Spectroscopic Studies of some Heterocyclic Hydrazones and their Metal Complexes

Thesis submitted for the Degree of Doctor of Philosophy

by

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I

Consult ere thou begin'st,
that done, go on
With all wise speed for execution.

Robert Herrick
1591-1674

Acknowledgements

I wish to thank my supervisor, Dr. C.F. Bell, for his help and guidance over the past three years. Thanks are also due to Dr. E.L. Short and Dr. G. Reed for their considerable assistance with computing, and Dr. C. Shaw for making available a Hanovia Photochemical Reactor.

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Abstract

The PMR spectra of the two isomers of pyridine-2-aldehyde-2'-pyridyl hydrazone in carbon tetrachloride, dimethyl sulphoxide, and benzene solutions have been studied. Specific associations between PAPHY molecules and solvent molecules have been proposed to account for the observed solvent shifts.

Dilution studies have shown that there are PAPHY-PAPHY molecular associations in solution. In the E-isomer these are of the n-donor type involving the lone pair electrons of the ring nitrogen atoms, whereas the Z-isomer association is a dipole-dipole interaction involving the aldehyde ring of different PAPHY molecules.

Evidence from long range coupling shows that the uncomplexed E and Z-PAPHY molecules possess a different configuration to the complexed molecules.

The chemical shift changes on isomerisation of the E to Z-isomer have been measured and those for the aldehyde ring are consistent with the withdrawal of charge from this ring via the nitrogen atom.

Metal complexes of the two isomers of PAPHY have been prepared and their PMR spectra studied. The chemical shifts changes on complex formation have been interpreted in terms of the variation in magnetic anistropy of the ring nitrogen atoms in the ligand molecule and the degree of back donation of d-electrons from the metal atom.

Contents

Abbreviations

ASIS	Aromatic Solvent Induced Shifts
Bipy.	2',2'-bipyridyl
Δ_x^y	Chemical shift of a proton in state x minus the shift of that proton in state y ($\nu_x - \nu_y$).
HMDS.	Hexamethyldisiloxane
Hz	Hertz
PAPHY.	Pyridine-2-aldehyde-2' -pyridylhydrazone
Phen.	1,10-phenanthroline
ppm.	Parts per Million
py.	Pyridine
TMS	Tetramethyl silane.

General Introduction

Theory of NMR

Some atomic nuclei act as though they are spinning and possess angular momentum and thus magnetic moments. The angular momentum is quantized in units of the modified Planck constant $\hbar (= \frac{h}{2\pi})$ The maximum measurable component of the angular momentum I in any direction may be written $I\hbar$ where I is integral or half integral and is known as the spin quantum number ($= \frac{1}{2}$ for ^1H). Thus

$$p = I\hbar \qquad 1$$

All nuclei with a spin quantum number greater than zero possess a magnetic moment μ and the magnetic moment vector is parallel to I. The maximum observable component along any direction (Z-direction) is given by

$$\mu_z = \gamma(I_z) \qquad 2$$

where I_z can take the values I, I-1,---- - I and γ is a constant for a nuclear species known as the magnetogyric ratio.

A nucleus thus has 2I+1 distinct states in which the angular momentum along a selected vector has values $I\hbar$, $(I-1)\hbar$, ------ $-I\hbar$ and the observed magnetic moment has values of $\gamma I\hbar$, $\gamma(I-1)\hbar$---$\gamma I\hbar$. In an external magnetic field H_0 taken in the Z-direction the nucleus will possess energy E given by

$$E = -\mu_z H_0 = \gamma(I_z H_0) \qquad 3$$

Therefore, there will be 2I+1 energy levels between which transitions may occur by the absorption or emission of energy quanta of magnitude $\gamma\hbar H_0$. If a small oscillating magnetic field is placed perpendicular

to the external field H_o energy may be absorbed from it into the nuclear spin system resulting in transitions between the energy levels. These transitions are governed by certain selection rules, one of which states that transitions may only occur between adjacent levels.

The frequency, ν, of the field required to induce a transition between adjacent levels is

$$\nu = \frac{E}{h} = \frac{\gamma H_o}{2\pi} \quad . \qquad 4$$

The Boltzmann distribution may be used to calculate the ratios of the number of nuclei in the energy levels between which transitions occur and it is found that at room temperature the lower energy level is slightly more populated. Thus a nett absorption of energy will occur. This absorption of energy is detected electronically and reproduced graphically giving the observed peaks in the NMR spectrum.

From equation 4 it can be seen that resonance for a particular nucleus will occur at a certain combination of ν and H_o. This resonance condition may be reached by variation of ν, keeping H_o constant or vice versa. On modern spectrometers ν is generally kept constant and the magnetic field swept until resonance occurs.

For the proton in a field of 14,100 gauss resonance is at 60MHz and at 23,500 gauss it is at 100MHz.

The Chemical Shift

From the preceding discussion it would appear that all nuclei of the same type would resonate at the same field value. For example in the case of the proton absorbing radiation at 60MHz resonance of all compounds of hydrogen might be expected to occur at 14,100 gauss. However, it is found that electrons surrounding nuclei in molecules modify the applied magnetic field experienced by protons in different parts of the molecule. The nuclei are thus magnetically screened and the magnitude (and sign) of the screening depends on the local electron density and neighbouring groups. Protons in different chemical environments will be shielded to different degrees and will resonate at different field values which will be characteristic of that particular chemical environment.

The modified field, H, experienced by the proton in particular environment is given by

$$H = H_0(1 - \sigma) \qquad 5$$

where σ is the nuclear screening constant which is independent of H_0 depending only on the electronic environment of the proton concerned.

From equation 4 it may be seen that resonance will occur at the frequency ν,

$$\nu = \frac{\gamma H}{2\pi} = \frac{H_0(1-\sigma)}{2\pi} \qquad 6$$

It is usual to measure the resonance position of a nucleus from a zero point reference which is the resonance of a suitable compound.

In PMR tetramethyl silane is frequently chosen as the reference compound as the single resonance from the methyl protons occurs at a higher field than the majority of other proton resonances. If the sample and reference protons resonate (at constant radio frequency) at fields H_S and H_R respectively then

$$\nu = \frac{H_S(1 - \sigma_S)}{2\pi} \qquad 7$$

and

$$\nu = \frac{H_R(1 - \sigma_R)}{2\pi} \qquad 8$$

If the chemical shift of the sample protons Δ_S is to be measured in hertz then

$$\Delta_S = H_R - H_S \qquad 9$$

H_R is arbitrarily taken as zero and chemical shifts downfield of this resonance are taken as positive. The difference between H_R and H_S will be proportional to the applied field and therefore chemical shifts are often measured on a dimensionless scale given the symbol δ defined by

$$\delta = \frac{H_R - H_S}{H_R} \times 10^6 = \frac{\sigma_R - \sigma_S}{1 - \sigma_S} \times 10^6 = \sigma_R - \sigma_S \times 10^6$$

Values of δ are given in parts per million (ppm). For the TMS resonance $\delta = 0$. On the τ scale the TMS resonance is assigned the arbitrary

position of 10 ppm.

It has been shown[1-5] that for aromatic systems there is a linear correlation between the variation in the chemical shift of a proton and the variation in charge at the carbon atom to which the proton is bonded. Proton magnetic resonance therefore provides a convenient means of studying variation of charge in aromatic systems induced by substitution into the ring or by bonding of an aromatic compound such a pyridine to a metal.

Spin-Spin Coupling.

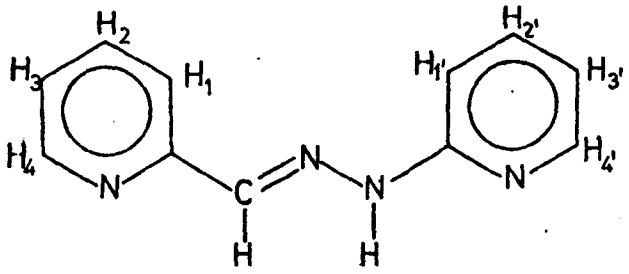
If a compound contains two or more protons which are chemically different then the PMR spectrum will frequently show fine structure in the proton resonances. This is a result of interaction between nuclei through the bonding electrons which causes splitting of energy levels and therefore several transitions in place of the single expected one. In general the resonance of a particular nucleus will be split into (n + 1) lines by n equivalently placed nuclei of spin $\frac{1}{2}$. For nuclei with $I > \frac{1}{2}$ more lines will be observed.

If the chemical shift between two protons A and B is large compared with the coupling constant J_{AB} (in Hz) then the spectrum is said to be first order and analysis is fairly straight forward. Coupling constants may be obtained readily from the multiplets. Non-first order spectra in which $\nu_A - \nu_B \not\ll J_{AB}$ are more difficult to analyse.

Unlike the chemical shift which is induced by, and proportional to, the applied field spin-spin coupling is independent of applied field strength.

Introduction to the Chemistry of Pyridine-2-Aldehyde-2'-Pyridylhydrazone.

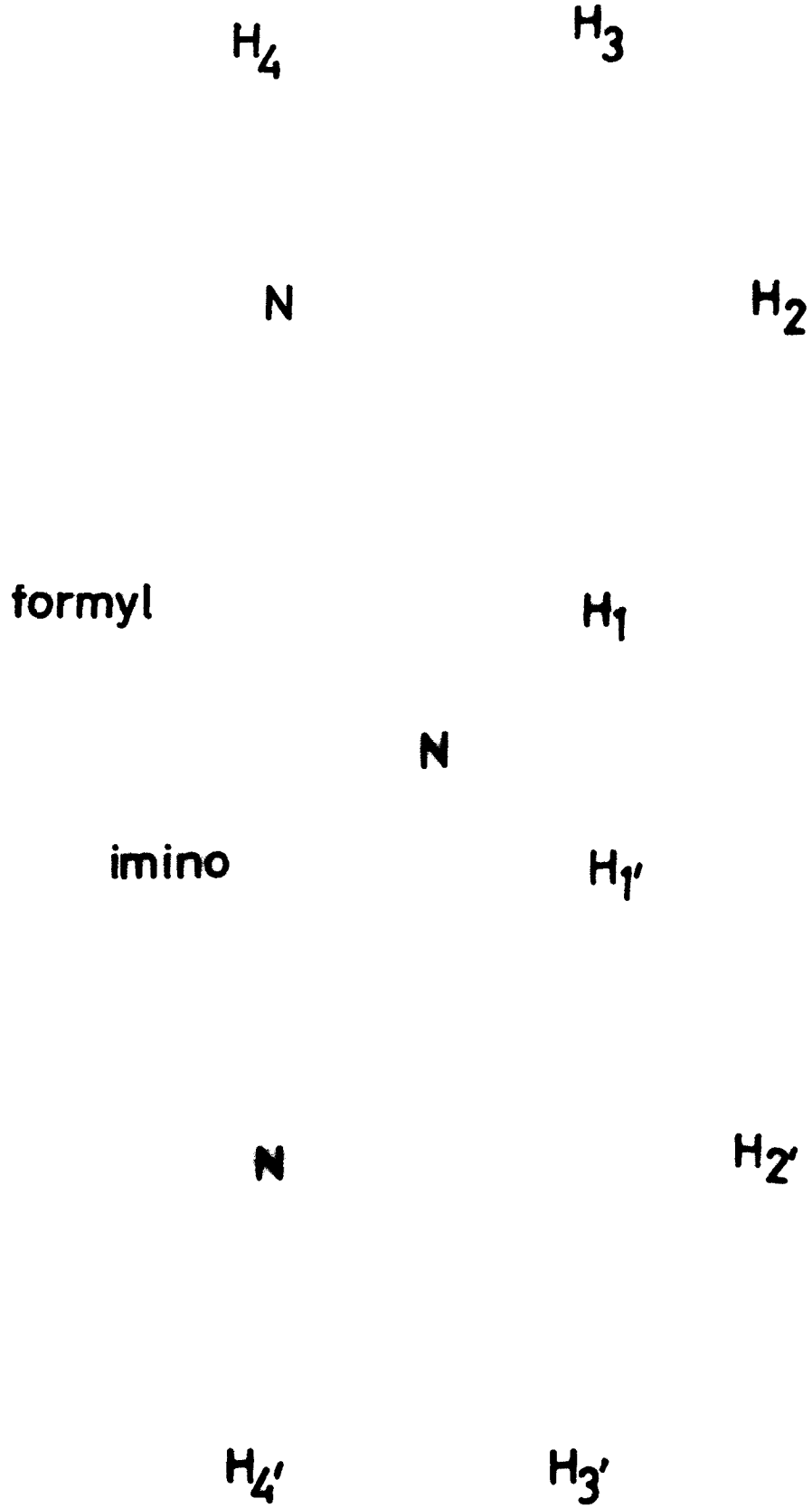
Condensation of pyridine-2-aldehyde and 2-pyridylhydrazine in ethanol gives the product pyridine-2-aldehyde-2'-pyridylhydrazone (1,3 bis-(2'-pyridyl)-2,3-diaza-1-propene) abbreviated to PAPHY (I).



