{2.48}$$

where k_0 applied to the reactions of CH_3CO_2R' and B and A refered to basic and acid hydrolyses. The factor of 2.48 put the σ^* values on approximately the same scale as σ values.

Taft suggested that the term $\log(k/k_0)_B$ gave the sum of steric, polar, and resonance effects of R, while $\log(k/k_0)_A$ gave the sum of steric and resonance effects of R, and hence the difference gave the polar effect of R. A further equation $E_s = \log(k/k_0)_A$, gives a steric contribution, but for systems which are conjugated to CO_2R', E_s contains a resonance contribution and it is assumed that the steric effects are the same in acidic and basic reactions, whereas the transition states may differ in charge and shape. It was decided not to investigate this factor.

Taft[274] also suggested a quantitative separation of substituent effects into inductive and resonance contributions, and later Exner[275] gave a modified analysis of this type, based on the equations:-

$$\sigma_M = \sigma_I + \alpha\sigma_R$$

$$\sigma_p = \lambda\sigma_I + \sigma_R$$

In the present case, however, where interest was in the overall polar effect of the substituent, this further separation was not investigated. Exner, however, showed that $\sigma_I \simeq 0.45\sigma^*$ and this was useful if σ_I data only was available.

The present study was limited to X=O dipoles. Molecular interactions between the X=O group and the solvent will clearly involve a hydrogen atom on the solvent. Considering the solvent as RH, correlation was attempted with the Taft factor σ^* of the solvent residue R. The data presented in Appendix 4, required considerable mathematical manipulation to cover an extensive range of solvents. Newman[276] presented an extensive list of σ^* values. Two principles outlined by Newman were used in the calculation of further Taft factors. The additive nature of Taft factors could be applied together with the reduction principle, $\sigma^*_R = 2.5\sigma^*_{CH_2R}$, in the calculation of further data. The Taft factor for the bromoform, CBr_3, residue was estimated at 2.5 by comparison of the value of 1.0 for CH_2Br with the values of 1.05 and 2.65 for CH_2Cl and CCl_3 respectively. In cases where the use of data after Newman was insufficient, Taft factors were calculated from σ_I values using the relationship, $\sigma_I = 0.45\sigma^*$, from various sources.[277-281] The σ^* values for tetrachloroethylene, carbon tetrachloride and carbon disulphide were taken as zero, and correlations under study C were performed twice, including and excluding the values for these solvents. The Taft factors for anisole, benzonitrile, o-dichlorobenzene, nitrobenzene and

toluene are given in brackets in Appendix 4. In the preliminary study the values for toluene were calculated by considering the residue R as $CH_3C_6H_4$- and $C_6H_5CH_2$-, as 0.60 and 0.21 respectively. The latter value is calculated from the Taft factor of the benzene residue, C_6H_5, using the reduction formula. The former value was taken as being the same as for benzene, as it was not possible to translate into mathematical terms the effect of the methyl group on the Taft factor of the phenyl residue. Correlation was always closer if a value of 0.60 was accepted and in the latter study, the principal was extended to other aromatic solvents.

The one parameter equations predicted under study C are given in Table 78. For each solute, two correlations are quoted. Correlation A, involves the Taft factor of any solvent given in Appendix 4, with the exception of those in brackets. In correlation B, the choice was limited, in that data for tetrachloroethylene, carbon tetrachloride and carbon disulphide were excluded. In one parameter equations it would appear that the Taft factor is as good as the KBM function. This would suggest that it is dangerous to consider dielectric effects (KBM function) or interaction effects(σ^*) in isolation. When the solvents studied were limited to exclude carbon tetrachloride, carbon disulphide and tetrachloroethylene, several correlations based on the KBM function, are changed to equations based on the Taft factor. This obviously substantiates the view that the effect of the three excluded solvents is best explained on a dielectric basis.

The results of the two parameter correlations under study C, are given in Tables 79 and 80. Table 79 deals with the extended range of solvents. These results were considered to be by far the most interesting obtained in the feasibility study. It will be noticed that Table 80 deals with less solutes than the previous table, this being because the results as collected in Table 80, supported the hypothesis that carbon tetrachloride, carbon disulphide and tetrachloroethylene could be represented by zero Taft factors and the study was discontinued. The results of Table 80 show a higher multiple correlation coefficient for the data than for the corresponding solute in Table 79. This is taken as being indicative of the expected importance of the Taft factor in a relatively small group of solvents which contained several of the more polar solvents. For cyclohexanone, Table 81, which was chosen as being a representative solute, the correlation based on the fifteen solvents shows greatest discrepancy for the nonpolar solvents, this confirming the trend observed in the earlier studies. This is particularly interesting as older studies, for example, those based on the KBM function, had found that nonpolar solvents were more readily correlated. This apparent anomaly may result from the failure of earlier workers to derive the best line statistically.

Table 78

The predicted one factor equations for the multiple regression analysis under study C.

Solute	Relationship A	Relationship B	Multiple correlation A	Multiple correlation B
Ethylene carbonate[14]	97.22KBM	93.04KBM	0.966	0.968
Glutaric anhydride[14g]	24.60KBM	24.68KBM	0.951	0.945
N-acetyl iminazole[15]	12.26KBM	13.18KBM	0.945	0.927
Dimethyl formamide[17b]	46.43KBM		0.941	
Dimethyl sulphoxide[14h]	57.11KBM	14.58 σ^*	0.937	0.959
N-acetyl pyrrole[16]	27.20KBM	7.51 σ^*	0.932	0.957
Thionyl chloride[10h]	16.78KBM		0.928	
Benzophenone[15]	23.29KBM	6.27 σ^*	0.920	0.957
Dimethyl formamide[17a]	51.72KBM		0.919	
Diphenyl sulphoxide[15h]	6.57 σ^*		0.966	
Acetyl pyrrolidine[16]	19.09 σ^*	19.09 σ^*	0.944	0.977
Methyl acetate[16]	8.64 σ^*	8.64 σ^*	0.944	0.977
Cyclohexanone[15]	9.96 σ^*	9.96 σ^*	0.939	0.972
N-acetyl indole[16]	7.53 σ^*	7.53 σ^*	0.931	0.965
Acetone[15]	5.70 σ^*	5.70 σ^*	0.931	0.963
Acetophenone[15]	6.78 σ^*	6.78 σ^*	0.928	0.965
Dimethyl hydrogen phosphonate[14]	13.01 σ^*	13.01 σ^*	0.927	0.959
Acetyl chloride[16]	3.95 σ^*	3.95 σ^*	0.886	0.945
N-acetyl tetrazole[16]	0.008 M_V	0.0064 M_V	0.456	0.359

The numerical suffixes refer to the number of solvents used in the derivation of relationship A. The sources for the data are given in Table 73 together with the meaning of suffixes a and b.

(g) Ref. 246 (h) Ref. 282

Table 79

The predicted two parameter equations under Study C. Data for tetrachloroethylene, carbon tetrachloride and carbon disulphide is included.

Solute	N	Relationship		M.C.
		σ^*	E_T	
Diphenyl sulphoxide	15	4.99(11.21)	0.071(4.74)	0.988
Acetyl pyrrolidine	16	12.81(10.17)	0.282(6.82)	0.987
Cyclohexanone	15	6.77(9.40)	0.150(6.23)	0.985
N-acetyl pyrrole	16	4.50(8.18)	0.135(7.47)	0.985
N-acetyl indole	16	4.75(8.44)	0.125(6.76)	0.984
Acetophenone	15	4.38(8.38)	0.113(6.45)	0.983
Benzophenone	15	3.88(7.67)	0.113(6.65)	0.982
Methyl acetate	16	5.99(8.66)	0.119(5.24)	0.981
Acetone	15	3.89(7.37)	0.085(4.84)	0.976
N-acetyl triazole[d]	15	1.50(3.11)	0.063(3.92)	0.934
		σ^*	KBM	
Dimethyl hydrogen phosphonate	14	7.75(7.70)	26.78(7.04)	0.986
Glutaric anhydride	14	2.59(4.73)	17.03(8.09)	0.983
N,N-dimethyl formamide[b]	17	4.69(3.22)	35.20(7.33)	0.966
		E_T	M_V	
Thionyl chloride	10	0.305(10.45)	-0.66(5.86)	0.983
Ethylene carbonate	14	1.24(7.87)	-0.16(2.33)	0.975
		E_T	R_d	
N-acetyl iminazole	15	0.23(6.19)	-1.65(3.31)	0.964
N,N-dimethyl formamide[a]	17	1.11(10.55)	-9.57(6.45)	0.975
		σ^*	R_d	
Acetyl chloride	16	2.89(5.38)	0.75(3.16)	0.935
		E_T	KBM	
N-acetyl tetrazole	16	0.17(2.87)	-17.11(2.60)	0.652

Suffixes, data sources and abbreviations as Tables 73 and 78. Figs. in brackets - T-statistic values of relevant parameters.

Table 80

The predicted two parameter equations under study C. Data for tetrachloroethylene, carbon tetrachloride and carbon disulphide is excluded.

Solute	N	Relationship		M.C.
		σ^*	E_T	
Cyclohexanone	12	7.53(10.81)	0.114(4.50)	0.991
Acetophenone	12	4.89(9.75)	0.089(4.85)	0.990
Dimethyl sulphoxide	11	9.79(8.07)	0.227(4.99)	0.989
Methyl acetate	13	6.85(10.78)	0.080(3.56)	0.989
N-acetyl indole	13	5.35(9.54)	0.098(4.93)	0.989
N-acetyl pyrrole	13	4.99(8.51)	0.113(5.42)	0.988
Benzophenone	12	4.30(8.47)	0.093(5.02)	0.988
N-acetyl iminazole	13	1.66(3.34)	0.077(4.36)	0.963
		σ^*	KBM	
N-acetyl pyrrolidine	13	13.83(13.12)	24.09(6.06)	0.995
Dimethyl hydrogen phosphonate	11	8.64(8.32)	22.25(5.31)	0.990
Glutaric anhydride	11	3.28(4.90)	15.90(6.84)	0.985
Acetone	12	4.13(6.86)	7.63(3.23)	0.982
Ethylene carbonate	13	6.72(2.18)	71.01(5.90)	0.979
		σ^*	M_V	
Acetyl chloride	13	3.55(7.93)	0.010(1.62)	0.956
		E_T	KBM	
N-acetyl tetrazole	13	0.171(2.18)	-17.02(2.04)	0.572

Data sources and abbreviations are given after Tables 73 and 78. Figures in brackets refer to the T-statistic values of the relevant parameters.

Table 81

A comparison of the observed and predicted solvent shifts(cm^{-1}) for cyclohexanmeunder study C.

Solvent	Observed shift y	A		B	
		y_{est}	$y-y_{est}$	y_{est}	$y-y_{est}$
Hexane	0	3.55	-3.55	2.33	-2.33
Cyclohexane	2	3.49	-1.49	2.30	-0.30
n-Butyl ether	3	5.09	-2.09	3.92	-0.92
Ethyl ether	4	6.28	-2.28	5.16	-1.16
Tetrachloroethylene	6	4.89	1.11		
Toluene	7	9.15	-2.15	8.39	-1.39
Carbon tetrachloride	7	4.88	2.12		
Carbon disulphide	9	4.89	4.11		
Benzene	11	9.24	1.76	8.46	2.54
Iodomethane	13	11.76	1.24	10.97	2.03
Nitromethane	17	16.42	0.58	15.83	1.17
1,2-Dichloroethane	17	15.22	1.78	14.72	2.27
Dichloromethane	18	19.30	-1.30	19.30	-1.30
Chloroform	21	23.80	-2.80	24.42	-3.42
Bromoform	25	22.77	2.23	23.28	1.72

D. COMPREHENSIVE STUDY

The method followed in the feasibility study, was pursued for an extended range of solvents. Data (Appendix 5) were obtained for twenty solutes in twenty-five to thirty solvents, the experimental method being that pursued for the solvent effect work on the νNH band of imidates (Section 2.C). Because of the relative unavailability of compounds with S=O and P=O dipoles, it was decided to limit the programme to solutes with carbonyl groupings. As it was desired to find if a general relationship existed for all carbonyl systems, the choice of solutes was deliberately wide, including aldehydes, ketones and esters, but carboxylic acids were excluded due to the broadness of the νC=O absorption and the possibility of ester formation with ethanol and methanol.