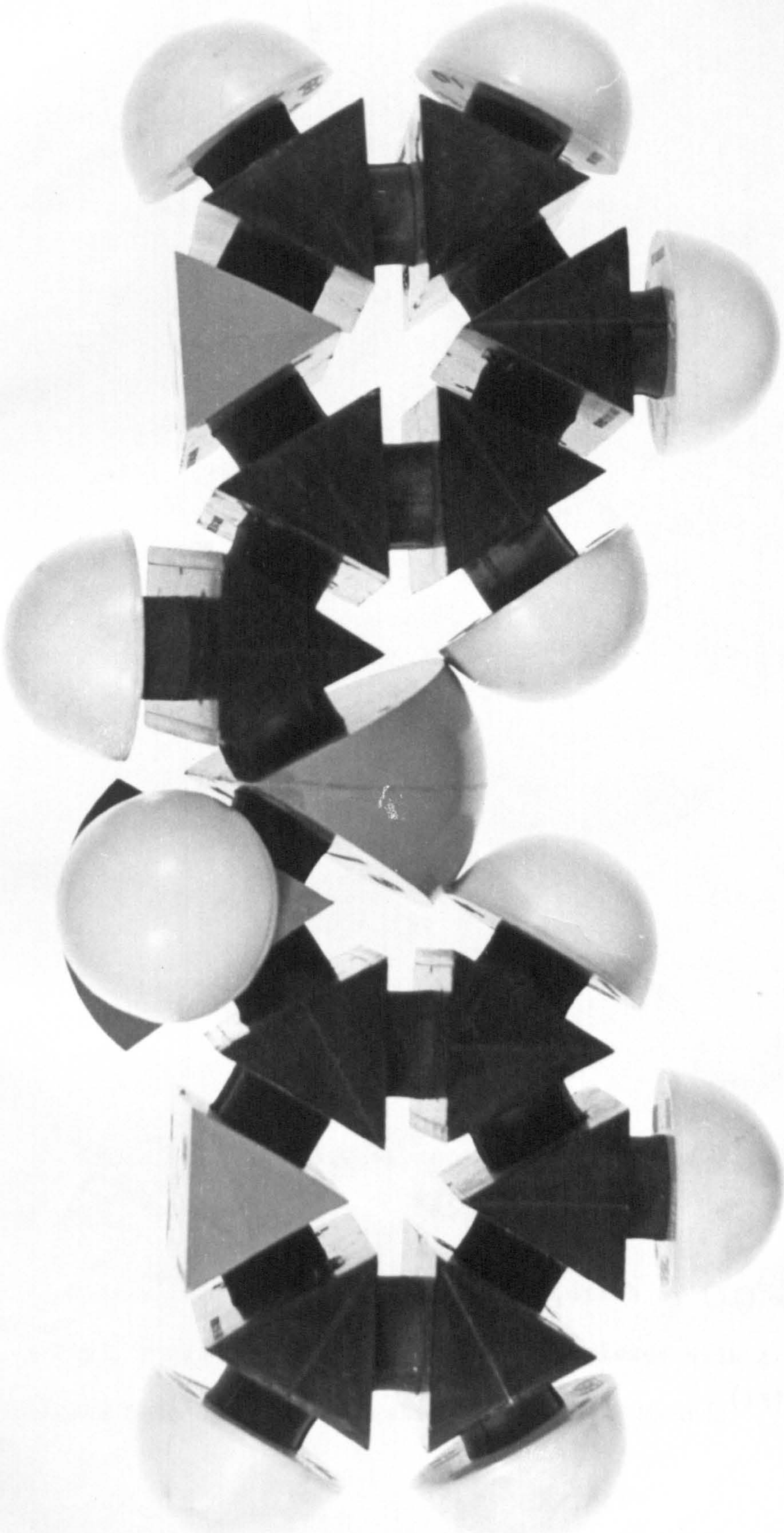
(I)

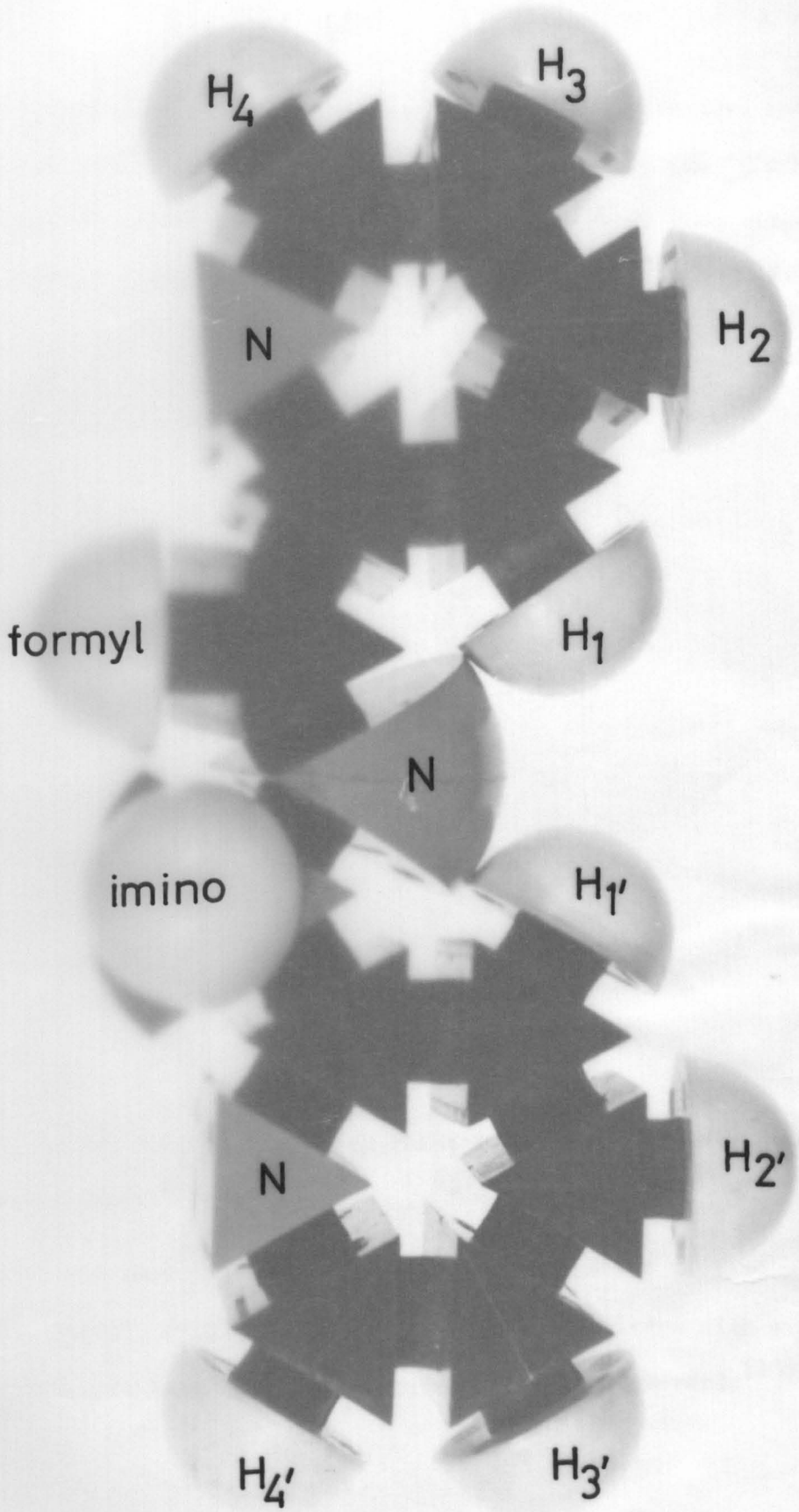
In this form designated the E-form PAPHY generally acts as a tridentate donor molecule forming mono or bis metal complexes. Reports have been published of E-PAPHY acting as a bidentate donor by means of the aldehyde ring nitrogen and the $\geq C{=}N-$ linkage nitrogen[8]. Considerable work on the metal complexes of E-PAPHY has been done by Lions et al[6,7] and Bell and Rose[9-11].

The imino proton is acidic as shown by its lowfield resonance position in the PMR spectrum of PAPHY. Electron withdrawal from the ligand by the metal ion when complexed enhances this acidity so that addition of alkali to the metal complexes results in removal of this proton. The resulting complex (designated $M(PAPY)_2$ where the absence of the H in PAPHY represents the loss of the imino proton) is highly coloured because of the increased charge delocalisation.



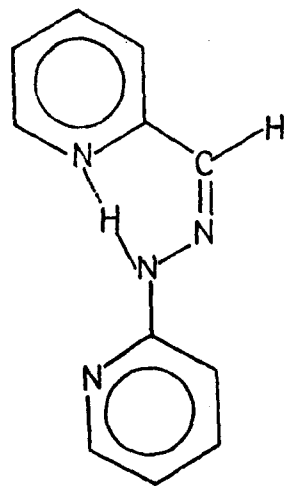
Courtaulds model of
E-PAPHY.(I)





Courtaulds model of
E-PAPHY.(I)

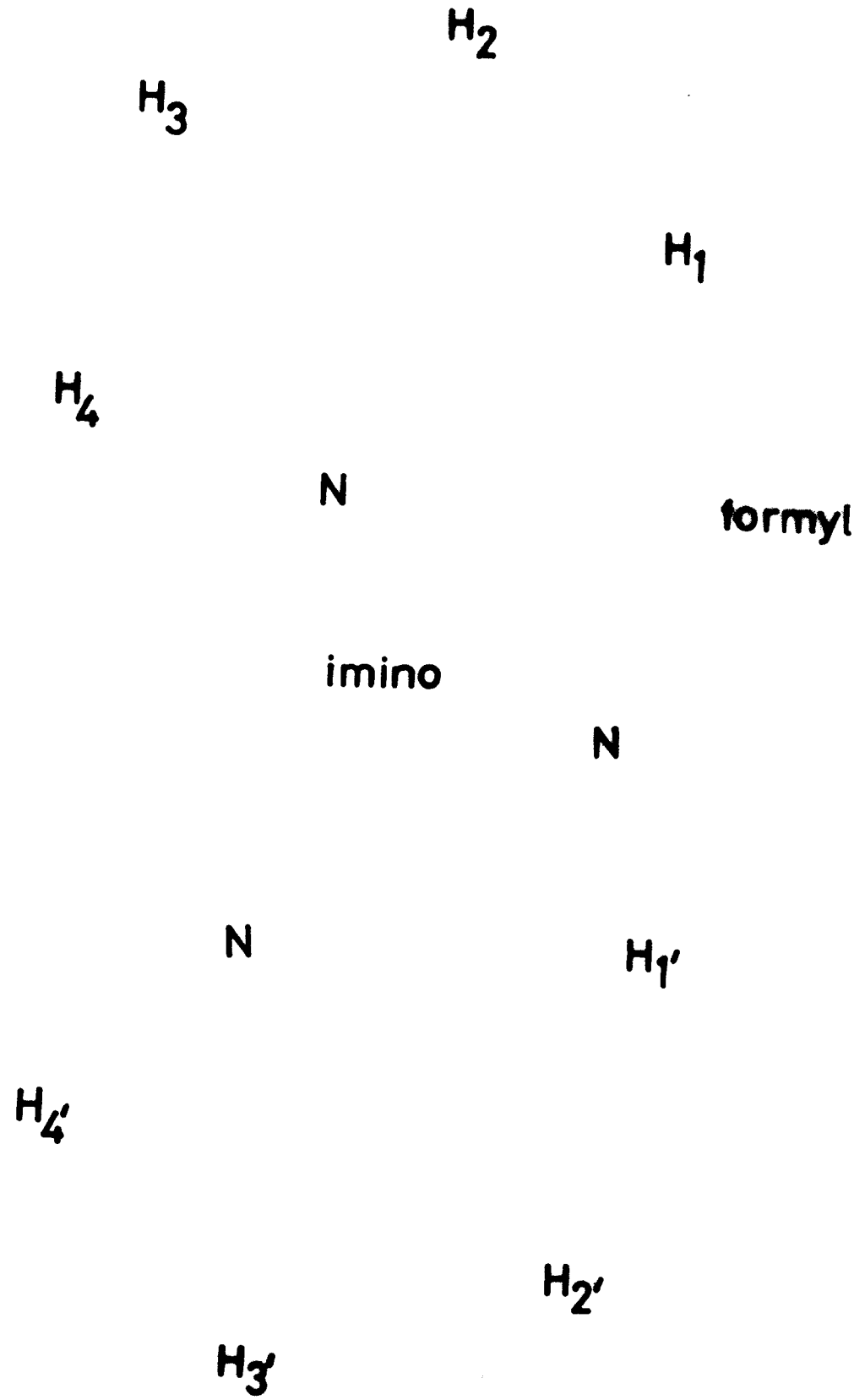
Irradiation of a benzene solution of E-PAPHY with u.v. radiation of the correct wavelength causes isomerisation about the >C=N- bond and subsequent hydrogen bonding between the aldehyde ring nitrogen and the imino proton. This compound is designated Z-PAPHY (II).



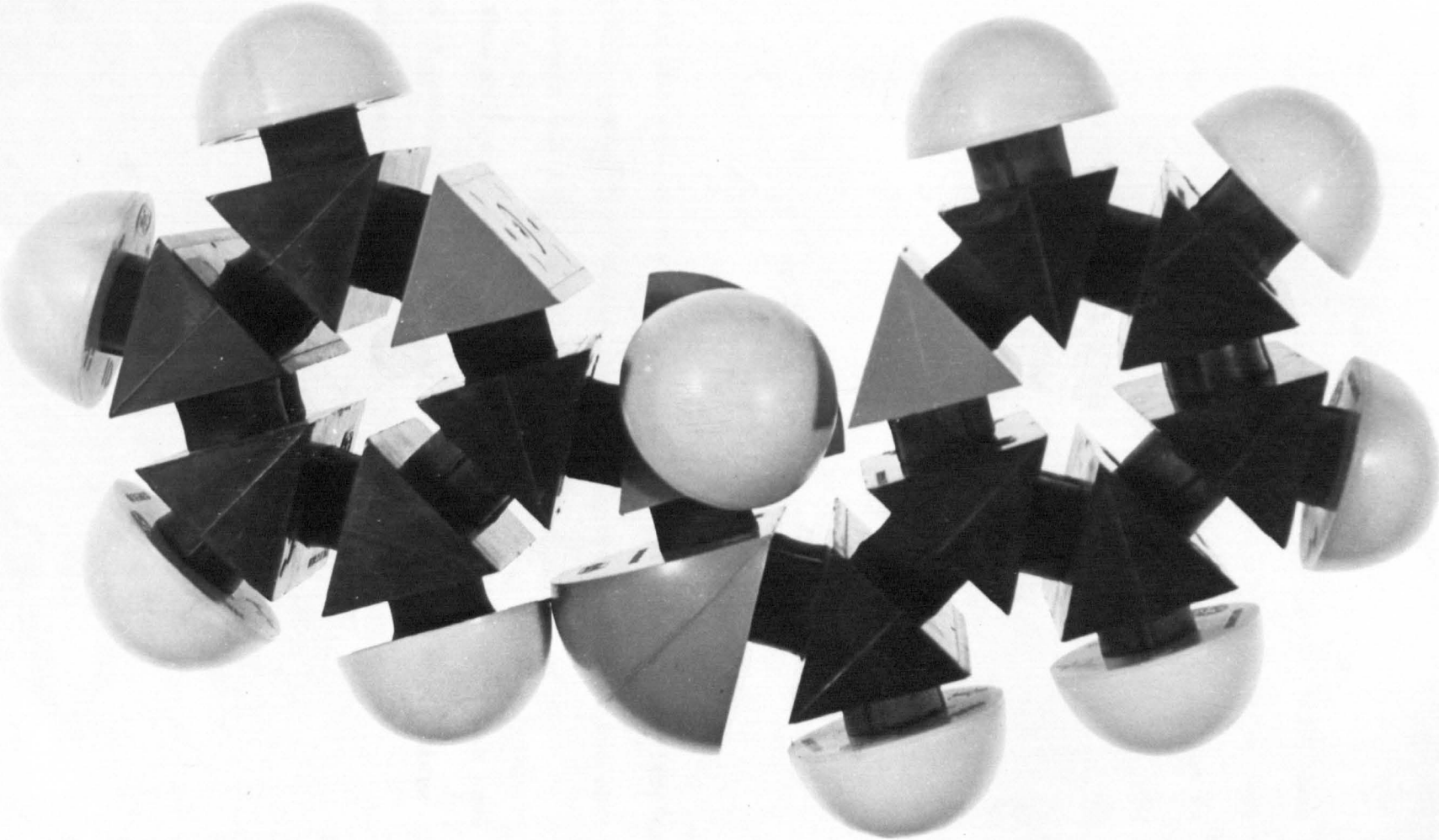
(II)

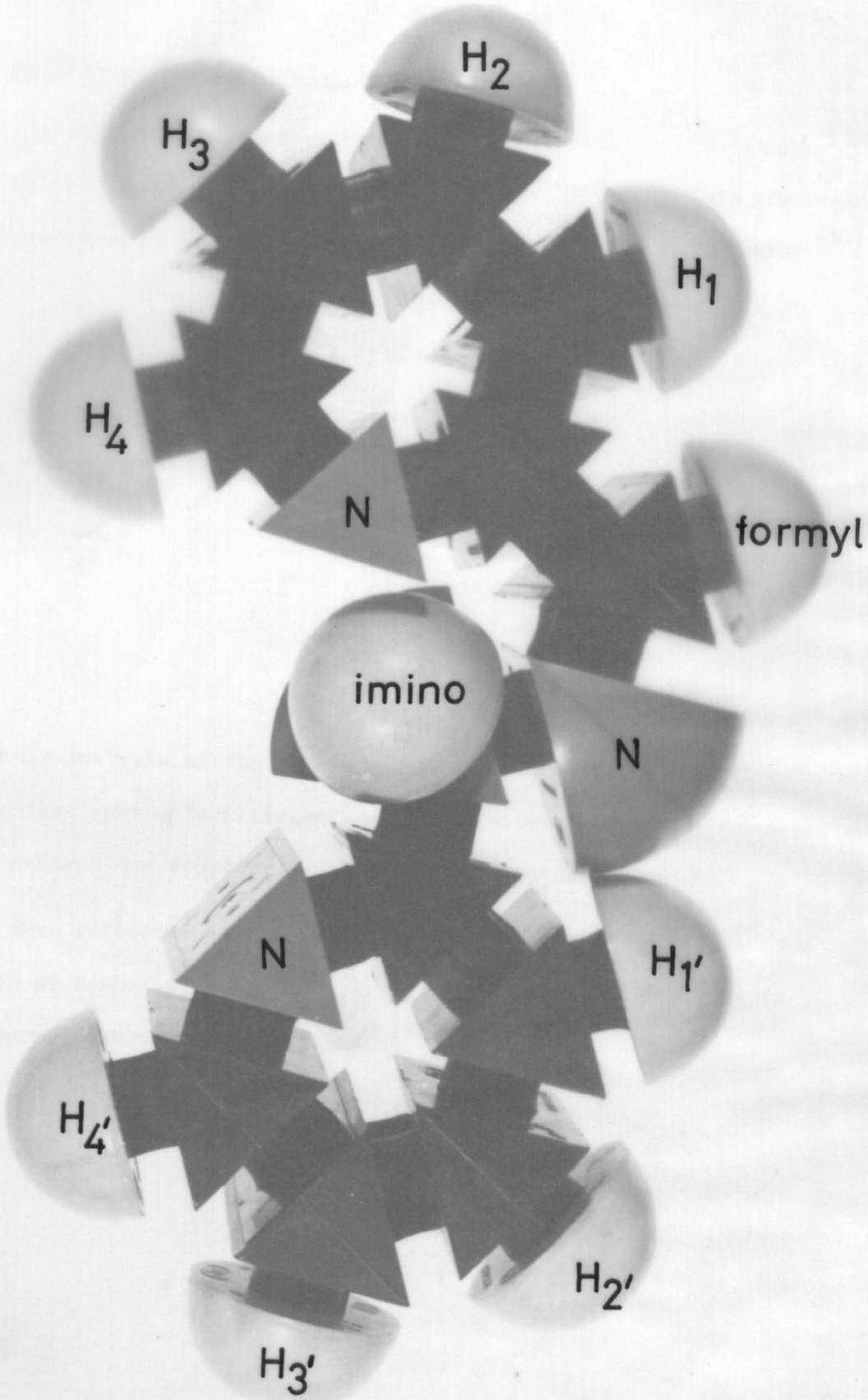
It is now only possible for PAPHY to act as a bidentate donor to a metal atom.

Bell and Rose[9,12] have investigated complexes of (II) with Rh(III), Fe(II), Pd(II), Mn(II) and Cd(II). Complexes with group VI metal carbonyls have been investigated by Dunn and Edwards[13].



Courtauld's model of
Z-PAPHY.(II).

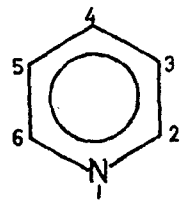




Courtauld's model of
Z-PAPHY.(II).

The Numbering of Heterocyclic Ring Systems

In this work the numbering of the ring protons of PAPHY does not follow that generally used for pyridine (III) and its derivatives. The numbering in (I) follows that originally used by Cooper et at[14]



(III)

in their analysis of the PMR spectrum of PAPHY in deuteriochloroform. Using this system facilitates comparison between computed and observed band centres and coupling constants.

When reference is made to methyl substituted PAPHYs this same method of numbering is used. For all other pyridine derivatives the normal numbering is employed.