In Correlation 1, nine solvent parameters were investigated, the KBM function, dielectric permittivity, E_T value, molar volume, refractive index, molar polarization, dipole moment, standard entropy, and the δ value. Equations involving from one to three of these parameters were statistically derived from correlations involving twenty-four to twenty-seven solvents. For the one parameter equations, a correlation involving the KBM function was obtained in every case, Table 82, this confirming the trend observed in the feasibility study.

The two parameter equations predicted under Correlation 1, are given in Table 83. These show a marked departure from

the $k_1E_T - k_2M_V$ relationship derived (Section 6.C), this relationship being accepted in only five of the twenty correlations. In this study a $k_1E_T - k_2S^0$ relationship, where S^0 is the standard entropy, was favoured in half of the correlations performed. This emphasises the need, when undertaking a multiple correlation study, to treat as much data as can be reasonably obtained.

In sixteen of the twenty relationships the E_T value is statistically the more favourable parameter for correlation, and all these relationships involve a negative contribution from the other parameter. The E_T value, having been deduced from measurements on charge transfer spectra, where the effect of the solvent may be increased by the charge on the solute, may overemphasise the role of the solvent in relation to less polar solutes. The E_T value as described in Section 6.C depends on the arrangement of solvent molecules about the solute. This arrangement could be considered in terms of the entropy of the solvent molecules or in relation to the diameter or volume of 'cavities' within the solvent. On this basis the inclusion of the molar volume and standard entropy in the two parameter relationships would appear to be theoretically significant. Also of significance is the E_T/S^0 ratio, which is approximately constant, and allows reduction of the relationship to the general form:-

$$\Delta\nu = k_1(3E_T - S^0)$$

Table 82

The predicted one parameter equations under correlation 1. All correlations are based on the KBM function

Solute	R.G.	E.S.S.	T-statistic	M.C.
Di-isobutyl ketone[27]	29.96	254	17.96	0.962
Salicylaldehyde[25]	15.67	45	17.35	0.962
Acetonyl acetone[27]	30.89	279	17.66	0.961
Diethyl ketone[27]	29.50	293	16.45	0.955
Methyl vinyl ketone[26]	27.53	252	16.12	0.955
m-Nitro acetophenone[26]	23.44	175	16.05	0.955
p-Amino acetophenone[25]	37.43	443	15.23	0.952
Benzophenone[24]	25.38	204	14.77	0.951
Benzaldehyde[27]	26.54	274	15.32	0.949
Cinnamaldehyde[27]	35.51	498	15.20	0.948
Di-n-heptyl ketone[26]	33.51	466	14.43	0.945
Di-isopropyl ketone[26]	28.92	352	14.33	0.944
Methyl chloroacetate[25]	45.69	888	13.63	0.941
Acetaldehyde[26]	18.77	160	13.82	0.940
Benzyl acetate[25]	33.68	461	13.42	0.939
Diacetyl[27]	13.64	89	13.84	0.938
Methyl isopropyl ketone[27]	29.11	417	13.62	0.937
Methyl ethyl ketone[27]	32.27	520	13.51	0.936
Amyl butyrate[27]	38.38	807	12.91	0.930
Methyl chloroformate[25]	13.16	195	8.34	0.862

Suffixes refer to the number of solvents correlated.
E.S.S. Error sum of squares, M.C. Multiple correlation coefficient, R.G. Regression coefficient.

Table 83

The predicted two factor equations for the multiple regression analysis, correlation 1.

Solute	Relationship	E.S.S.	M.C.
Di-n-heptyl ketone	$0.577E_T(15.06)-0.209S^O(7.35)$	168	0.981
Di-iso-butyl ketone	$0.441E_T(13.01)-0.128S^O(5.08)$	137	0.980
Acetonyl acetone	$0.444E_T(11.68)-0.123S^O(4.38)$	173	0.976
Benzaldehyde	$0.438E_T(12.90)-0.152S^O(6.06)$	138	0.975
Salicylaldehyde	$0.202E_T(9.28)-0.054S^O(3.53)$	32	0.974
Diethyl ketone	$0.463E_T(12.04)-0.150S^O(5.27)$	176	0.973
Methyl vinyl ketone	$0.411E_T(11.08)-0.122S^O(4.41)$	156	0.972
m-nitro-acetophenone	$0.376E_T(10.74)-0.123S^O(4.86)$	122	0.969
Acetaldehyde	$0.309E_T(11.01)-0.107S^O(5.11)$	89	0.967
Benzophenone	$0.413E_T(8.19)-0.130S^O(3.64)$	161	0.962
Methyl ethyl ketone	$0.487E_T(14.65)-0.086M_V(6.38)$	231	0.972
Methyl isopropyl ketone	$0.446E_T(12.92)-0.077M_V(5.63)$	211	0.968
Cinnamaldehyde	$0.505E_T(11.72)-0.77\ M_V(4.51)$	329	0.966
Benzyl acetate	$0.562E_T(11.04)-0.100M_V(5.28)$	267	0.965
Amyl butyrate	$0.597E_T(11.89)-0.107M_V(5.33)$	446	0.962
Diacetyl	$6.03n\ (9.05)-0.043M_V(4.24)$	58	0.960
Methyl chloro-formate	$6.21n\ (5.36)-0.047M_V(2.72)$	158	0.890
Di-isopropyl ketone	$43.37KBM(11.81)-0.111S^O(4.34)$	197	0.969
p-Amino aceto-phenone	$1.11E_T\ (7.38)-28.74\ (5.13)$	289	0.969
Methyl chloro-acetate	$63.37KBM(11.58)-0.075M_V(3.72)$	555	0.964

The figures in brackets refer to the T statistic value of the corresponding parameter. Data taken from Appendix 5. The meaning of the abbreviations and the number of solvents correlated are given after Table 82.

in which the wavenumber shift $\Delta\nu$ is related to the constant k_1, which is characteristic of the solute.

In the second study of these data, Correlation 2, the use of the transformation facilities of the program was again pursued. In this study, the molar volume M_V, E_T value, KBM function, standard entropy S^0, refractive index, and dielectric permittivity ε were retained from Correlation 1, and in addition the following transformations were investigated:-

$$\text{KBMVOL} = \frac{\text{KBM function}}{\text{molar volume } M_V} \qquad \text{ETOVMV} = \frac{E_T \text{ value}}{\text{Molar volume } M_V}$$

$$\text{REFSQD} = (\text{refractive index n})^2$$

$$\text{RADIUS} = \left\{\frac{3}{4\pi} \times M_V\right\}^{1/3} \qquad \text{DILMOV} = \frac{\text{Dielectric permittivity } \varepsilon}{\text{molar volume } M_V}$$

Of the one parameter equations predicted under Correlation 2, fifteen were based on the KBM function, being identical to those in Correlation 1, Table 82, the correlations for the remaining solutes are given in Table 84.

The relationships under correlation 2, are generally statistically favoured by small increases in the T statistic and multiple correlation values. The biggest increase is for di-n-heptyl ketone where the multiple correlation coefficient rises from 0.945 to 0.955. These increases do not alter the conclusion that the KBM function is the most powerful single parameter. The low correlation observed with methyl chloroformate is thought to be consistent with the lower chemical

Table 84

Predicted one parameter equations under correlation 2 which differ from those under correlation 1

Solute	Relationship	E.S.S.	M.C.
di-n-heptyl ketone	2373KBMVOL(16.08)	383	0.955
di-isopropyl ketone	2031KBMVOL(14.66)	338	0.946
methyl isopropyl ketone	2052KBMVOL(14.05)	394	0.940
amyl butyrate	2712KBMVOL(13.53)	743	0.936
methyl chloroformate	$2.23n^2(8.48)$	190	0.866

Figures in brackets refer to the T-statistic values of the respective parameters. The number of solvents correlated and the meaning of the abbreviations is given in Table 82.

stability of this solute, as was apparent from the reaction which occured with pyridine. It is noted that the values for the multiple correlation coefficients are generally higher for the data obtained in the present study than for the data used in the feasibility study.

The predicted two parameter equations under Correlation 2 are given in Table 85. The comments pertaining to the results under Correlation 1, in this section still hold, although it would appear, as was found in the feasibility study, Section 6.C, that the molar radius is superior to the solvent molar volume for correlation purposes.

As with the S^0, E_T relationship discussed earlier in this section, the E_T, R_d relationship, can be expressed approximately in terms of a solute dependent constant k_2:-

Table 85

The predicted two factor equations for the multiple regression analysis, correlation 2.

Solute	Relationship	M.C.
Di-isobutyl ketone	$0.441E_T(13.01)-0.128S^O(5.08)$	0.980
Acetonyl acetone	$0.444E_T(11.68)-0.123S^O(4.38)$	0.976
Benzaldehyde	$0.438E_T(12.90)-0.152S^O(6.06)$	0.975
Salicylaldehyde	$0.202E_T(9.28)-0.054S^O(3.53)$	0.974
Diethyl ketone	$0.463E_T(12.04)-0.150S^O(5.27)$	0.973
Methyl vinyl ketone	$0.411E_T(11.08)-0.122S^O(4.41)$	0.972
m-Nitro acetophenone	$0.376E_T(10.74)-0.123S^O(4.86)$	0.969
Acetaldehyde	$0.309E_T(11.01)-0.107S^O(5.11)$	0.967
Di-n-heptyl ketone	$0.690E_T(13.27)-5.39\ R_d(7.49)$	0.981
Methyl iso-propyl ketone	$0.587E_T(10.17)-4.52\ R_d(5.68)$	0.969
Benzyl acetate	$0.800E_T(5.62)-6.53\ R_d(5.62)$	0.968
Amyl butyrate	$0.813E_T(10.34)-6.54\ R_d(6.02)$	0.967
p-Amino acetophenone	$0.810E_T(8.16)-6.21\ R_d(4.78)$	0.966
Methyl chloroacetate	$0.909E_T(9.23)-6.97\ R_d(5.13)$	0.964
Benzophenone	$0.501E_T(6.86)-3.56\ R_d(3.69)$	0.962
Methyl ethyl ketone	$0.487E_T(14.65)-0.086M_V(6.38)$	0.972
Cinnamaldehyde	$0.505E_T(11.72)-0.77\ M_V(4.51)$	0.966
Diacetyl	$6.39n^2\ (7.59)-3.20\ R_d(4.93)$	0.969
Methyl chloroformate	$7.68n^2\ (5.43)-4.24\ R_d(3.90)$	0.922
Di-iso-propyl ketone	$43.37KBM(11.81)-0.111S^O(4.34)$	0.969

Figures in brackets refer to the T statistic values for the respective parameters. The number of solvents correlated and the meaning of the abbreviations are given after Table 82.

$$\Delta\nu = k_2(0.13E_T - R_d)$$

This would again suggest a genuine relationship, and also suggest the interdependence of the E_T value with the solvent molar radius. As in Correlation 1, the three parameter equations under this section showed little statistical improvement over the two parameter equations, the improvement often being produced upon the introduction of parameters, from which the T-statistic value was less than 3.0, and these and higher correlations will not be discussed.

In the third and final study under this section, Correlation 3, six parameters, the standard entropy, E_T value, molar volume, molar radius, Taft factor and KBM function were selected. The inclusion of the Taft factor necessitated a reduction in the number of solvents which could be correlated, twenty to twenty-three being used.