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Chapter 1

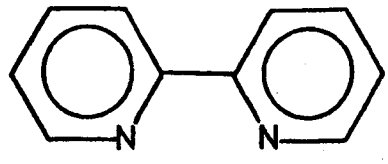
PMR Spectra of Pyridine and Related Nitrogen Heterocycles.

An early analysis of the spectrum of pyridine at 40MHz was performed by Schneider et al[1,2] using deuterated derivatives to simplify the spectrum. Castellano et al[3] analysed the spectrum of pyridine under conditions of nitrogen decoupling. The ^{13}C spectrum has been studied by Lauterbur[4].

Considerable work has been done on substituted pyridines[5-14], particularly by Brugel[5] and the Kowalewskis[6].

Pyridine protons resonate at quite low field because of the presence of an aromatic ring current (cf. benzene) in the molecule. The electronegative nitrogen atom causes the ring protons to resonate at lower field than those in benzene. The fact that the α-proton is further downfield is a result of the anisotropy of the sp^2 hybridised nitrogen atom[29], associated with the lone pair, which has a deshielding effect on protons in the plane of the ring.

The spectrum of bipyridyl has been fully analysed by Gil[16], who also determined the signs of the couplings, Kramer and West[17] and Castellano[15]. The molecule (I) is symmetrical and the corresponding protons in each ring are magnetically and chemically equivalent and



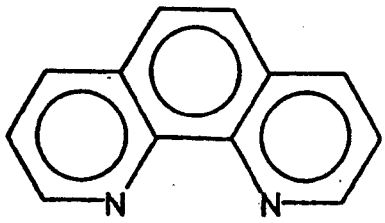
(I)

give rise to four separate resonances.

The study by Castellano et al[15] was in a variety of solvents and they concluded that the bipyridyl molecule assumed different conformations depending on whether the solvent was inert or proton donating, a conclusion later disputed by Spotswood and Tanzer[18]. The coupling constants did not vary much from solvent to solvent and were similar to a number determined for 2-substituted pyridines[13,11].

Considerable work has been done by Spotswood and Tanzer[18-20] on the spectrum of 2,2'-bipyridyl and its dimethyl derivatives[18]. They attributed the large chemical shift changes shown by the ring protons, when changing from an inert solvent to a hydrogen bonding solvent, to a masking of the pyridine ring dipole moment associated with the nitrogen lone pair.

The spectrum of 1,10-phenanthroline (II) has been investigated



(II)

by a number of workers[21-27]. The effect on the spectrum of substituting a methyl group into the rings was investigated by Carmen and Hall[21]

using deuterochloroform solutions. Their spectral parameters for the unsubstituted ligand agreed well with those obtained by Donckt et al[22] using carbon tetrachloride as solvent. Those obtained in dichloromethane by Blears and Danyluck[23] differed quite substantially, possibly partly due to differences in concentrations, these were not specified in references (22) and (23), and to a difference in degree of solute interaction with the solvents.

The Effect of Protonation on the PMR Spectra of Nitrogen Heterocycles

The protonation of pyridine using trifluoroacetic acid was investigated by Smith and Schneider[28]. All resonances shifted down field on protonation in the order $\gamma > \beta > \alpha$, consistent with the withdrawal of electron density from the ring via the nitrogen atom. Gil and Murrell[29] have shown that the low shielding of the α-proton compared with the β and γ-protons is partly a result of the magnetic anisotropy of the nitrogen atom and the dipole moment of the molecule, both associated with the nitrogen lone pair. On protonation the paramagnetic effect of the nitrogen atom's anisotropy on the α-proton is considerably reduced thus offsetting the deshielding effect of the positive charge and reducing the downfield shift of the α-proton.

It was noticed[29] the β and γ resonances were considerably broadened on protonation probably due to rapid proton exchange between the nitrogen atoms and the acid.

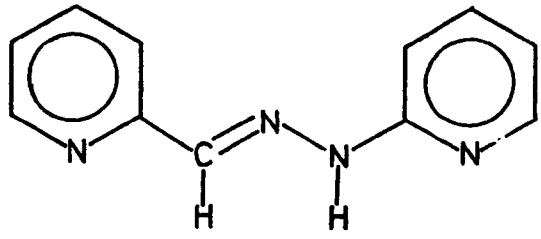
Palmer and Semple[30] found that salts of various azines with trifluoroacetic acid had different coupling constants to the parent heterocycles. They suggested that the change was a result of differences in bond angles and orders and charge densities in the heteroaromatic ring.

Merry and Goldstein[31] obtained the nitrogen decoupled spectrum of aqueous pyridine and the pyridinium ion. As in trifluoroacetic acid[28] all proton resonances moved down field.

The spectrum of protonated 1,10-phenanthroline was reported by Blears and Danyluck[23] and the changes in chemical shifts were similar to those observed for pyridine.

Recently (1970) Rund and Keller[24] studied the spectrum of 1,10-phenanthroline in various concentrations of aqueous acid and considered that the three protonated species ($phenH_2^{2+}$), ($phenH^+$) and ($phen_2H^+$) were present.

A partial analysis of the spectra of the E and Z isomers of pyridine-2-aldehyde-2'-pyridylhydrazone (III) and (IV), was performed



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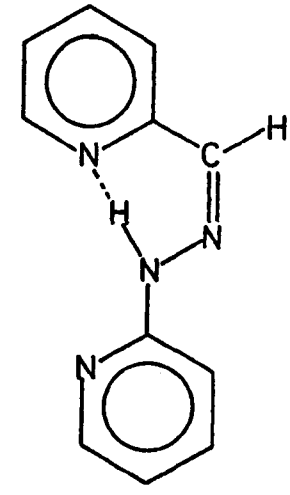


(IV)

by Bell and Rose[32] and a full analysis for the E-isomer was later reported by Cooper et al[33] who used deuterochloroform as solvent.

1.1 E-PAPHY in Dimethyl Sulphoxide

The spectrum (S.2.1) of E-PAPHY (III) in dimethyl sulphoxide consists of two overlapping ABCD type spectra (one for each ring). In addition single resonances were observed for the formyl and imine protons. A repetitive first order procedure[37] was used to analyse the spectrum. Assignments were confirmed by spin decoupling and PMR measurements on methyl substituted derivatives of PAPHY (see 1.4).

Each aromatic heterocyclic ring in the molecule gave a spectrum (which appeared to be independent of the other ring) consisting of four octets as is expected from a 2-substituted pyridine. Thus the spectrum of the whole molecule in the aromatic region consists of 64 lines plus a single resonance due to the formyl proton. Another single resonance due to the imino proton occurs much further downfield than the rest because of its acidic nature. Small coupling (0.5Hz) was observed between the formyl proton and H_2. There was no overlapping of resonances of protons in the same ring.

Coupling constants generally agreed well with those obtained by other workers for 2-substituted pyridines[5,6] (Table.1.1). The full set of spectral parameters for E-PAPHY is given in Table 1.2.

At about the time when this present work was started Cooper et al[33] published the 100MHz spectrum of E-PAPHY in deuteriochloroform. Their results are listed in Table.1.2 and it may be seen that there are some differences in the spectral parameters, particularly the chemical shifts, which are the result of different types of solute-solvent interaction present in the two solvents. The overall shapes of the multiplets are very similar.

Table 1.1. Coupling Constants (Hz) for 2-substituted pyridines.

	PAPHY[a]				
	Ring 1.	Ring 2.	2-Cl-Py[b].	2-Me-Py[b].	2-NO_2-Py[b].
$J_{1,2}$.	7.90.	8.31	8.2.	8.0.	8.2.
$J_{1,3}$.	1.35.	0.97.	0.97[c].	-	-
$J_{1,4}$.	0.90.	0.87.	0.88[c].	-	-
$J_{2,3}$.	7.03.	7.15.	7.8.	7.8.	8.1.
$J_{2,4}$.	1.73.	1.93.	1.97[c].	-	-
$J_{3,4}$.	4.72.	4.90.	4.8.	5.0.	5.2.

(a) Ring 1: aldehyde ring.
Ring 2: hydrazine ring.
(b) W. Brügel, Z. Electrochem., 66, 159, (1962).
(c) R.H.Cox and A.A.Bothner-By, J.Phys. Chem., 73, 2465, (1969).

Table 1.2. Spectral paremeters (in Hz) for E-PAPHY in various solvents (measured at 100 MHz).

Proton \ Solvent	T.F.A.	$CDCl_3$*.	d_6DMSO.	C_6D_6.	CCl_4.
H_1	829.95.	798.19.	796.46.	785.92.	787.08.
H_2	873.20.	763.35.	779.73.	714.30.	752.0
H_3	813.65.	715.29.	728.98.	665.10.	701.9.
H_4	906.95.	855.0.	853.28.	845.06.	843.62.
$H_{1'}$	752.95.	742.12.	730.37.	736.10.	726.26.
$H_{2'}$	835.70.	759.42.	766.78.	721.96.	746.86.
$H_{3'}$	746.50.	679 78.	680.97.	644.93.	667.79.
$H_{4'}$	842.0.	822.88.	814.00.	817.85.	808.50.
-CHO.	848.70.	796.0.	808.48.	768.90.	785.0.
imino	-	-	1110.0	900.0.	932.0.
$J_{1,2}$.	7.90.	7.88.	7.90.	8.10.	7.91.
$J_{1,3}$.	1.10.	1.13.	1.35.	1.29.	1.16.
$J_{1,4}$.	0.80	0.93.	0.90.	0.88.	0.96.
$J_{2,3}$.	7.70.	7.53.	7.03.	7.12.	7.42.
$J_{2,4}$.	1.30.	1.78.	1.73.	1.75.	1.62.
$J_{3,4}$.	5.80.	4.93.	4.72.	5.0.	4.82.
$J_{1',2'}$.	8.90.	8.53.	8.31.	8.49.	8.40.
$J_{1',3'}$.	1.0.	1.01.	0.97.	1.02.	1.04.
$J_{1',4'}$.	0.70.	0.88.	0.87.	0.90.	0.75.
$J_{2',3'}$.	7.0	7.34.	7.15.	7.34.	7.05.
$J_{2',4'}$.	1.60.	1.86.	1.93.	1.90.	1.715.
$J_{3',4'}$.	6.66.	5.18.	4.90.	4.86.	4.92.
Conc mol l^{-1}	sat. soln.	10% w/v	0.12.	0.12.	0.1.
Temp. ^oC.	AMB.	AMB.	AMB.	60.	70.

*Ref.33.

1.2 Z-PAPHY in Dimethyl Sulphoxide (and chemical shift changes, Δ_E^Z, on isomerisation)

The spectral parameters for Z-PAPHY in dimethyl sulphoxide are given in Table 1.3. and Fig. 1.1. shows the changes in chemical shift

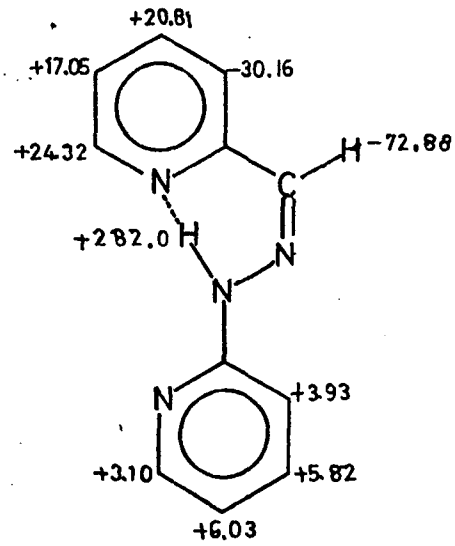


Fig.1.1

(Δ_E^Z = $\nu_{E\text{-isomer}}$ - $\nu_{Z\text{-isomer}}$) on isomerisation of the E- to the Z-isomer. A positive sign before the value of Δ_E^Z indicates a shift downfield of the proton resonance.