The values for the Taft factors are those given in Appendix 4. The results of the feasibility study suggested that the acceptance of a zero Taft factor for carbon disulphide, carbon tetrachloride and tetrachloroethylene, and a value of 0.6 for toluene were reasonable. In this study the data for anisole, benzonitrile, O-dichlorobenzene and nitrobenzene were included by assuming that the Taft factors of the solute residues would be close to that of benzene, that is 0.6.

Nineteen of the twenty single parameter equations, Table 86, were based on the KBM function. The multiple correlation

coefficient was generally slightly lower than for the treatment of the same data under Correlation 1, Table 82. This may simply be due to the fact that the solvents excluded, because of the unavailability of Taft factor data, may include those which are adequately correlated with the KBM function. It is interesting to note that the regression coefficient associated with the KBM function is little altered by the exclusion of these solvents.

In the two factor equations predicted, Table 87, two distinct sets were observed. The $k_1E_T - k_2$ (Molar volume M_V or molar radius R_d) type was found in half the cases studied, but, of the remaining ten correlations, nine involved the Taft factor. In all cases high multiple correlation coefficients were obtained, the lowest value of 0.959 being for methyl chloroformate, and hence all the equations are of high predictive value. The relationships were also examined to determine if there was a direct relationship between the type of equation predicted and the environment of the carbonyl group. Only for the aliphatic ketones did there appear to be a genuinely useful relationship, this involving the E_T and molar volume parameters. For the three aromatic ketones, a relationship involving the Taft factor and KBM function was obtained, this type of relationship being shared with benzyl acetate and acetaldehyde. This equation corresponds to the Buckingham equation as modified by Caldow and Thompson[232] in which the constant is zero and the two KBM type terms are combined.

In the final set of correlations, Table 88, multiple regression analysis was extended to obtain three parameter equations. If the parameters were chosen randomly there would be twenty possible combinations of the six parameters involved. If additionally it is considered that these may have positive or negative contributions, with the exception that all three may not be negative, there are seven further combinations in each set, leading to one hundred and forty combinations. It is therefore significant that only seven combinations were selected, and of these two particular sets accounted for fifteen of the twenty correlations.

In examining the predicted equations under Correlation 2, Table 85, it was suggested that the negative contributions from the standard entropy or molar radius terms, were indicative of the ability of the E_T value to overemphasise the role of the solvent on account of its calculation from charge transfer spectra. Returning to the three parameter equations, Table 88, sixteen of the twenty equations, contain an E_T term modified by the molar volume M_V, molar radius R_d, or standard entropy S^0 of the solvent. In every case there is a positive contribution from the Taft factor of the solvent residue which would be consistent with the formation of intermolecular hydrogen bonds with polar solvents. Again the ratios of E_T/R_d and E_T/S^0 are reasonably constant, suggesting reduction of the equations to the form:-

$$\Delta\nu = k_1(0.13E_T - R_d) + k_2\sigma^*$$

$$\Delta\nu = k_A(3.5E_T - S^0) + k_2\sigma^*$$

where k_2 is approximately 2.5 for ketones.

Table 86

The predicted one factor relationships from the multiple regression analysis, Correlation 3.

Solute	Relationship	E.S.S.	M.C.
Di-isobutyl ketone[23]	29.33KBM(16.37)	223	0.961
Acetonyl acetone[23]	30.25KBM(16.10)	245	0.960
Salicylaldehyde[21]	13.22KBM(15.10)	41	0.959
Diethyl ketone[23]	29.14KBM(14.52)	280	0.952
Methyl vinyl ketone[23]	26.91KBM(14.22)	249	0.950
m-Nitroacetophenone[22]	22.96KBM(13.87)	169	0.950
p-Aminoacetophenone[21]	35.95KBM(13.21)	400	0.947
Benzophenone[20]	25.09KBM(12.78)	191	0.946
Cinnamaldehyde[23]	34.37KBM(13.68)	438	0.946
Benzaldehyde[23]	26.23KBM(13.55)	260	0.945
Di-n-heptyl ketone[23]	33.68KBM(12.92)	472	0.940
Methyl chloroacetate[21]	44.28KBM(12.23)	772	0.939
Methyl ethyl ketone[23]	31.51KBM(12.59)	435	0.937
Di-isopropyl ketone[23]	28.40KBM(12.52)	358	0.936
Diacetyl[23]	13.05KBM(12.40)	77	0.935
Benzyl acetate[21]	33.13KBM(11.71)	433	0.934
Acetaldehyde[22]	17.55KBM(11.88)	134	0.933
Methyl isopropyl ketone[23]	28.85KBM(11.97)	404	0.931
Amyl butyrate[23]	37.24KBM(11.28)	758	0.923
Methyl chloroformate[22]	4.80σ*(10.29)	118	0.914

E.S.S. Error sum of squares M.C. Multiple correlation coefficient. Numerical suffixes refer to the number of solvents correlated. Figures in brackets refer to the T statistic values of the corresponding parameter.

Table 87

The statistically derived two parameter equations for carbonyl solutes under correlation 3.

Solute	Relationship	M.C.
Di-n-heptyl ketone	$0.520E_T(15.21)-0.090M_V(6.62)$	0.979
Diethyl ketone	$0.414E_T(11.90)-0.063M_V(4.52)$	0.978
Di-isobutyl ketone	$0.396E_T(12.60)-0.053M_V(4.25)$	0.975
Benzaldehyde	$0.384E_T(12.12)-0.062M_V(4.86)$	0.969
Cinnamaldehyde	$0.494E_T(11.54)-0.076M_V(4.46)$	0.968
Methyl vinyl ketone	$0.368E_T(10.92)-0.051M_V(3.77)$	0.967
Methyl isopropyl ketone	$0.441E_T(11.78)-0.076M_V(5.07)$	0.966
Methyl ethyl ketone	$0.475E_T(11.48)-0.080M_V(4.87)$	0.965
Amyl butyrate	$0.800E_T(9.92)-6.55R_d(5.77)$	0.968
Di-iso-propyl ketone	$0.595E_T(9.82)-4.82R_d(5.65)$	0.968
Benzyl acetate	$5.51\sigma^*(8.16)+20.45KBM(9.88)$	0.986
p-Amino acetophenone	$4.60\sigma^*(5.19)+25.36KBM(9.33)$	0.979
Benzophenone	$3.30\sigma^*(5.22)+8.72KBM(8.72)$	0.979
m-Nitroacetophenone	$2.40\sigma^*(3.55)+17.67KBM(8.85)$	0.969
Acetaldehyde	$2.27\sigma^*(4.05)+12.66KBM(7.69)$	0.964
Acetonyl acetone	$3.10\sigma^*(4.04)+0.226E_T(10.86)$	0.974
Salicylaldehyde	$1.03\sigma^*(2.76)+0.105E_T(9.50)$	0.968
Diacetyl	$1.54\sigma^*(3.61)+0.094E_T(8.12)$	0.968
Methyl chloroformate	$3.53\sigma^*(8.14)+0.77R_d(4.57)$	0.959
Methyl chloroacetate	$63.78KBM(12.16)-0.085M_V(4.31)$	0.970

The figures in brackets refer to the T statistic values of the corresponding parameter. The number of solvents correlated are as given in Table 86. M.C. Multiple correlation.

Table 88

The predicted three parameter equations under the multiple regression analysis, Correlation 3.

Solute	Relationship	M.C.
Di-isopropyl ketone	$0.49E_T - 4.03\ R_d + 2.66\sigma^*$	0.983
Methyl isopropyl ketone	$0.46E_T - 3.61\ R_d + 2.98\sigma^*$	0.982
Methyl chloroacetate	$0.72E_T - 5.70\ R_d + 4.26\sigma^*$	0.981
Cinnamaldehyde	$0.51E_T - 3.62\ R_d + 3.05\sigma^*$	0.980
Acetaldehyde	$0.29E_T - 2.26\ R_d + 1.80\sigma^*$	0.979
Benzaldehyde	$0.43E_T - 3.17\ R_d + 1.87\sigma^*$	0.978
Amyl butyrate	$0.69E_T - 5.74\ R_d + 2.72\sigma^*$	0.977
Methyl ethyl ketone	$0.38E_T - 0.063M_V + 2.90\sigma^*$	0.979
Benzyl acetate	$0.36E_T - 0.110S^0 + 4.64\sigma^*$	0.989
Di-isobutyl ketone	$0.37E_T - 0.110S^0 + 2.03\sigma^*$	0.984
Acetonyl acetone	$0.36E_T - 0.094S^0 + 2.54\sigma^*$	0.984
Diethyl ketone	$0.37E_T - 0.116S^0 + 2.71\sigma^*$	0.983
Di-n-heptyl ketone	$0.53E_T - 0.196S^0 + 1.66\sigma^*$	0.982
Methyl vinyl ketone	$0.33E_T - 0.095S^0 + 2.20\sigma^*$	0.978
m-Nitroacetophenone	$0.27E_T - 0.079S^0 + 2.20\sigma^*$	0.976
Salicylaldehyde	$0.15E_T - 0.029S^0 + 0.72\sigma^*$	0.971
p-Aminoacetophenone	$4.06\sigma^* - 0.045S^0 + 32.91KBM$	0.980
Benzophenone	$3.37\sigma^* - 0.045E_T + 12.41KBM$	0.979
Diacetyl	$3.01R_d - 0.049M_V + 3.19\sigma^*$	0.964
Methyl chloroformate	$1.38R_d - 0.061M_V + 3.31\sigma^*$	0.960

The number of solvents correlated are as given in Table 86.

M.C. Multiple correlation.

E. CONCLUSION

The results presented in Sections 6C and 6D have shown the use of multiple regression analysis as a predictive tool in infra-red solvent shift calculations. The problems that arise from chance correlations have been shown to be largely overcome by treating as much data as is readily obtainable. There still remains a need, however, for more accurate data. When there is a fairly close agreement with the observed data from two sets of parameters, an error in any of the readings may result in the acceptance of a different correlation.

The choice of the carbonyl system for this initial study on the basis of known correlations involving the Taft factor of the solvent residue R of the solvent RH, has been vindicated by the inclusion of this factor in many of the statistically derived equations. The limited data treated in the feasibility study for S=O and P=O systems suggests that the study may be extended to other X=O dipoles. There is evidence to suggest that carbonyl bands retain vibrational structure in the liquid phase, although the measurements in the present study support the presence of overtone bands. Even with high precision spectrometers the position of the νC=O absorption may be determined with difficulty due to the breadth of the band. Despite these disadvantages the carbonyl band would still appear the most suitable for this type of study.

The other major error in the correlations is associated

with the parameters themselves. In the derivation of any relationship of the type, $y = a + bx_1 + cx_2 + \ldots$ on a least squares principle, it is assumed that the errors are confined to the dependent variable y. In this case, this is clearly not so, but the results of the present study suggest it is reasonable to estimate the missing solvent parameters wherever possible in order to allow the inclusion of as many solvents as possible. It is, however, fortunate that data is readily available for the molar volume, E_T and KBM parameters which have featured in the majority of the correlations.

The superiority of the KBM function for single parameter correlation has been clearly demonstrated. The possible correlation with a parameter, KBMVOL, which is the KBM function divided by the solvent molar volume, has also been investigated and shown to be inferior to the KBM function itself. One parameter correlations with the Taft factor have also been observed, when solvents with zero Taft factors have been excluded. These results would seem to suggest that whilst specific interactions exist, bulk dielectric effects are probably more important for carbonyl systems. This would not appear unreasonable, if the size of the observed shifts are considered in comparison to those for the νOH band of alcohols where specific interactions have been established.[283] The KBM function has been critised both from the theoretical standpoint of the model chosen, and for its inapplicability to polar solvents. In the present study the regression coef-

ficients have been statistically derived and it is interesting to note that on this basis the greatest error is exhibited in the nonpolar solvents such as hexane, heptane, di-n-butyl ether, and ethyl ether (Tables 89 and 90)

The extension of the work to equations containing two or more variables resulted in a marked increase in the multiple regression coefficient. This improvement was considered in relation to the increasing complexity of the equations produced and the inclusion of parameters with low T-statistic values these being indicative of poor linear correlation of this particular parameter with the dependent variable. Additionally the actual calculated shifts for each solvent were examined because a small decrease in the error sum of squares for a particular correlation, may or may not be significant in the present study. This apparent anomaly arises principally from the inbuilt error in the measurement of the solvent shifts. The program considers any variation from the observed value as an error, whereas a spectroscopist would accept a variation of $\pm 1 cm^{-1}$ as being within experimental error. Additionally readings may be subject to a bias error as a result of an incorrect measurement of the n-pentane or n-hexane standard.