It may be seen from Fig.1.1. that apart from H_1 the aldehyde ring protons are deshielded as a result of the intra-molecular hydrogen bonding between the imino proton and the ring nitrogen. This observation is consistent with the withdrawal of electronic charge from the ring via the nitrogen atom. The extent and order of the proton downfield shifts are not the same as when protonation in trifluoroacetic acid takes place.

Table 1.3. Spectral parameters (in Hz) for Z-PAPHY in various solvents (measured at 100MHz).

Proton \ Solvent	d_6DMSO.	C_6D_6.	CCl_4
H_1	766.30.	650.08.	722.01
H_2	800.54.	687.42.	769.70.
H_3	746.03.	637.03	715.91.
H_4	877.60.	804.95.	873.44.
$H_{1'}$	734.2.	770.30.	732.10.
$H_{2'}$	771.6.	723.64.	750.20.
$H_{3'}$	687.0	646.44.	667.70.
$H_{4'}$	817.1	824.93.	808.50.
-CHO	735.60.	697.90.	702.5.
imino	1392.0.	1448.50.	1375.6.
$J_{1,2}$	7.87	7.87.	7.57.
$J_{1,3}$	1.15.	1.16.	0.83.
$J_{1,4}$	0.78.	0.811.	0.83.
$J_{2,3}$	7.65.	7.52.	7.53.
$J_{2,4}$	2.04.	1.80.	1.83.
$J_{3,4}$	4.74.	4.90.	5.00.
$J_{1',2'}$	8.40.	8.36.	8.35.
$J_{1',3'}$	1.25.	1.05.	1.40.
$J_{1',4'}$	0.86.	0.84.	0.91.
$J_{2',3'}$	7.20.	6.88.	6.80.
$J_{2',4'}$	1.90.	1.95.	1.77.
$J_{3',4'}$	4.90.	4.89.	4.95.

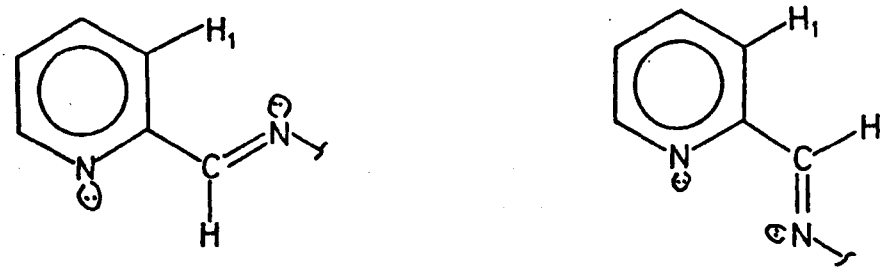
All solutions 0.1 mol l^{-1}; ambient temperature.

The spectrum (S.2.5) shows that coupling between H_2 and the formyl proton has disappeared but H_4 is coupled and $H_{2'}$ now couples with the imino proton.

The imino proton resonance exhibits an extremely large downfield shift on isomerisation which is expected for a proton involved in hydrogen bonding[34]. Further deshielding may result from this proton being placed in the plane of a second pyridine ring and hence in the deshielding region of the aromatic ring current.*

As expected the chemical shifts of the protons in the hydrazine ring show very little change on isomerisation.

The substantial shielding of H_1 may be a result of the re-orientation of the $\rangle C{=}N-$ bond. In Chapter 3 (Long Range Coupling) it is shown that the $\rangle C{=}N-$ bond must have the orientation shown in Fig.1.2a. with



(a) (b)

Fig.1.3

respect to the heterocyclic ring rather than orientation (b). Inspection

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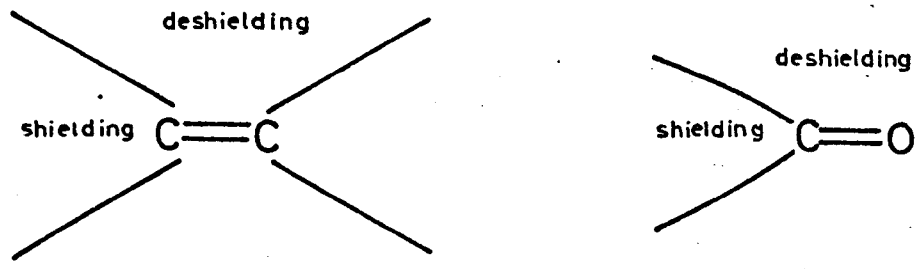
* For explanation of ring current effect see Chapter 2, Introduction.

of a Courtauld's model of PAPHY shows that in the conformation shown in Fig.1.2a. H_1 will lie directly above the $\rangle C{=}N-$ bond. A double bond involving carbon and another atom possesses considerable anisotropy when placed in a magnetic field[35]. For example, because of this anisotropy in the carbon-carbon double bond,[36] protons in the region above the bond will experience deshielding and those along the axis will experience shielding (Fig.1.3a).



(a) (b)

Fig.1.3

For the carbonyl group, the anisotropy leads to a general deshielding except for a region where shielding occurs at the carbon end of the bond around the bond axis (Fig.1.3b). It is this anisotropy that is the reason for the downfield position of the formyl proton resonance in aldehydes.

It is reasonable to assume that the anisotropy of the $\rangle C{=}N-$ bond is not vastly different from that of the carbonyl group, especially as the formyl proton in PAPHY resonates at low field in the aromatic region of the spectrum.

In the light of the foregoing it can be seen that in lying above the $\rangle C{=}N-$ bond H_1 will experience some deshielding. In the Z-isomer

the *intra*-molecular hydrogen bonding will force the molecule to adopt the *configuration* below (Fig.1.4).

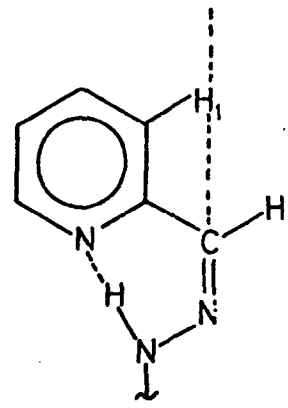


Fig.1.4

H_1 will then lie directly along the axis of the $\rangle C{=}N-$ bond, i.e. in the shielding region. Thus on isomerisation H_1 will experience a considerable increase in shielding.

Support for the above theory may be obtained from previous work on substituted pyridines by Brügel[5]. Fig.1.5. shows the chemical shift (ppm.)

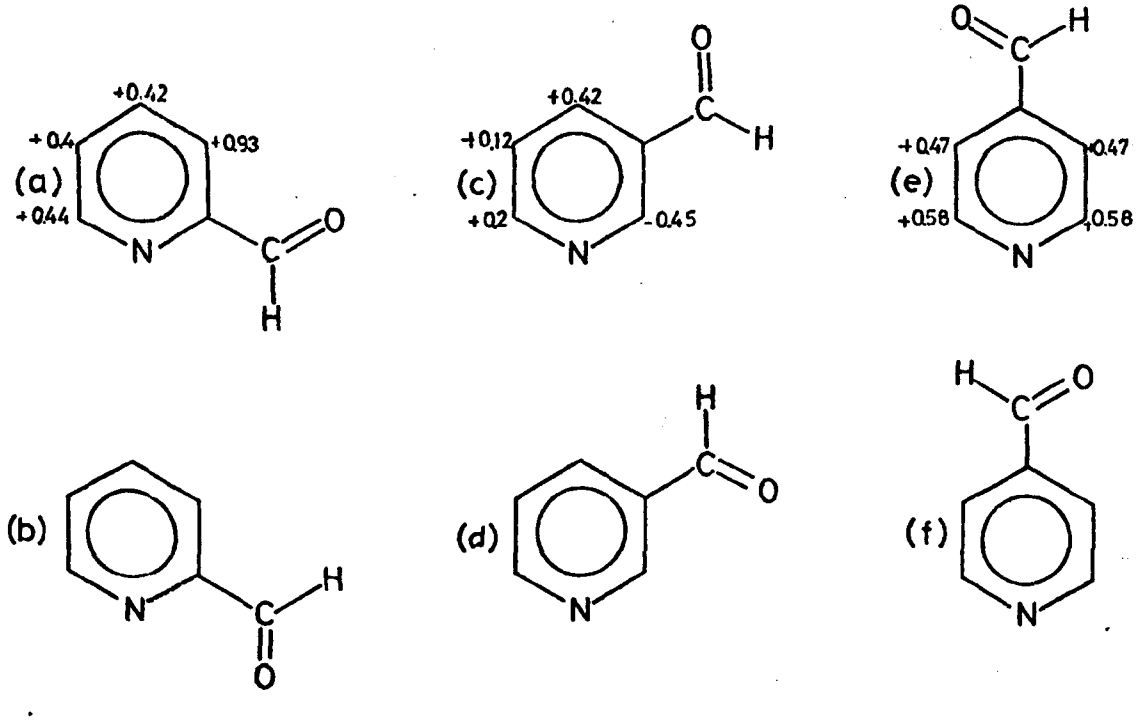


Fig.1.5

changes, Δ_{py}^{py-CHO}, that take place for various protons in pyridine when an aldehyde group is substituted into the ring at different positions.

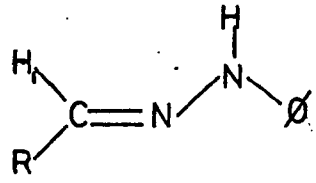
It may be seen from Fig.1.5a that substitution of the aldehyde group into the 2-position in the ring causes a particularly large downfield shift for H_3. Long range coupling evidence shows[40] that although there exists the possibility of unrestricted rotation about the C-CHO bond the compound exists approximately 80% as the conformation (a), (probably as a result of nitrogen one-pair-oxygen lone-pair repulsion). Thus 80% of the time H_3 will be above the -C=O bond and will experience deshielding. When the substituent is in the 3-position the aldehyde exists as 70% conformation (c). H_2 and H_4 are deshielded to approximately the same extent but not as much as H_3 in (a). It has been shown[40] that pyridine-4-aldehyde exists as 50% conformation (e) and 50% (f) and thus one would expect no preferential shielding of H_3 or H_5 by the carbonyl double bond anisotropy.

An additional factor contributing to the upfield shift of H_1 is that it is quite close to the sp^2 hybridised nitrogen atom in the E-isomer (Fig.1.2a) and may experience deshielding as a result of the anistropy of the nitrogen lone pair[35]. In the Z-isomer (Fig.1.1) this nitrogen atom is far removed from H_1.

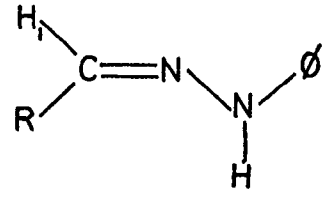
On isomerisation a large upfield shift of the formyl proton resonance is observed. This is considered to be due to the removal of this proton away from the deshielding effect of the magnetic anisotropy of the sp^3 nitrogen atom. From the photographs of the Courtaulds models of E and Z-PAPHY (Pages 8 and 10) it is clear that in the E-isomer the formyl proton

is quite close to the sp^3 nitrogen atom and is far removed from it in the Z-isomer.

Karabatsos and Taller[41,42] studied some phenylhydrazones of the type (V) and (VI) and found that on isomerisation of the E (cis) to the



(V)



(VI)

Z (trans) form an upfield shift of the H_1 resonance (equivalent to the formyl proton resonance in PAPHY) occurred. As the isomerisation in this case did not involve any intra-molecular hydrogen bonding it is unlikely that redistribution of charge within the molecule is the reason for the upfield shift. Thus a change in the shielding due to the anisotropy of the sp^3 nitrogen atom seems the most likely explanation. The shift changes observed by Karabatsos and Vane were in the region of 12-30Hz. The larger value observed in the case of PAPHY may be a result of the formyl proton being deshielded in the E-isomer both by the anisotropy of the sp^3 nitrogen atom and by that of the aldehyde ring nitrogen, to which it is quite close in the E-isomer but far removed in the Z-isomer.