On the basis of previous discussion, the equations involving four or more independent variables were rejected as being statistically unsound.

The favoured two parameter equations have been shown to be much more sensitive to the range of solvents investigated.

This particularly applied to relationships involving the molar volume or molar radius of the solvent, these parameters being largely inter-changeable, but the molar radius was found to be slightly more significant overall. No exclusive two parameter relationships have been found, but the results indicated that certain relationships are worthy of closer theoretical consideration.

The most significant of these is the $\Delta\nu = k_1 E_T - k_2 R_d$ relationship, which will be refered to as the ETR relationship. This offers a working relationship for a large proportion of the solutes studied. In the feasibility study 6.C, the inclusion of the Taft factor often resulted in the inclusion of this parameter in the two parameter equations, on the basis of a small improvement the multiple correlation coefficient. In all cases the multiple correlation coefficient was sufficiently large to suggest a genuine relationship. It was, however, found difficult to compare directly the multiple correlation coefficients from studies B and C, because of the smaller number of solvents investigated in the Taft factor study, and hence the reduced number of degrees of freedom. In this respect it is interesting to compare these results with the results under Correlations 2 and 3 (Section 6.D), in the comprehensive study where there was less tendancy for relationships based on the Taft factor to be favoured, and this may be simply due to the larger range of solvents being studied.

With the ETR relationship, it was noticed that the ratio of the regression coefficients k_1/k_2 was approximately constant

and this suggested a reduction of the equation as follows:-

$$\Delta\nu = k_3(0.13E_T - R_d)$$

In the comprehensive study a similar relationship involving the E_T and S^0(standard entropy) parameters was also found (Section 6.D Correlations 1 and 2) and here there was again an apparent relationship between the regression coefficients which suggested a general equation of the form:-

$$\Delta\nu = k_4(3E_T - S^0)$$

This equation, which will be referred to as the ETS relationship, and the preceding ETR relationship, both involve a positive E_T term and a negative corrective term.

The E_T values are calculated from the displacement of the solvato-chromic band of charge transfer spectra. This displacement is thought to be due to the inability of the solvent molecules to rearrange themselves around the excited state, in which the solute dipole is perpendicular to that in the ground state. The E_T value might therefore be expected to be related to the entropy of the solvent system, as both represent in different units 'the degree of randomness' within the system. The solvation may also be affected by the distance of approach of the solvent molecule and this may in turn be related to the molar radius of the solvent. It is possible that the E_T value, because of its origin in charge transfer systems, will over estimate the effect of the solvent with

respect to nonpolar solutes. The negative contributions of the R_d and S^0 terms in the ETR and ETS relationships may allow the E_T parameter to be extended to less polar solutes.

The importance of the Taft factor is difficult to assess on the basis of the two parameter equations alone and it is clear that a larger number of solutes would need to be correlated in order to obtain a clear trend. The feasibility study suggested the possibility of a $\Delta\nu = k_1\sigma^* + k_2E_T$ relationship, but this was only favoured in three cases in the comprehensive study, Correlation 3, Table 87. Whilst the Taft factor is associated with a higher T statistic value in most cases, mathematically it accounts for less than half the shift.

The only other relationship of interest would appear to be that based on the KBM function and Taft factor. This relationship was only favoured three times in the feasibility study and five times in the comprehensive study, Table 87. This equation corresponds to the Buckingham equation as modified by Caldow and Thompson,[232] in which the constant term is zero and the two KBM function terms are combined. It was concluded that solvent-solute interactions were of relatively minor importance in carbonyl solutes.

These observations have been extensively confirmed by the predicted three parameter equations for the Comprehensive study, Table 88. Eighty percent of the data could be predicted using equations of the form.

$$\Delta\nu = k(0.13E_T - R_d) + k_2\sigma^*$$

$$\Delta\nu = k(3.5E_T - S^0) + k_2\sigma^*$$

The values of $k(0.13E_T - R_d)$ and $k(3.5E_T - S^0)$ generally account for the measured shift in nonpolar solvents. Only in such solvents as chloroform and bromoform does the contribution of the $k_2\sigma^*$ term become the more significant. The value of the regression coefficient k is generally lower than the constant in the corresponding two parameter equation. These three parameter equations give the best fit to the experimental data. In many cases the statistical improvement of the three parameter equations over the ETS and ETR relationships is not very significant and the simplicity of these latter relationships and the greater number of solvents that can be treated may favour these for predictive purposes. The three parameter equations, however, satisfy the original criteria of solvent shifts, Section 6.A, as these are in the general form:-

$$\Delta\nu = k_1 f(\text{bulk solvent effects}) + k_2 f(\text{interaction effects})$$

Whilst much work remains to be done, the undoubted usefulness of the derived equations as predictive organs has been established. The data, Tables 89 and 90, for di-n-heptyl ketone show clearly the improvement of the two and three parameter equations in relation to the KBM relationship. The general applicability to a wide range of carbonyl compounds

has been established, and, in particular, excellent agreement observed for the series of ketones studied. These observations are consistent with the general linearity of the BHW type plot for X=O systems.

The extension of the work to νOH systems, presents an interesting problem. The ETR and ETS relationships observed for carbonyl systems may not be statistically favoured as it is anticipated that bulk solvent effects will be less significant than solvent-solute interaction effects. On this basis it is very important to include parameters such as the Taft factor which represent the inductive nature of the solvent. Interaction with the O-H dipole may be expected to occur through the hydrogen atom. In the solvent there may be C=O, C≡N or C-X dipoles, where X is a halogen, involved in intermolecular interaction and it may be necessary to include further factors to bring the Taft factors of the solvent residues of the three systems onto a common basis.

Table 89

The predicted infra-red solvent shifts (cm^{-1}) for di-n-heptyl ketone

Solvent	Observed shift	Predicted shift		
		A	B	C
Acetonitrile	15	16.2	19.2	19.6
Anisole	12.5	11.6	9.5	9.0
Benzene	10.0	7.8	8.2	11.2
Benzonitrile	14.0	15.9	12.5	12.4
Bromoform	17.0	11.7	12.3	13.9
Carbon disulphide	9.0	8.8	11.4	10.3
Carbon tetrachloride	8.5	7.6	8.1	7.2
Chloroform	15.5	13.3	13.0	15.7
Cyclohexane	1.5	6.8	5.7	6.1
n-butyl ether	4.0	9.7	6.2	6.0
o-Dichlorobenzene	11.5	14.4	9.0	8.7
1,2-Dichloroethane	14.0	14.5	14.6	14.7
Dichloromethane	14.5	14.2	15.5	16.7
Ethanol	26.0	15.8	21.7	20.4
Ethyl ether	5.5	11.6	8.5	6.8
n-Heptane	0.5	8.1	2.8	0.8
n-Hexane	0.5	7.9	4.2	2.3
Iodomethane	17.0	13.5	15.2	15.1
Methanol	24.0	16.4	25.2	24.5
Nitrobenzene	14.0	16.1	12.5	12.8
Nitromethane	15.5	16.4	19.4	18.9
Tetrachloroethylene	5.5	10.4	7.6	5.5
Toluene	10.0	8.0	7.9	8.7
E.S.S.		473	170	144
M.C.		0.940	0.979	0.982

E.S.S. Error Sum of Squares. M.C. Multiple correlation coefficient. A. $\Delta\nu = 33.68KBM$. B. $\Delta\nu = 0.52E_T - 0.090M_V$.
C. $\Delta\nu = 0.532E_T - 0.196S^0 + 1.66\,\sigma^*$.

Table 90

The predicted infra-red solvent shifts (cm^{-1}) for di-iso-propyl ketone.

Solvent	Observed shift	Predicted shift		
		A	B	C
Acetonitrile	13	13.6	16.2	16.7
Anisole	11.5	9.8	7.9	7.9
Benzene	7.5	6.6	7.1	5.8
Benzonitrile	13.5	12.3	11.0	10.5
Bromoform	15.5	9.9	9.9	14.7
n-butyl ether	3.0	8.2	3.1	2.4
Carbon disulphide	6.5	7.4	7.6	6.2
Carbon tetrachloride	5.0	6.4	5.6	4.4
Chloroform	16.5	11.3	10.3	15.4
Cyclohexane	1.0	5.8	3.6	2.4
o-Dichlorobenzene	10.5	12.2	7.6	7.7
1,2-Dichloroethane	13.0	12.2	12.1	13.3
Dichloromethane	14.0	12.0	12.5	15.3
Ethanol	18.0	13.4	19.3	16.3
Ethyl ether	3.5	8.8	6.5	5.6
n-Heptane	0.0	6.8	4.2	2.9
n-Hexane	0.0	6.7	3.2	2.0
Iodomethane	9.0	11.3	11.9	11.9
Methanol	21.0	13.8	22.8	20.1
Nitobenzene	13.5	13.6	11.0	10.5
Nitromethane	14.5	15.2	16.4	17.1
Tetrachloroethylene	4.0	8.8	5.4	4.3
Toluene	6.0	6.8	6.0	6.3
E.S.S.		403	294	218
M.C.		0.936	0.968	0.983

E.S.S. Error Sum of Squares. M.C. Multiple correlation coefficient. A. $\Delta\nu = 28.41KBM$. B. $\Delta\nu = 0.595E_T - 4.82R_d$.
C $\Delta\nu = 0.49E_T - 4.03R_d + 2.66\sigma^*$.

CHAPTER 7

Temperature effects on the infra-red spectrum of phthalic anhydride

A. INTRODUCTION

Where there are related vibrations of the same frequency, in small molecules, it is quite common for coupling to occur, leading to the splitting of the band into two components, above and below the expected frequency. This effect has only been observed in certain carbonyl systems, principally peroxides (acyl and aroyl) and acid anhydrides. Structurally, the anhydrides differ from the peroxides in the greater proximity of the two carbonyl groups. Spectral studies of the carbonyl stretching region of anhydrides have been numerous.[286,287] The compounds are relatively stable, although drying of the solvent is essential to avoid hydrolysis to the acid.

Complete vibrational assignments of anhydrides are uncommon. Of the published assignments, that of Mirone and Chiorboli of maleic anhydride[287] is of particular interest as the Raman spectrum was used to simplify and endorse the assignment.

The twenty-one fundamental vibrations are shared among the symmetry species as follows:-

$$8a_1 + 7b_1 + 3a_2 + 3b_2$$

Of these, the a_1 species give polarised Raman lines and the a_2 are infra-red inactive. The carbonyl stretching modes were assigned as shown (Table 91).

Table 91

The assignment of the infra-red and Raman effect spectra of maleic anhydride in the region 1750-1900cm^{-1}.

Liquid Raman	Liquid Infra-red	Vapour Infra-red	Assignment
1873vw.p	1876vw		Combination band 1235+633 (A_1)
1846vs.p	1852s	1887-1873m	a_1 fundamental (C=O stretch)
		1852w	Combination band 1235+615 (B_2)
	1800m		Combination band 1235+560 (B_1)
			Combination band 1262+537 (B_2)
1775s.dp	1774vs	1816	b_1 fundamental (C=O stretch)
		1809	
		1801vs	

Mirone and Chiorboli recorded solution spectra in five solvents of varying polarity, (cyclohexane, carbon tetrachloride, benzene, chloroform, and n-butanol), and noted the splitting of the lower wavenumber carbonyl band. In view of the complex nature of the carbonyl region of phthalic anhydride, their observations are of interest. It was suggested that the band at 1795cm^{-1} could be explained as a combination tone (560+1235) of species B_1 enhanced by Fermi resonance with the carbonyl vibration of the same specis at 1785cm^{-1}, but this was dismissed due to the strong dependence of the intensity ratio on the nature of the solvent, whilst there was little change in wavenumber. The possibility of the splitting being due to

interactions with two different orientations of the solvent molecules with respect to the carbonyl groups was also dismissed, as splitting was observed in carbon tetrachloride, a spherical molecule. No alternative explainations were given.

Mirone and Chiorboli[288] had previously calculated the wavenumber separation in anhydrides on the basis of mechanical coupling alone. The observed splitting was, however, generally much greater than the calculated value (succinic anhydride, calculated value $10cm^{-1}$, observed value[289] $72cm^{-1}$), whilst better agreement was found in the calculations of splitting in orthoquinones. Mirone and Chiorboli also noted that the splitting in O=C-X-C=O systems only approached that observed in anhydrides when the central atom X was nitrogen (e.g. the splitting is $40-60cm^{-1}$ in phthalimide derivatives[290]).

The higher wavenumber absorption in maleic anhydride and succinic anhydride[291] was assigned to the in-phase vibration and the lower wavenumber band to the out-of-phase vibration, principally on the basis of the Raman effect evidence. Dauben and Epstein[289] and Bellamy et al,[292] reached a similar conclusion on the basis of the intensity ratio of the two carbonyl bands in a series of anhydrides.

Phthalic anhydride has featured in several general studies of anhydrides. The anhydride ring consists of five members; and due to the proximity of the benzene ring, conjugation is possible and the ring is probably stabilised by resonance.

Studies of the Raman spectrum in the carbonyl region, performed by Kohlrausch et al,[293] yielded two bands at 1775cm^{-1} and 1841cm^{-1}.

Cooke[294] quotes the following values for the infra-red spectrum of phthalic anhydride:

	Band position (cm^{-1})		
Nujol	1766	1791	1854
Chloroform	1775	1789	1854
Carbon tetrachloride	1779	1793	1858

Fayat and Foucaud[295] measured absolute intensities for a number of cyclic anhydrides in carbon tetrachloride solution. The results included a detailed infra-red spectrum of phthalic anhydride in the carbonyl region:

In carbon tetrachloride solution, four peaks at 1778cm^{-1} (b_1), 1791cm^{-1} (b_1), 1808cm^{-1} (b_1) and 1857cm^{-1} (a_1) were observed, these being shifted in nujol to 1762, 1789, 1806 and 1850cm^{-1} respectively. The assignment of three of the bands to b_1 modes would appear to be based on the Kohlrausch Raman effect evidence alone.

Fayat and Foucaud assumed that two bands were due to overtones enhanced by Fermi resonance, and the following combination bands were suggested as possibilities:-

$$534 + 1250 = 1784\ (B_1)$$

$$896\ (a_1) + 916\ (b_1) = 1808\ (B_1)$$

On this basis the bands at 1791 and 1857cm^{-1} (carbon tetrachloride) are accepted as the antisymmetric and symmetric carbonyl stretching modes respectively.

The majority of the literature dealing with the effects of temperature on spectra is concerned with measurement of infra-red spectra at low temperatures. Hermann, Harvey and Honts[296-298] have condensed much of this literature into a series of review articles.

In this study an attempt was made to determine if the observations were truly temperature effects, and not due to reaction or solvent evaporation. This was shown by recording the spectra in a rising and falling sequence for a chosen solvent. If the pattern obtained was due to temperature effects alone, the pattern should be repeated on cooling. If, however, irreversible reaction occurs the pattern observed on cooling will be radically altered. To avoid evaporation the study was terminated when the temperature came within 20^{o} of the boiling point of the solvent. In an attempt to minimise temperature effects on the solvent a compensating cell was used in the reference beam of the spectrometer.

B. EXPERIMENTAL

Phthalic anhydride of BDH laboratory reagent, guaranteed assay of 99%, was used in this study. The anhydride was purified by sublimation.

Solute concentrations of 1%w/v were used where possible, but in certain cases the low solubility of the solute necessitated the use of more dilute solutions. Wavenumber positions of the peaks in the region 1900-1700cm^{-1} are given in Table 92. Table 93 presents ratios of the heights of the peaks at the higher temperature to the lower temperature. The position of the peaks in various solvents, as presented in Table 92 were obtained on a Perkin Elmer 457 Spectrometer. Calibration of the region was based on a polystyrene spectrum.[114] The temperature effects were recorded on a Unicam SP 100 spectrometer using 1mm cells manufactured by the Research and Industrial Instrument Company. A degree of compensation was ensured by filling the reference cell with the solvent under investigation, but the cells were not accurately compensated. To obtain continuity of procedure the same cell was used for the pure solvent throughout. With compensating cells it is normal procedure to compensate with both cells filled with the solvent and later alter the path length to allow for the solute concentration. This was not possible with the equipment available. Errors on this account are thought to be small as the path length was small, solute concentrations were uniformly

low and the solvents used exhibited few, if any, absorptions in this region. The cells had provision for electrical heating. Temperatures were originally recorded by a thermocouple. It was found more convenient, however, to calibrate the VARIAC settings with the thermocouple and by using a standard procedure calibrate the voltage settings in terms of temperatures. The temperatures of the two cells were found to agree within $\pm 2^{o}$ at temperatures below 373K. The temperatures quoted in the results are those of the solute cell. The temperature and solvent effects were repeated at least twice on each solvent, The results quoted in Table 93 are attributable to one of these determinations.

All spectra were recorded at least three times at each temperature to ensure reproducibility and observations were also made at intermediate temperatures. The "room temperature" readings were taken after the cells had equilibrated in the thermostat. After reaching the maximum temperature, the cells were allowed to cool back to the temperature of the equipment and further readings taken.

Table 92

Wavenumber positions of the peaks in the carbonyl stretching region of phthalic anhydride in various solvents at 299K.

Solvent	Wavenumber Position			
Acetonitrile	1855.5		1791	1778
Anisole	1853		1789	1776.5
Benzaldehyde	1851.5		1788	1774.5
Benzene	1854.5		1789	1777
Bromoform	1852.5		1787	1774
Carbon disulphide	1856.5		1790	1777.5
Carbon tetrachloride	1857.5	1808	1790.5	1778
Chloroform	1855.5	1808	1789.5	1776.5
o-Dichlorobenzene	1853.5	1808	1788.5	1776.5
1,2-Dichloroethane	1854.5	1808	1789.5	1777
Dioxan	1855.5		1790	1778
Ethanol*	1854.5		1791	1777
Ethyl ether	1856	1807.5	1790.5	1778
Methanol*	1855.5	1808.5	1791	1777.5
Methyl ethyl ketone	1854.5	1806	1788.5	1776.5
Nitrobenzene	1852.5	1806	1788	1775
Tetrachloroethylene	1857	1807.5	1790	1777
Toluene	1853.5	1807	1789	1777.5
Trichloroethylene	1854.5	1807.5	1789	1777

Data are quoted to the nearest $0.5cm^{-1}$. The concentration of solutions in cyclohexane and n-hexane were not sufficient to allow accurate measurements, other solutions were 1% w/v

cont.

except for carbon disulphide, carbon tetrachloride and tetrachloroethylene which were saturated at < 1% w/v.

* Peak observed at 1725cm^{-1} due to formation of ester.

Table 93

The ratio of the height of the peaks in the carbonyl stretching region of phathalic anhydride at high and low temperatures.*

Solvent	Maximum Temperature	Ratio		
		1860	1790	1780
Acetonitrile	339K	0.833	0.994	0.864
Anisole	354K	0.872	0.972	0.813
Benzaldehyde	354K	0.847	0.975	0.832
Benzene	339K	0.827	0.948	0.781
Bromoform	354K	0.827	0.952	0.849
Carbon tetrachloride	339K	0.923	1.034	0.889
Chloroform	323K	0.976	1.016	0.950
o-Dichlorobenzene	385K	0.707	0.876	0.667
1,2-Dichloroethane	339K	0.867	0.930	0.832
Dioxan	339K	0.880	1.000	0.850
Ethanol	357K	0.0	0.0	0.0
Methanol	323K	0.0	0.0	0.0
Methyl ethyl ketone	339K	0.867	0.921	0.830
Nitrobenzene	339K	0.852	0.926	0.869
Toluene	339K	0.916	0.967	0.867

* All cells were left to equilibrate in the equipment before heating commenced, room temperature is thus considered as the thermostated temperature of the SP 100, that is (299 $\pm$ 1K).

C. DISCUSSION

The results obtained have been analysed for information on:-

(a) The effect of temperature on the shape, intensity (based on peak height measurement) and wavenumber position of all peaks in the carbonyl stretching region of phthalic anhydride.

(b) The effect of solvents on the relative intensity of selected peaks in the carbonyl stretching region at room temperature.

(c) The effect of varying the solvent on the wavenumber position of the peaks at room temperature.

C.1. Temperature effects

Phthalic anhydride has been studied in fifteen solvents at various temperatures. Reproduction of the spectra obtained is limited to two solvents, 1,2-dichloroethane (Fig. 39) and methanol (Fig. 40), as these adequately represent the two distinct trends observed.

No attempt has been made to calculate the absolute or relative intensities of the peaks. Observations have been based on the variation in the heights of the peaks in the spectra of a particular solution with temperature. In this instance where the 1780, 1790cm^{-1} doublet in the spectrum of phthalic anhydride is of interest comparison of the relative

intensity of the peaks obtained by the fitting of triangles. is unlikely to produce a substantially more accurate result. The effect of temperature on the peak at approximately 1810cm^{-1} was not investigated.

The results, with the exception of methanol and ethanol fall into a distinct pattern. The peak at approximately 1790cm^{-1} is much less susceptible to changes in temperature than the other two peaks (Table 93). In all cases the ratio of this peak at the higher temperature to the lower temperature is larger than the corresponding ratios of either the 1780 or 1860cm^{-1} peak. In ten of the solvents the 1780cm^{-1} peak was the most susceptible to the effect of temperature, while in three solvents it was the 1860cm^{-1} peak. If the observed ratios are averaged over the thirteen solvents studied, the result is as follows:-

Peak (cm^{-1})	1860	1790	1780
Average ratio	0.861	0.962	0.838

Even allowing for the inaccuracies in measurement, (choice of baseline, evaporation of solvent, etc.) the above ratios suggest that the 1860 and 1780 peaks are affected similarly by temperature.

All the peaks studied decreased in intensity as the temperature rose. This is in agreement with the findings of Kamhawy[299] who studied solutions of water, acetone and piperazine over the range 283K to 322K (carbon tetrachloride)

Fig. 39

Spectra for phthalic anhydride in 1,2-dichloroethane at room temperature (299K) - - - and 339K - . - .