The above results are considered to be evidence for the existence of considerable anisotropy associated with an sp^3 hybridised nitrogen atom .

Previous evidence for the presence of such anisotropy has not been conclusive[43] although it has been shown to be present when the atom is sp^2 hybridised[43].

1.3 Z-PAPHY in Carbon Tetrachloride

When carbon tetrachloride is used as a solvent the values of Δ_E^Z (Fig.1.6) agree fairly well with those obtained in dimethyl sulphoxide

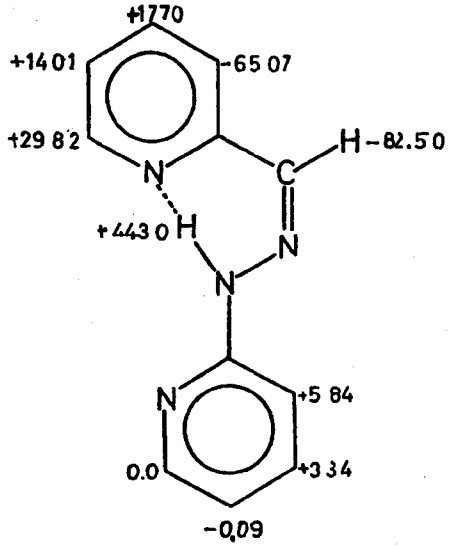


Fig. 1.6

(Fig.1.1) apart from those for H_1 and the imino proton.

It is clear from a Courtauld's model of E-PAPHY that H_1 is in close proximity to the nitrogen atom of the $\rangle C = N-$ bond and this may be effective in partially shielding H_1 from interaction with dimethyl sulphoxide solvent molecules. In the Z-isomer H_1 is considerably more exposed and thus more accessible to solvent molecules. The increased interaction will lead to a downfield shift and will appear to give a reduced value of Δ_E^Z for H_1. The increased value of Δ_E^Z for the imino proton in carbon tetrachloride is probably because in solutions of E-PAPHY in dimethyl sulphoxide this proton is involved in hydrogen bonding with solvent molecules (as indicated by its lower field position

at 1110Hz compared with 932Hz in carbon tetrachloride). Thus the change in chemical shift on hydrogen bonding to the ring nitrogen in the Z-isomer is not as great as when carbon tetrachloride, which does not interact with the imino proton, is the solvent.

Values of Δ_E^Z in benzene are very different from those discussed above. This is a result of a stereospecific solvent interaction which is fully discussed in Chapter.2.

1.4 Protonation of PAPHY in Trifluoracetic Acid

As co-ordination of PAPHY to a metal atom results in the withdrawal of some charge from the pyridine rings of the ligand it was considered of interest to observe the spectrum of protonated PAPHY.

The spectrum of E-PAPHY in trifluoroacetic acid (S1.1) is substantially different to its spectrum obtained in carbon tetrachloride, benzene or dimethyl sulphoxide (S.2.1-3). The spectral parameters are given in Table 1.2.

There is a general shift to low field for all protons in both rings (indicating that both rings are protonated) which is consistent with the deshielding of the protons by withdrawal of electronic charge from the rings by protonation of the ring nitrogen atoms. Shown in Fig.1.7 are values of $\Delta^{TFA}_{CCl_4}$ and it can be seen that the lowfield shift for the

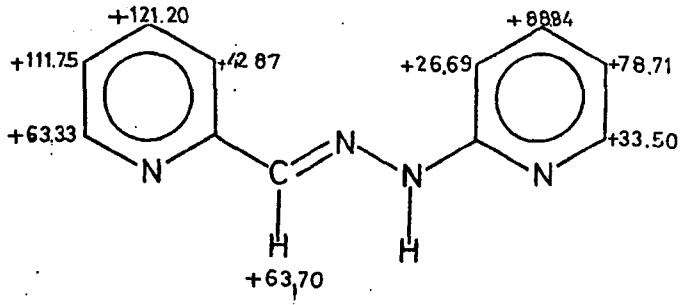


Fig.1.7

protons in the hydrazine ring is generally less than the shift for the protons in the aldehyde ring. This could indicate the more powerful protonation of one ring nitrogen compared with the other. The order of downfield shifts (neglecting $H_{1(1')}$ is the same as observed by Smith and Scheider[28] for pyridine (i.e. $\gamma > \beta > \alpha$)

The resolution of the spectrum is not as good as that obtained using carbon tetrachloride as a solvent (S.2.2). There is considerable broadening of the peaks, a feature also observed in the spectrum of pyridine[28] and 1,10-phenanthroline[23] in trifluoracetic acid. Numerical results are necessarily less accurate than those obtained from spectra run in carbon tetrachloride because of this broadening which has been attributed[24] to proton exchange between the acid and the heteroaromatic ring nitrogens.

Protonation of the ligand also affected the coupling constants but because of the error in measurement the extent is uncertain. Palmer and Semple[30] suggested that such changes in various azines on protonation were a result of changes in bond angles and orders and charge densities in the heteroaromatic ring.

It is of interest to note the changes in $\nu_4 - \nu_3$ and $\nu_4 - \nu_2$ (Table 1.4) on changing the solvent from carbon tetrachloride

	T F A (Hz)	CCl_4
$\nu_4 - \nu_3$	93.3	141.72
$\nu_4 - \nu_2$	33.75	91.62
$\nu_{4'} - \nu_{3'}$	95.5	140.71
$\nu_{4'} - \nu_{2'}$	6.3	61.64

Table.1.4

to trifluoroacetic acid. A decrease is apparent indicating a deshielding of H_2 and H_3 relative to H_4 which is a result of the removal on protonation

32

of the anisotropy of the nitrogen atom associated with the lone pair (see the Introduction). Attempts to prepare the protonated form of Z-PAPHY resulted in isomerisation to the E-isomer.

1.5. Changes in the Spectrum of E-PAPHY on Substitution of a Methyl Group into one of the Rings.

In order to confirm assignments of resonances in the spectrum of E-PAPHY a number of methyl substituted PAPHYs were prepared (Fig.1.8) and their spectra recorded (S.1.2-6). The spectral parameters are listed in Table.1.5. All the compounds give well resolved spectra in which clearly defined multiplets can be observed except for the 1'-methyl substituted compound (S.1.2). Difficulty was experienced in the preparation and purification of this compound and the spectrum is of poor quality showing the presence of impurities.

Substitution of a methyl group into an aromatic ring will change the spectrum in a number of ways. Coupling involving the proton that it replaces is removed as well as the resonance due to that proton thus simplifying the spectrum. The resonances of the methyl groups occur well away from the aromatic region at around 200-240Hz.

In addition to the above effects on the spectrum the diamagnetic shielding of the protons in the ring undergoing substitution will increase because of the release of electronic charge into the ring by the methyl group by an inductive and/or hyperconjugative mechanism. This will cause an upfield shift of the proton resonance positions. Substitution of a methyl group into an aromatic ring activates the ortho and para position towards electrophilic attack and the increase in electron density at the ortho and para carbons should be reflected in the PMR spectrum by an upfield shift of the protons attached to those carbon atoms. Shown in Fig.1.8 are values of $\Delta^{\text{Me-PAPHY}}_{\text{PAPHY}}$. A negative sign indicates an upfield shift and in general this upfield

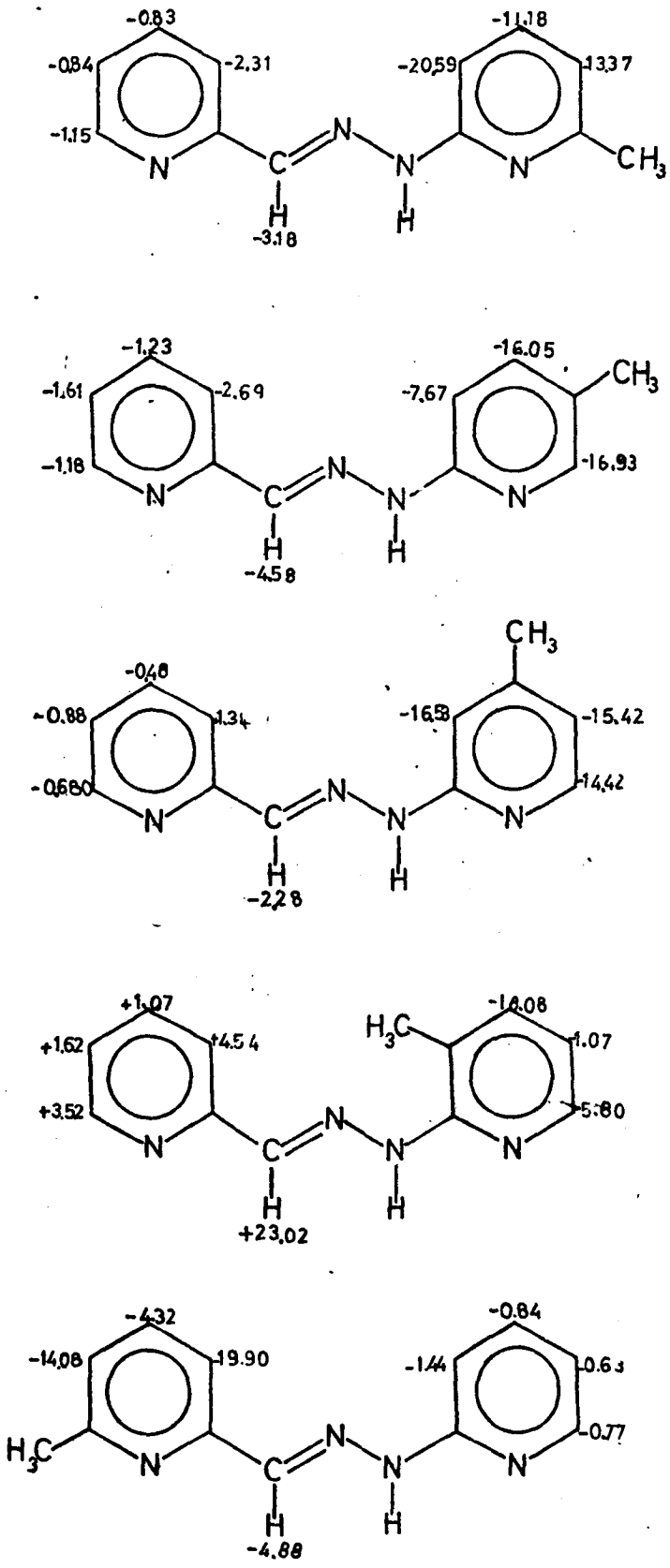
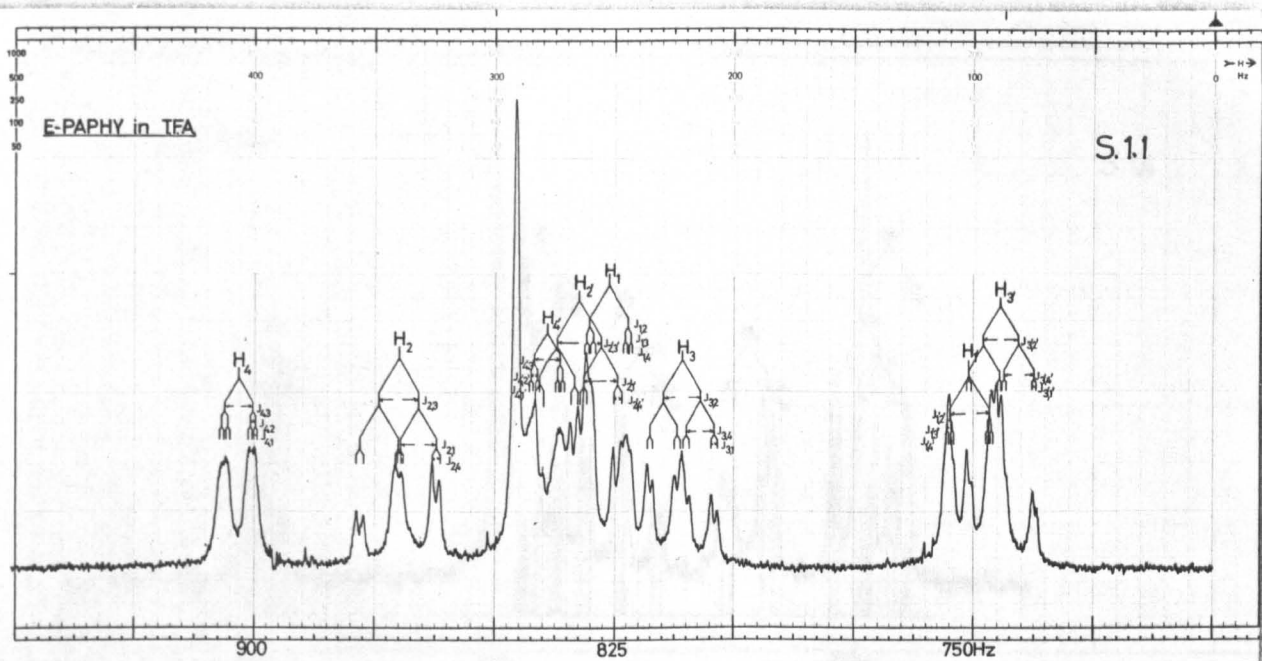
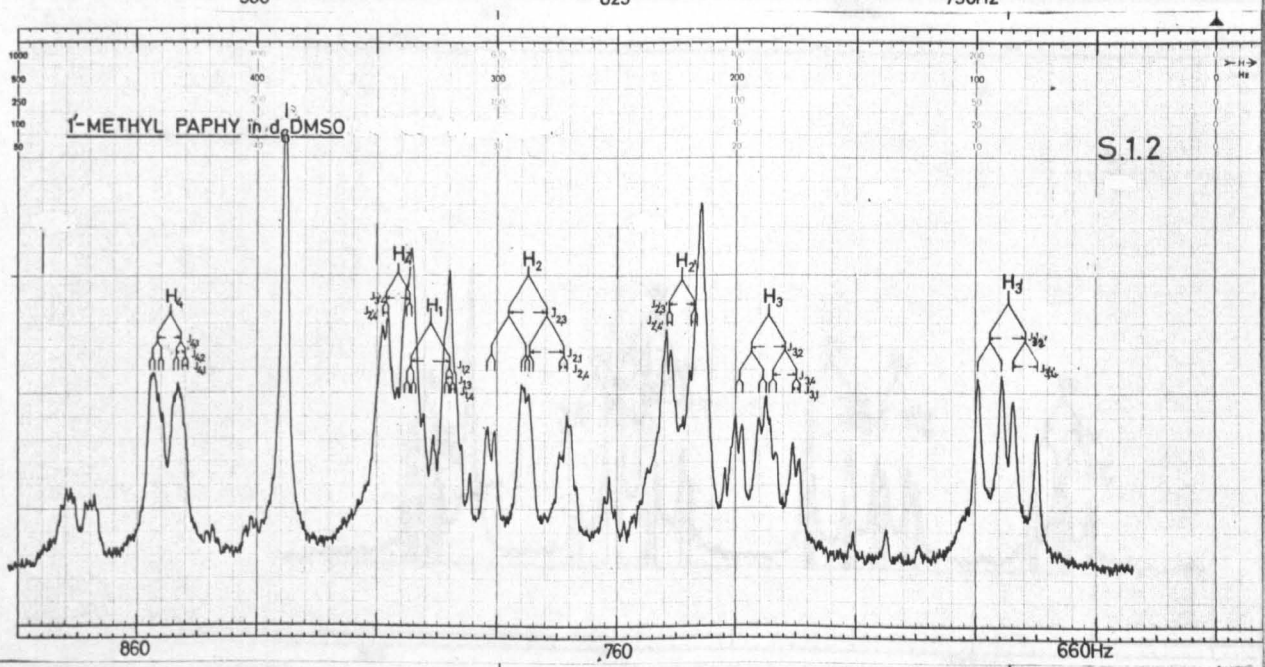

-0.83
-11.18
-0.84
-2.31
-20.59
13.37
-1.15
N
C
N
N
N
CH3
H
-3.18
H
-1.23
-16.05
CH3
-1.61
-2.69
-7.67
-16.93
-1.18
N
C
N
N
N
H
-4.58
H
CH3
-0.48
-0.88
1.34
-16.53
-15.42
-0.680
N
C
N
N
N
14.42
H
-2.28
H
+1.07
-16.08
H3C
+1.62
+4.54
1.07
+3.52
N
C
N
N
N
5.80
H
+23.02
H
-4.32
-0.84
-14.08
19.90
-1.44
0.63
H3C
N
C
N
N
N
-0.77
H
-4.88
H

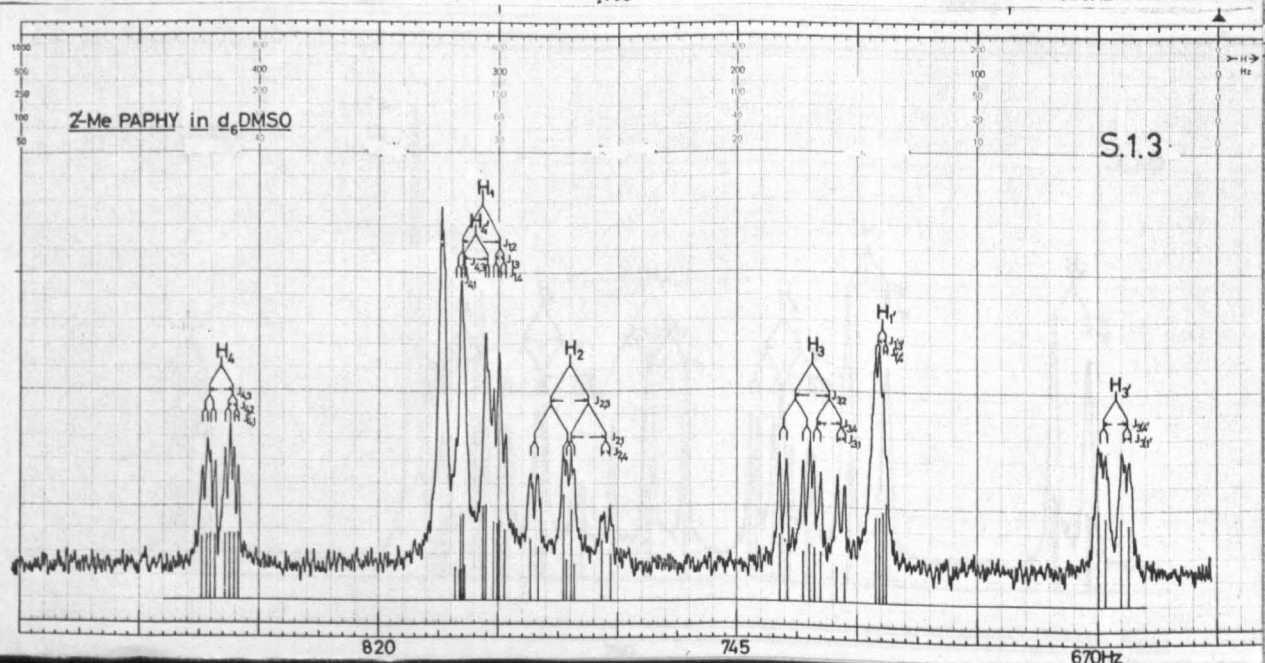
Fig.1.8.

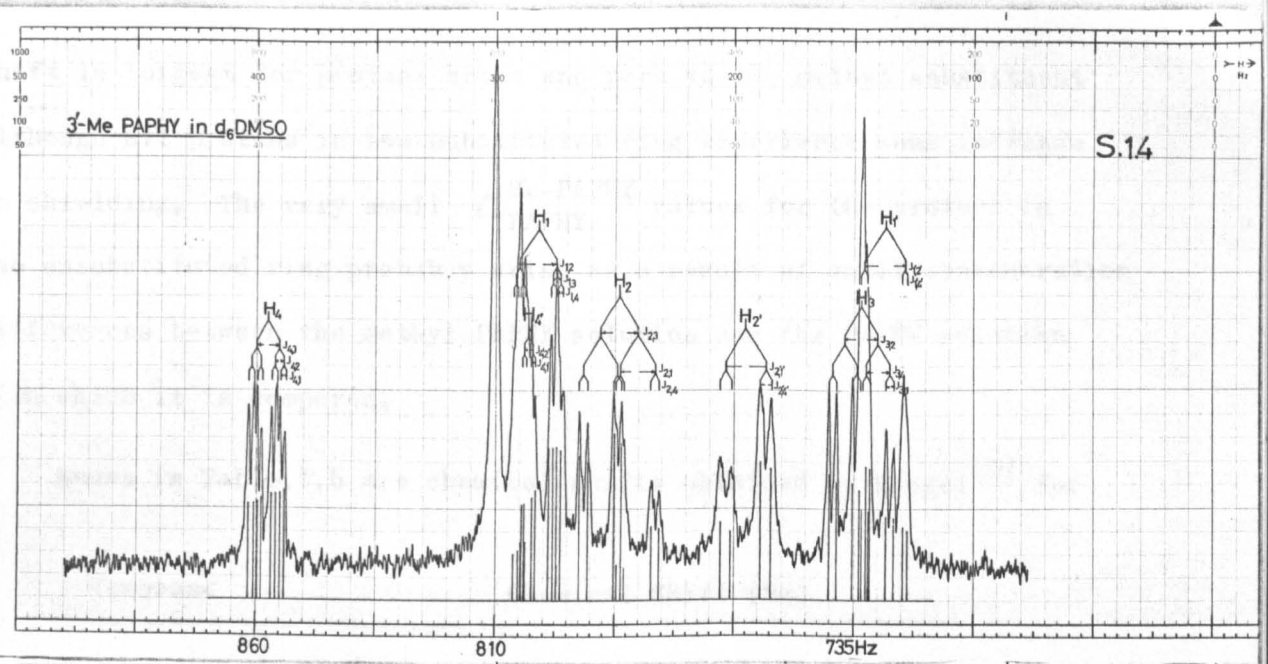
Table. 1.5. Spectral Parameters (Hz) for methyl substituted PAPHYs (measured at 100MHz).