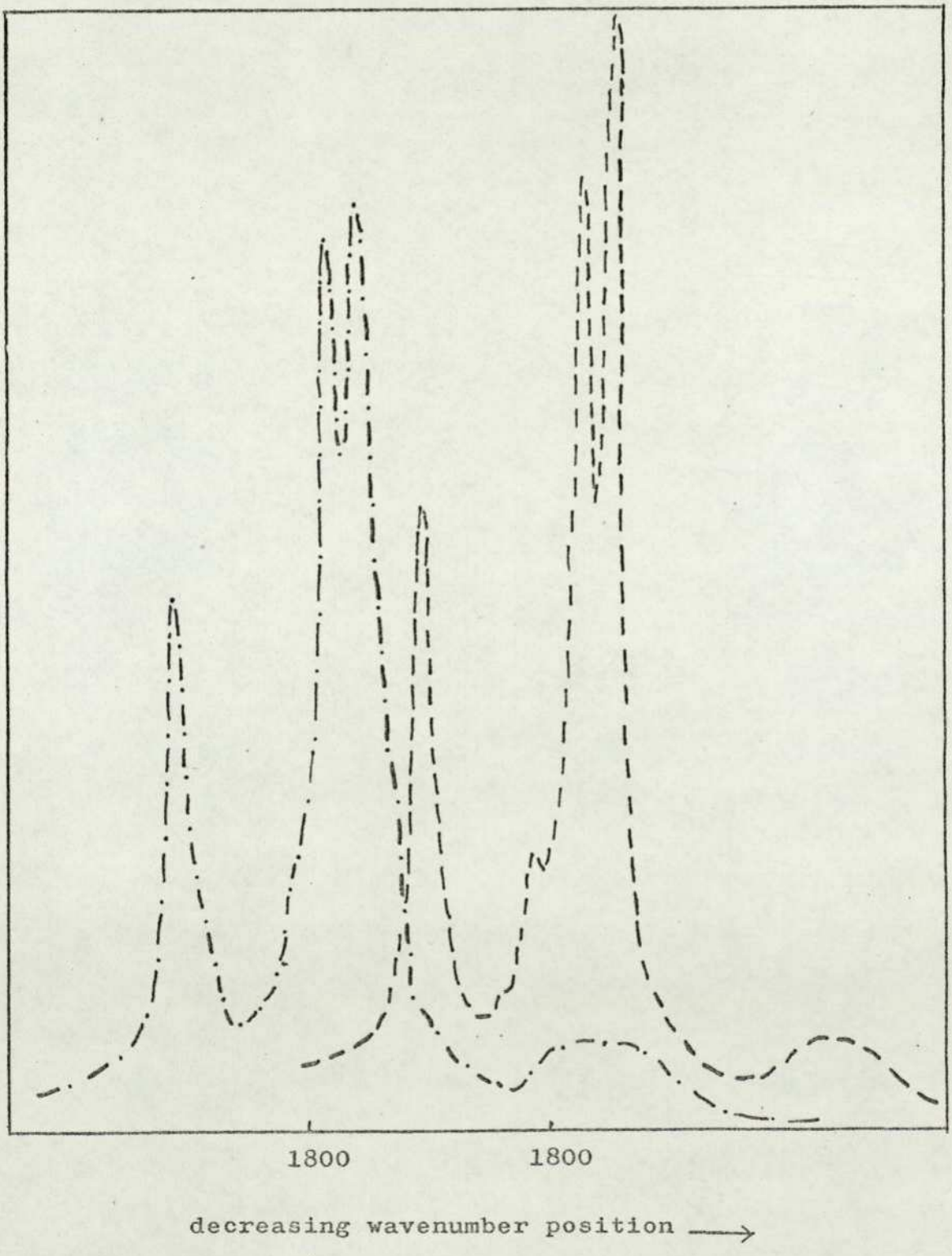
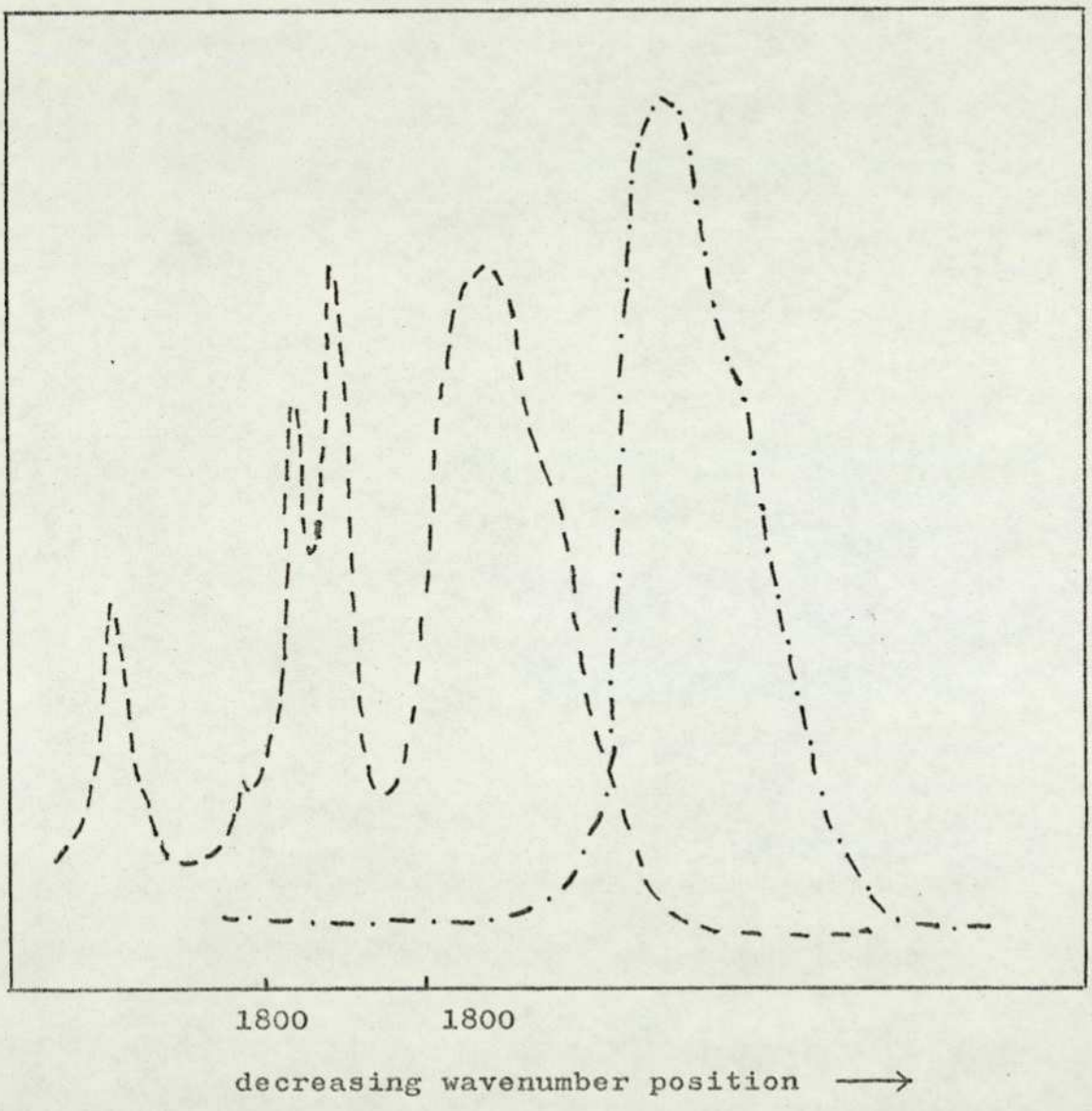


Fig. 40

Spectra for phthalic anhydride in methanol at room temperature (299K) - - - and 339K - • -



and 284K to 353K (toluene). The absorption of the functional groups studied decreased as the temperature was increased. The magnitude of the decrease was dependent on the functional group, the mode of vibration and the solvent. Density corrections were made and the spectra were repeated on cooling.

Kamhawy suggested that, as solvation is temperature dependent, highly polar groupings would be more solvated than less polar groups and hence their absorptivities would be more sensitive to temperature. The fact that solvent effects at room temperature on carbonyl band frequencies[232] cannot be explained simply on a bulk dielectric theory such as the KBM relationship but require an interaction term such as the Taft factor would also appear to support Kamhawy's hypothesis.

The results of the present study do not substantiate this interpretation. It would be anticipated that the rate of change of peak height with temperature would be more marked in the case of those solvents capable of bonding with the carbonyl group of the anhydride. No marked trend in this respect was observed. Due to the low solubility of phthalic anhydride in non-polar solvents, only carbon tetrachloride could be classified as non-polar. In non-polar solvents (carbon tetrachloride), the effect of temperature on the peak height was relatively small, but not as small as the effect in chloroform.

Solvation of the carbonyl group may not be a linear function of temperature. The removal of solvent molecules may

be accelerated, as the thermal energy approaches the energy of the solvent-solute bond. Conversely, as the temperature rises more solvated species will be broken down, releasing solvent and solute molecules, speculation then arising as to the difference in heat capacity between the solvent, solute and solvated species. The increased number of species in solution as the temperature rises may result in a greater portion of the supplied thermal energy per degree temperature rise to be absorbed by unassociated species and hence the number of complexed molecules broken down will decrease as the temperature rises and the rate of decrease in the peak height will be less as the temperature increases.

In discussing the effect of temperature on the intensity of bands in terms of solvation, the effect of rupture of bonded species on the band position has been neglected. If the rupture of the bonds resulted in a shift in the band position, a decrease in the intensity of this band would automatically be expected. This was not the case and this will be discussed later. For phthalic anhydride, however, the temperature range studied was probably too small to allow sufficient solute species unassociated with solvent molecules to be formed to shift the band centre significantly. This is expected by comparison of the effect of solvents on hydroxyl bands and carbonyl bands. The observed shift in carbonyl bands is generally much smaller than for hydroxyl bands, while the effect of altering the concentration of a

liquid carbonyl compound in non-polar solvents, fails to give distinct monomer and associated bands, but rather a gradual shift in band centre.

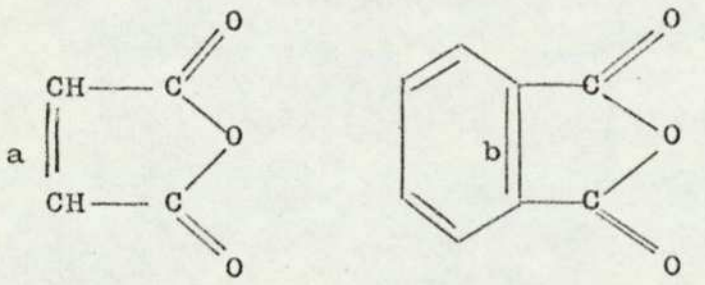
Theoretically the problem has been tackled by Ovander[300] who deduced that anharmonic interaction between intramolecular and intermolecular vibrations in the liquid phase leads to a fall in the integrated intensity with increasing temperature. This treatment suffers from the need to approximate in certain instances and the assumption that the complexed species are stable over the range of temperature considered. This is definitely not the case for hydrogen-bonded alcohol species[301] where temperature causes a disproportionately large decrease in the intensity of the polymer band. Illinger and Freeman[302] have deduced a more complex expression using a broadly similar approach to Ovander. Whilst useful deductions can be made on the effect of temperature on gas spectra, the relationship deduced has too many variables in the case of the condensed phase for useful information to be obtained.

On the basis of the present study it is suggested that the bands at 1860 and 1780cm^{-1} are characteristic of the coupled carbonyl vibrations and that the 1790cm^{-1} band is probably an overtone. A nujol mull spectrum of phthalic anhydride showed a strong band at 906cm^{-1} which would produce an overtone band in the 1800cm^{-1} region. The 1800cm^{-1} band. may also be less susceptible to solvent effects as it is probably a combination band involving skeletal vibrations,

which are usually little altered in wavenumber position by changes in solvent polarity.

In phthalic anhydride there are two effects, the coupling of the two carbonyl bands and Fermi resonance of one of the carbonyl bands with an overtone band of the same symmetry species. Cooke[294] sought comparison for the splitting of the bands with the spectrum of maleic anhydride. If we consider the structures of maleic and phthalic anhydrides (Fig. 41):-

Fig. 41



maleic anhydride

phthalic anhydride

the bonds a (maleic anhydride) and b (phthalic anhydride) involved in the five membered anhydride ring will differ in bond order, in that, whereas bond a can be conjugated to the carbonyl group, bond b is also conjugated within the benzene ring. This difference, together with the Fermi resonance effect could be sufficient to produce the observed separation.

D. WAVENUMBER POSITION

The wavenumber position of the peaks in the carbonyl region of phthalic anhydride was measured in the solvents listed in Table 92, at room temperature and at various temperatures up to the maximum recorded (Table 93). In no case was a significant wavenumber shift observed. Variations were not systemmatic and could be reasonably attributed to experimental errors.

The absence of a measureable shift for phthalic anhydride would appear consistent with the observed solvent effects at room temperature (Table 92). The maximum shifts for the three main solute bands at approximately 1850, 1790 and 1780cm^{-1}, from the observed wavenumber positions in carbon tetrachloride are respectively 6.0, 2.5 and 4.0cm^{-1}. These are remarkably small shifts and lead to the expectation of a correspondingly small shift in the position of these bands under the influence of temperature.

The analysis of the temperature effects on the infra-red spectrum of phthalic anhydride leads to the following conclusions:-

1) Increase in temperature causes rupture of solute-solvent bonds.
2) There is no noticeable change in band position, as the peaks due to monomer and solvent-solute associated species are virtually superimposed.

3) All bands decrease in intensity as the temperature is raised. The intensity decrease is probably due to three factors:-

   a) Rupture of associated species.

   b) Anharmonic interaction between intermolecular and intramolecular vibrations in the liquid phase.

   c) Reactionary effects, limited to studies in methanol and ethanol.

E. THE RATIO OF THE 1780/1790cm^{-1} PEAKS AT ROOM TEMPERATURE (299K)

The discussion of the small solvent shifts observed for the three peaks in the carbonyl stretching region mitigate against a solvent-solute interaction theory for the effect of temperature on the intensity of bands, however, the observations discussed in this section support this hypothesis.

The relative intensities of the 1780/1790cm^{-1} peaks varies, either peak of the doublet being stronger, depending on the solvent (Table 94). Although the trend is not completely regular, it is generally true that, the ratio of the 1780/1790cm^{-1} peaks increases as the E_T value, dielectric permittivity or dipole moment of the solvent increases. From the earlier study of solvent effects (Chapter 6), it is clear that no single parameter is perfect in describing solute interactions. For the tabulated parameters, the lowest ratios are observed in the case of non-polar solvents.

Macroscopically this is interpreted on the basis of the 1790cm^{-1} peak being an overtone and the 1780cm^{-1} peak a carbonyl fundamental vibration. The 1790cm^{-1} peak should then be little affected in its intensity by the solvent, whilst the intensity of the 1780cm^{-1} peak will increase in polar solvents due to association. The relatively low values for the ratio in ethanol and methanol are probably due to the polymeric nature of these solvents. The choice of a simple model to explain the observed effects has been deliberate as the effect

of coupling and Fermi resonance collectively are too complex for them to be reasonably included.

Table 94

The ratio of the heights of the peaks occuring in the carbonyl region at 1780 and 1790cm^{-1} at room temperature in various solvents. The solvents are listed in order of E_T values.

Solvent	Ratio	E_T[267] value	Dipole[284] moment	Dielectric[284] permittivity
Carbon tetrachloride	0.790	32.5	0	2.238
Carbon disulphide	0.717	32.6	0	2.641
Tetrachloroethylene	0.938	32.6	0	2.30
Toluene	0.924	33.9	0.39	2.379
Benzene	1.037	34.5	0	2.284
Ether	0.735	34.6	1.15	4.335
Trichloroethylene	1.01	35.0	0.9	3.42
p-Dioxan	1.579	36.0	0.45	2.209
o-Dichlorobenzene	1.02	37.0	2.26	9.93
Anisole	1.111	37.2	1.20	4.33
Bromoform	1.462	39.0	0.99	4.39
Chloroform	1.187	39.1	1.15	4.81
1,2-Dichloroethane	1.173	41.9	2.06	10.36
Nitrobenzene	1.215	42.0	3.99	34.82
Methyl ethyl ketone	1.131	42.2	2.75	18.51
Acetonitrile	1.515	46.0	3.37	37.5
Ethanol	0.98	51.9	1.68	24.30
Methanol	1.28	55.0	1.66	32.63

F. SOLVENT EFFECTS ON THE CARBONYL STRETCHING REGION AT ROOM TEMPERATURE

The positions of the peaks in the carbonyl region of phthalic anhydride are presented in Table 92. The solvents listed include those used for the temperature effect study together with other solvents unsuitable due to volatility or low solute solubility. Wavenumber positions for the 1810cm^{-1} peak are included where this peak was sufficiently pronounced to be measured with accuracy. The results themselves are remarkable only in the extent to which all the peaks are unaffected by the solvent. As such the results have not been treated under a multiple correlation analysis. The shift observed is smaller than that observed for open chain anhydrides.[289] Although the shift is small, the trend follows the known order of solvent polarity, and it would appear that the small shift is due to the constraints implanted by the anhydride ring, coupled with the conjugative effect of the benzene ring.

G. CONCLUSION

The results of the present study suggest that the effect of temperature on spectra could be used to distinguish between fundamental and overtone bands in Fermi resonance. The simplicity of the approach does not undermine the true importance of the principle deduced, namely that overtone bands are generally less affected than solvated fundamental bands in Fermi resonance.

Generally overtone bands are distinguished, as in the case of ethylene carbonate[303] by resorting to vapour studies, when the wavenumber position of the fundamental may be sufficiently displaced for the resonance effect to be removed. In the case of relatively unstable liquids or solids the attainment of the vapour phase may cause operating difficulties and a study along the present lines may prove profitable. It is, however, apparent that a more conclusive study could have been made had accurately recorded Raman effect data been available.

In a recent publication, Vledder et al[304] have given a detailed assignment for acetic anhydride. The vapour, liquid and solution infra-red spectra and Raman effect data have been substantiated by a force field treatment. The results obtained do not alter the foregoing conclusions.

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APPENDIX

APPENDIX 1

```
      MASTER J C HUGHES
      REAL INT1,M
      DIMENSION A(100),B(100),Y(100),R(100),X(100)
      WRITE (2,8)
    8 FORMAT (1H1,49H       METHYL TRICHLOROACETIMIDATE          )
      READ (1,1) NOS
      DO 100 NNOS=1,NOS
      DO 70 K=1,2
      READ(1,1)N
    1 FORMAT(IO)
      READ(1,2) (A(I),B(I),Y(I),I=1,N)
    2 FORMAT (3FO.O)
   87 DO 88 I=1,N
      X(I)=A(I)/B(I)
   88 CONTINUE
   35 IF(K-1)100,81,102
   81 DO 82 I=1,N
      Y(I)=2.2725+(0.00040303*Y(I))
   82 CONTINUE
      GO TO 101
  102 DO 65 I=1,N
      R(I)=Y(I)*Y(I)
      Y(I)=R(I)
   65 CONTINUE
  101 SUMX=0.0
      SUMY=0.0
      SUMXX=0.0
      SUMXY=0.0
      WRITE (2,3)
    3 FORMAT (1X 1HX 13X 1HY 13X 1HA 13X 1HB)
      WRITE(2,72) (X(I),Y(I),A(I),B(I),I=1,N)
   72 FORMAT (1H,F10.7,3X,F10.7,3X,F10.7,3X,F10.7)
      DO 4 I=1,N
      SUMX=SUMX+X(I)
      SUMY=SUMY+Y(I)
      SUMXX=SUMXX+X(I)*X(I)
```

cont.

Appendix 1 cont.

```
      SUMXY=SUMXY+X(I)*Y(I)
    4 CONTINUE
      WRITE(2,6) SUMX,SUMY,SUMXX,SUMXY
    6 FORMAT(7HO SUMX=F14.6/6H SUMY=F14.6/7H SUMXX=F17.8/7H
                                                SUMXY=F17.8)
      S1=SUMXY*N-SUMX*SUMY
      S2=SUMXX*N-SUMX*SUMX
      S3=SUMXX*SUMY-SUMX*SUMXY
      GRA1=S1/S2
      INT1=S3/S2
      WRITE(2,7)GRA1,INT1
    7 FORMAT(22HO GRADIENT OF LINE M=F13.9/24H INTERCEPT AT
                                          Y AXIS C=F20.12)
   36 IF(K-1)104,105,106
  104 STOP
  105 ZINT1=INT1
      ZGRA1=GRA1
      GO TO 70
  106 YINT=INT1
      YGRA1=GRA1
   70 CONTINUE
   37 READ(1,14)M
   14 FORMAT(F0.0)
   69 WRITE(2,71)M
   71 FORMAT(4HO M=F10.5)
      P=0.18811*M*ZGRA1-0.19064*M*YGRA1
      Q=SQRT(P*298.1)
      D=0.012812*Q
      WRITE(2,15),D
   15 FORMAT(16HO DIPOLE MOMENT=F10.7)
  100 CONTINUE
      STOP
      END
```

APPENDIX 2

X(weight fraction)	Y(dielectric permittivity)
0.00000	2.31700
0.06710	2.44060
0.12420	2.59310
0.17510	2.71980
0.22090	2.83220
0.26330	2.95780
0.30050	3.05170

Sum X = 1.151100
Sum Y = 18.912200
Sum XX = 0.25901201
Sum XY = 3.28352183
Gradient = 2.489114376
Intercept = 2.292425777442

X(weight fraction)	Y(refractive index squared)
0.00000	2.24700
0.06710	2.25000
0.12420	2.25060
0.17510	2.25691
0.22090	2.25961
0.26330	2.26172
0.30050	2.26653

Sum X = 1.151100
Sum Y = 15.792362
Sum XX = 0.25901201
Sum XY = 2.60143350
Gradient of line = 0.064432681
Intercept = 2.245456224336
M = 112.55975

Dipole Moment = 1.5846931

APPENDIX 3

XDS3 PROGRAM

```
JOB XDS3, 521022, J. C. HUGHES
SLOT 189
CHECKDISC 10
IN ED(PROGRAM XDS3)
LOAD #XDS3
CORE 1000
SWI ON 22,23
IN CRO/O (DATA)
ENTER 2
* * * * *
DOC DATA
HUGHES                    OUTPUTFILE        00000500
OBSERVATION MATRIX          HUGHES
COL NAMES                   HUGHES
ASHIFTDILECTMOLPOLDELVALMOLVOLSTENTRREFINDDIPMOMEEETTTKBMFUN
MATRIX      20      10      HUGHES           R0001010  LP

          (  DATA  CARDS  INTERPOSED  )

END OF DATA
CROS                        HUGHES
COVA                        HUGHES
CORR                        HUGHES
POBS                33      HUGHES           LP
PCOR                15      HUGHES           LP
PCOV                44      HUGHES           LP
REGR                        HUGHES           CROS  -9  1  4
DEPENDENT VARIABLE           ASHIFT          LP
INDE
DILECTMOLPOLDELVALMOLVOLSTENTRREFINDDIPMOMEEETTTKBMFUN
RESI
GET OFF
* * * * *
```

APPENDIX 4

Physical Data used in the infra-red solvent effect studies.

Solvent	D.P.[a]	R.I.(293K)[a]	δ value[c]	Molar volume[b]	D.M.[a]
Acetonitrile	37.5	1.344	11.9	52.253	3.37
Anisole	4.33	1.517	6.2*	108.630	1.20
Benzene	2.284	1.501	9.2	89.939	0.0
Benzonitrile	25.26	1.527	10.6	103.40	3.16
Bromoform	4.39	1.598[e]	8.6	88.233	0.99
Carbon disulphide	2.641	1.628[e]	10.0	61.003	2.20
Carbon tetrachloride	2.238	1.460	8.6	97.687	0.0
Chloroform	4.806	1.449	9.3	81.184	1.15
Cyclohexane	2.023	1.426	8.2	109.388	0.0
Cyclohexene	2.22	1.446	6.9*	101.482	0.28
Di-n-butyl ether	3.06	1.399	6.1*	170.031	1.22
o-Dichlorobenzene	9.93	1.551	10.0	113.053	2.26
1,2-Dichloroethane	10.36	1.445[e]	7.8*	79.920	2.06
Dichloromethane	9.08	1.425	9.7	64.950	1.55
Dioxan	2.209	1.422	9.9	85.799	0.45
Ethanol	24.3	1.361	12.7	58.704	1.68
Ethyl ether	4.335	1.353	7.4	105.576	1.15
n-Heptane	1.924	1.388	7.4	147.456	0.0
n-Hexane	1.890	1.375	7.3	131.596	0.08
Iodomethane	7.0	1.532	7.9*	63.06	1.35
Methanol	32.63	1.329	14.5	40.704	1.664
Nitrobenzene	34.82	1.553	10.0	103.154	3.99
Nitromethane	35.87	1.382	12.7	52.282	3.17
Pyridine	12.3	1.510	10.7	79.940	2.20
Tetrachloroethylene	2.3	1.506	9.4	103.242	0.0
Toluene	2.379	1.497	8.9	107.421	0.39
Trichloroethylene	3.42	1.478[e]	9.3	90.533	0.9

(a) Ref. 284 (b) Calculated from density values from Ref. 284
(c) Ref. 259 *Estimated value using SMALLS METHOD (Ref. 259)
(e) n_D values at 293K, calculated from n_D values at other temperatures using $\frac{\partial n}{\partial T}$. D.P. Dielectric permittivity. R.I. Refractive index. D.M. Dipole moment.

APPENDIX 4 (cont.)

Solvent	Taft factor[d]	E_T value[g]	KBM fun[h]	S^0_{298}[i]	Molar rad.[j]	Molar pol[a]
Acetonitrile	1.3	46.0	0.480	35.76	2.319	48.5
Anisole	(0.6)	37.2	0.345	60[f]	2.960	57.15
Benzene	0.6	34.5	0.231	41.41	2.779	26.96
Benzonitrile	(0.6)	42.0	0.471	56[f]	2.911	
Bromoform	2.5	39.0	0.347	59[f]	2.761	46.80
Carbon disulphide	0.0	32.6	0.261	36.1	2.442	21.58
Carbon tetrachloride	0.0	32.5	0.226	51.67	2.857	28.53
Chloroform	2.65	39.1	0.396	48.5	2.686	45.40
Cyclohexane	-0.15	30.0	0.203	48.84	2.966	27.82
Cyclohexene		30.5	0.224	51.67	2.893	29.32
Di-n-butyl ether	0.02	33.0	0.289	75[f]	3.436	69.36
o-Dichlorobenzene	(0.6)	37.0	0.428	61[f]	2.999	84.62
1,2-Dichloroethane	1.32	41.9	0.431	49.84	2.672	60.52
Dichloromethane	1.94	41.1	0.422	42.7	2.493	47.38
Dioxan		36.0	0.223	46.67	2.736	24.65
Ethanol	0.198	51.9	0.470	38.4	2.411	52.08
Ethyl ether	0.16	34.6	0.345	60.5	2.932	55.6
n-Heptane	-0.15	31.0	0.240	78.53	2.949	34.73
n-Hexane	-0.16	30.9	0.235	70.76	3.155	30.12
Iodomethane	0.555	40.0	0.400	38.9	2.469	37.85
Methanol	0.85	55.0	0.485	30.3	2.134	37.15
Nitrobenzene	(0.6)	42.0	0.479	53.60	2.909	94.71
Nitromethane	1.4	46.3	0.486	41.05	2.319	49.17
Pyridine		40.2	0.442	42.52	2.672	84.62
Tetrachloroethylene	0.0	32.6	0.232	60.4[f]	2.910	31.22
Toluene	(0.6)	33.9	0.239	52.81	2.949	33.85
Trichloroethylene		35.0	0.309	57.63	2.785	40.41

Taft factor values in brackets refer to approximate values only.
(d) Data from Refs 276-281. (g) Ref. 267. (h) Calculated from dielectric permittivity data from Ref. 284. (i) Ref. 285.
(j) Calculated from Molar Volume figures.

APPENDIX 5

Wavenumber positions of the $\nu C{=}O$ band in various solutes. The figures on the left hand side of each of the following tables refer to the following solvents.

Acetonitrile	1	Ethanol	16
Anisole	2	Ethyl ether	17
Benzene	3	n-Heptane	18
Benzonitrile	4	n-Hexane	19
Bromoform	5	Iodomethane	20
Carbon disulphide	6	Methanol	21
Carbon tetrachloride	7	Nitrobenzene	22
Chloroform	8	Nitromethane	23
Cyclohexane	9	n-Pentane	24
Cyclohexene	10	Pyridine	25
Di-n-butyl ether	11	s-Tetrachloroethane	26
o-Dichlorobenzene	12	Tetrachloroethylene	27
1,2-Dichloroethane	13	Toluene	28
Dichloromethane	14	Trichloroethylene	29
Dioxan	15	p-Xylene	30

APPENDIX 5 (cont.)

	Di-isopropyl ketone	Di-isobutyl ketone	p-Amino acetophenone	Di-n-Heptyl ketone
1	1708	1708.5	1666	1708
2	1709.5	1709	1667.5	1710.5
3	1713.5	1711.5	1671.5	1713
4	1707.5	1707	1664.5	1709
5	1705.5	1706	1660.5	1706
6	1714.5	1712	1673.5	1714
7	1716	1713.5	1676.5	1714.5
8	1704.5	1706	1664	1707.5
9	1720	1717	1681.5	1721.5
10	1711.5	1713.5	1677.5	1717.5
11	1718	1709	1676.5	1719
12	1710.5	1715.5	1670	1711.5
13	1708	1708	1667.5	1709
14	1707	1708	1667.5	1708.5
15		1708.5	1668.5	
16	1703	1703		1697
17	1717.5	1717	1674	1717.5
18	1721	1720	1683	1722.5
19	1721	1720.5	1683.5	1722.5
20	1712	1711	1669	1706
21	1700	1703		1699
22	1707.5	1708.5	1666	1709
23	1706.5	1707	1666.5	1707.5
24	1721	1721		1723
25	1707.5	1708	1663	1711
26	1705.5	1705.5	1662.5	1705
27	1717	1714	1678.5	1717.5
28	1715	1712.5	1673.5	1713
29	1713	1712	1671.5	1712
30				

APPENDIX 5 (cont.)

	Benzyl acetate	Benzo-phenone	Diacetyl	Cinnam-aldehyde	Acetonyl acetone	m-Nitro acetophenone
1	1738	1661	1717	1679	1713.5	1695.5
2	1743	1660.5	1715	1680	1713.5	1694.5
3	1744.5	1663	1716	1682	1716	1697.5
4	1741	1659.5	1715.5	1677.5	1713.5	1694
5	1734.5	1655	1712.5	1672	1709	1692
6	1746	1662.5	1716	1684.5	1716.5	1699
7	1747	1665.5	1717.5	1686.5	1719.5	1701
8	1732	1655.5	1715	1676	1712	1694.5
9	1753	1668.5	1720.5	1692	1724.5	1704.5
10	1750.5	1667	1718.5	1689	1720	1702
11	1751	1667	1718.5	1689	1720.5	1701.5
12	1744.5	1660.5	1716	1680.5	1715	1696.5
13	1739	1660	1715.5	1678	1713	1695.5
14	1738	1659.5	1716	1678.5	1712.5	1695
15	1743	1662.5	1716	1680.5	1713.5	1697
16			1716	1670.5	1709.5	
17	1750	1667	1719.5	1687	1720.5	1702.5
18	1754.5	1670	1721	1692.5	1726	1705
19	1754.5	1670	1721.5	1693	1725.5	1705
20	1742.5	1660.5	1714.5	1680	1714	1695
21			1717	1672	1709	1691.5
22	1738.5	1658.5	1715	1678.5	1713	1694
23	1737	1660	1716	1677.5	1713	1694.5
24	1755	1671	1721	1693.5	1726.5	1705.5
25	1741	1659.5	1714	1677.5	1713.5	1693.5
26	1732	1665.5	1714	1673	1711.5	1694
27	1748.5		1717.5	1688.5	1719.5	1701.5
28	1745.5	1663.5	1716	1683	1716.5	1699
29	1743	1662	1716	1682.5	1716	1699
30		1664.5	1716		1716.5	1698.5

APPENDIX 5 (cont.)

	Acet-aldehyde	Amyl butyrate	Methyl chloroformate	Diethyl ketone	Methyl iso-propyl ketone
1	1725	1729.5	1785.5	1714	1711.5
2	1726	1732	1784.5	1714.5	1713
3	1727.5	1734.5	1785	1717	1715
4	1725	1729	1783.5	1713.5	1712.5
5	1721.5	1721.5	1777	1709	1704.5
6	1729	1735	1784.5	1718.5	1716
7	1731	1735.5		1720.5	1718
8	1725	1724.5	1780	1712	1707.5
9	1733	1743	1789	1725	1723.5
10		1741	1788	1722.5	1721.5
11	1731.5	1740	1788.5	1722	1721.5
12	1727.5	1731	1784.5	1715	1714.5
13	1725.5	1728	1783.5	1713.5	1712
14	1725	1726.5	1782.5	1713	1711
15	1725	1732	1785.5	1715.5	1714
16	1722.5	1716.5	1788	1709	1705
17	1731.5	1740.5	1789	1722	1719.5
18	1733	1744	1790	1725.5	1724
19	1733.5	1744	1790	1725.5	1724
20	1725.5	1732	1783.5	1714.5	1713.5
21	1721.5	1714	1788	1708	1703.5
22	1725	1729	1783	1713	1712
23	1724.5	1728	1784	1712.5	1709
24		1744.5	1790	1726.5	1724
25	1724	1730.5	Reaction	1714	1712
26	1723	1724	1779	1710.5	1704.5
27	1731	1738.5	1787	1721.5	1718.5
28	1728	1735.5	1786	1718.5	1716
29	1727.5	1731	1785	1716.5	1714
30		1737.5	1786	1719.5	1717

APPENDIX 5 (cont.)

	Methyl chloroacetate	Salicyl aldehyde	Methyl vinyl ketone	Benz-aldehyde	Methyl ethyl ketone
1	1761	1666	1681	1703	1714.5
2	1763	1665	1680	1702	1716.5
3		1665.5	1682.5	1705.5	1719.5
4	1760.5	1664.5	1679.5	1702	1714
5	1755	1663.5	1675.5	1698.5	1708
6	1772.5	1666	1683	1706.5	1715
7	1775.5	1668	1686	1709.5	1722.5
8	1757	1665.5	1678	1702	1710.5
9	1778.5	1669.5	1690	1713	1727.5
10	1777.5	1667.5		1711	1724.5
11	1775.5	1668	1687.5	1710.5	1724.5
12	1762	1665.5	1682	1704	1716.5
13	1760.5	1665.5	1680.5	1703	1713.5
14	1759.5	1665.5	1681	1702	1713.5
15	1761.5	1666	1682.5	1704	1711.5
16	1753		1675.5	1696.5	1708.5
17	1775.5	1667.5	1687.5	1709.5	1723.5
18	1779.5	1670	1691	1713.5	1728
19	1780	1670	1691	1713.5	1728
20		1664.5	1683.5	1703.5	1716
21	1750		1674.5	1696	1707.5
22	1760	1664.5	1679.5	1702	1713
23	1760	1666	1680	1702	1712.5
24	1781	1671	1692	1714	1727.5
25	1759	1664	1679.5	1702	1713
26	1756.5	1664.5	1676.5	1702	1709
27	1775	1668	1687	1710	1723
28	1772.5	1666	1684	1707	1720
29	1761.5	1667	1682.5	1706.5	1718.5
30			1685.5	1707.5	1721