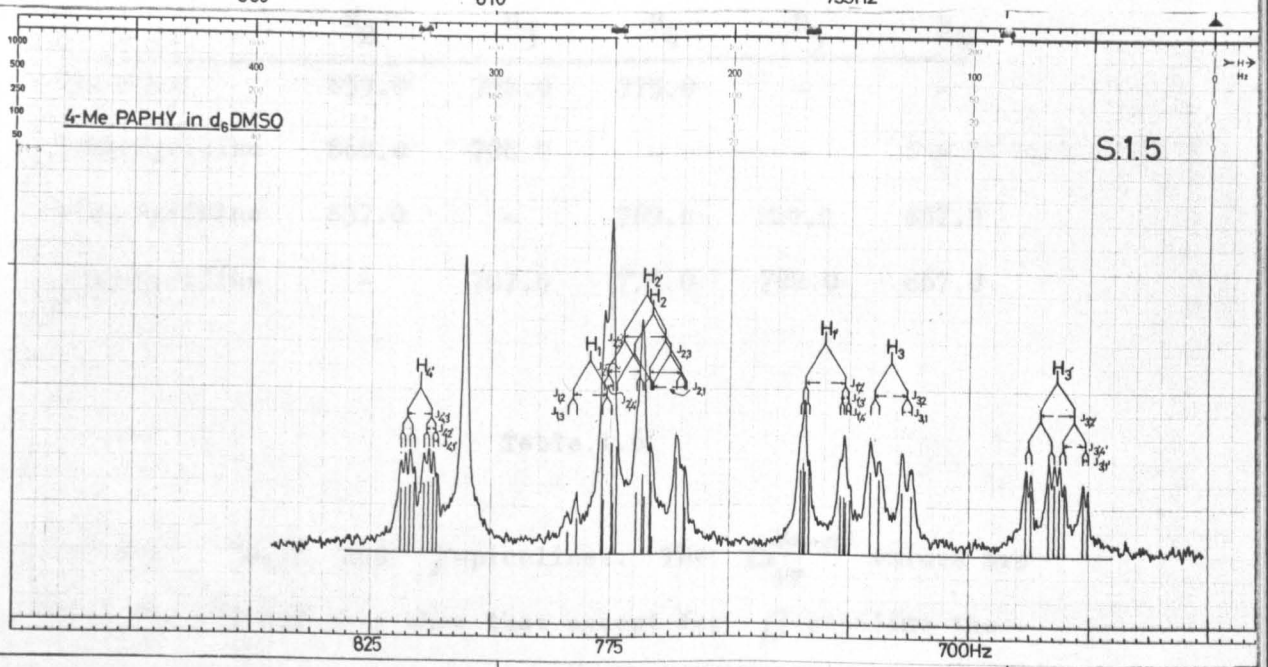
compound / proton	1'-me-PAPHY	2'-me-PAPHY	3'-me-PAPHY	4'-me-PAPHY	4-me-PAPHY
H_1	801.0.	797.80.	793.77.	794.15.	776.56.
H_2	780.80.	779.25.	778.50.	778.90.	766.40.
H_3	730.60.	728.10.	727.37.	728.14.	714.90.
H_4	856.8.	852.6.	852.10.	852.13.	-
$H_{1'}$.	-	713.84.	722.70.	709.78.	728.93.
$H_{2'}$	748.70.	-	750.73.	755.60.	765.94.
$H_{3'}$	679.90.	665.55.	-	667.60.	680.34.
$H_{4'}$	808.20.	799.58.	797.07.	-	813.23.
-CHO	831.50.	806.2.	803.9.	805.3.	803.6.
$-CH_3$	236.0.	203.0.	219.50.	236.50.	199.0.
$J_{1,2}$.	8.1.	8.00.	8.01.	7.930.	7.20.
$J_{1,3}$.	1.50.	1.50.	1.26.	1.20.	1.17.
$J_{1,4}$.	-	0.95.	0.94.	1.02.	-
$J_{2,3}$.	7.20.	7.20.	7.45.	7.38.	7.21.
$J_{2,4}$.	1.55.	1.70.	1.73.	1.47.	-
$J_{3,4}$.	5.0.	4.88.	4.88.	4.80.	-
$J_{1',2'}$.	-	-	8.45.	8.10.	8.38.
$J_{1',3'}$.	-	1.55.	.	0.50.	0.88.
$J_{1',4'}$.	-	0.60.	0.64 .	-	0.88.
$J_{2',3'}$.	7.40.	-	-	7.15.	7.20.
$J_{2',4'}$.	0.90.	-	2.38.	-	1.75.
$J_{3',4'}$.	5.4.	4.69.	-	-	4.87.
conc. mol. l^{-1}	sat soln.	0.84.	0.12.	0.10.	0.10.

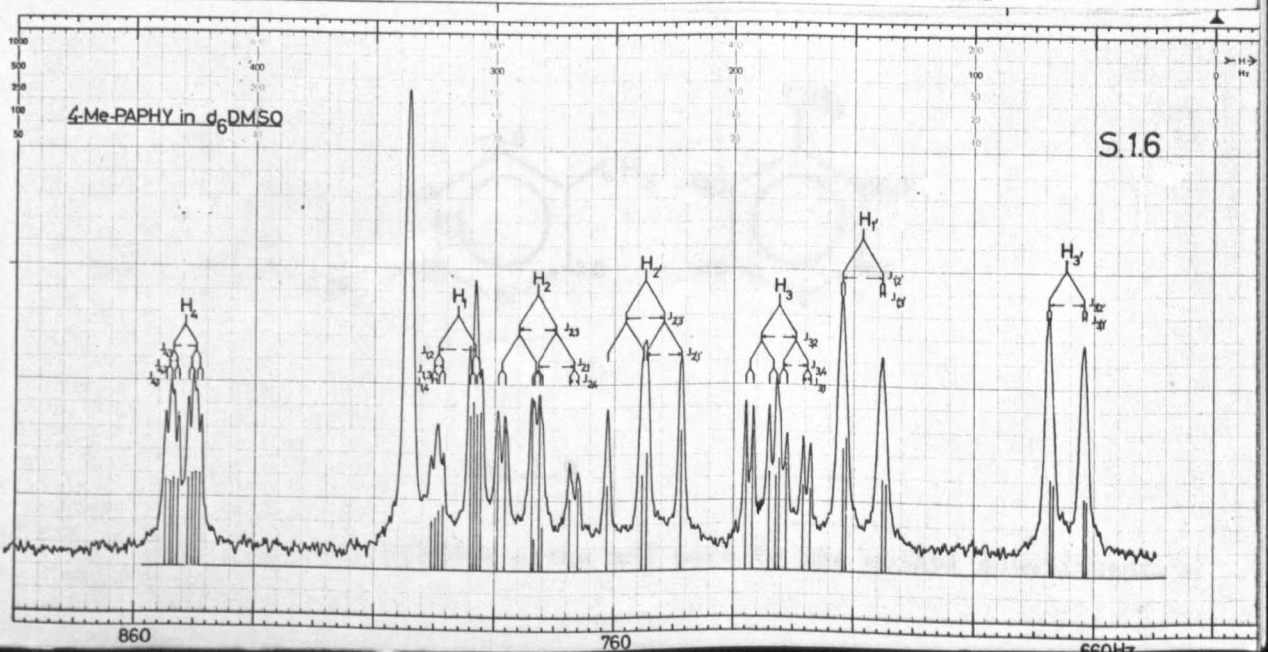

E-PAPHY in TFA
S.1.1
900
825
750Hz


1'-METHYL PAPHY in d6DMSO
S.1.2
860
760
660Hz


2'-Me PAPHY in d6DMSO
S.1.3
820
745
670Hz


3'-Me PAPHY in d6DMSO
S.1.4
860
810
735Hz


4-Me PAPHY in d6DMSO
S.1.5
825
775
700Hz


4-Me-PAPHY in d6DMSO
S.1.6
860
760

shift is largest for protons ortho and para to the methyl substituent although all protons in the substituted ring experience some increase in shielding. The very small $\Delta^{\text{Me-PAPHY}}_{\text{PAPHY}}$ values for the protons in the unsubstituted ring probably arise as a result of small concentration differences between the methyl-PAPHY solution and the PAPHY solution with which it is compared.

Shown in Table.1.6 are chemical shifts obtained by Brügel[5] for

Compound	Chemical Shift (Hz)				
	H_2	H_3	H_4	H_5	H_6
Pyridine	859.0	738.0	775.0	-	-
4-Me-Pyridine	860.0	728.0	-	-	-
3-Me-Pyridine	857.0	-	769.0	729.0	857.0
2-Me-Pyridine	-	727.0	774.0	722.0	867.0

Table.1.6

pyridine and α,β and γ-picolines. The $\Delta^{\text{Me-py}}_{\text{py}}$ values are given in Fig.1.9 and they show that except for β-picoline the

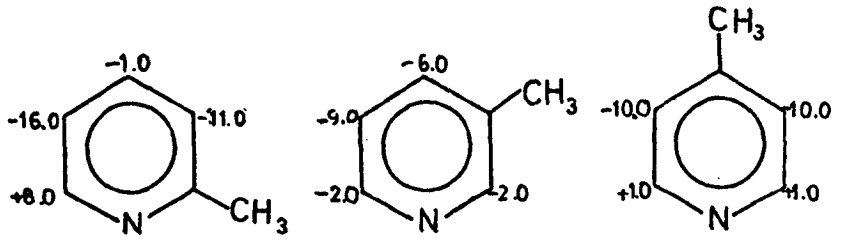


Fig.1.9

shielding is greatest for protons ortho and para to the methyl substituent.

1.6 Temperature Dependence of Chemical Shifts

In view of the desirability of using dimethyl sulphoxide as a solvent for metal complexes in PMR work and of obtaining chemical shifts as uncomplicated by solvent effects as possible, it was decided to carry out a preliminary investigation into the possibility of removing, or at least reducing to a very low level, the hydrogen bonding interaction of the solvent by running the spectra of samples in dimethyl sulphoxide at moderately elevated temperatures. ($\sim 70^{\circ}C$).

The procedure was as follows. The spectra of two solutions of PAPHY in dimethyl sulphoxide of different concentrations were obtained and the chemical shifts measured. As expected the shifts were different for corresponding protons in the two solutions. It was hoped that on elevating the temperature not only the chemical shifts obtained from the two solutions would move upfield to the same position but also that this final position would be close to that obtained for a particular proton in carbon tetrachloride.

The results of this experiment are presented in Table.1·7 and compared with the chemical shifts obtained in carbon tetrachloride. It can be seen from these results that elevating the temperature has the effect of decreasing the chemical shift and also decreasing the difference in chemical shift between protons in the 0.8M and 0.4M solutions. However, there still is a considerable difference between the shifts in dimethyl sulphoxide and those in carbon tetrachloride and a considerable further elevation of temperature would be required to remove the interaction of the solute and solvent.

	Chemical Shift (Hz) (Probe Temp. ~35°C)			Chemical Shift (Hz) (70°C)			Shift in CCl_4 (0.1M 70°C)
	0.8M	0.4M	Difference	0.8M	0.4M	Difference	
H_1	801.60	799.05	2.55	796.45	795.35	1.10	787.08
H_2	781.55	781.0	0.55	776.50	776.20	0.30	752.0
H_2	729.85	729.25	0.50	725.25	725.35	-0.10	701.9
H_4	857.65	855.45	2.20	854.20	853.20	1.0	843.62
H_1'	735.90	732.60	2.30	731.50	729.10	2.40	726.26
H_2'	770.55	768.80	1.75	766.20	765.10	1.10	746.86
H_3'	683.25	681.95	1.30	679.75	679.10	0.65	667.79
H_4'	818.55	816.45	2.10	815.30	813.75	1.55	808.50
Formyl	817.80	812.60	5.20	816.0	812.50	3.50	785.0

Table 1.7

References

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Chapter 2

Solvent Effects in PMR Spectroscopy

Introduction

It was shown in the general introduction to this thesis that the resonance frequency of a proton could be expressed by the equation

$$\nu = \frac{\gamma H_0(1 - \sigma)}{2\pi} \qquad (1)$$

in which σ is the shielding constant, determined by electronic distribution within the whole molecule, for the hydrogen atom under consideration. If the sample happens to be a gas at low pressure then the value of σ can be considered to be that for the isolated molecule. However, the spectra of compounds are very often measured in solution and the molecules can no longer be considered to be isolated. As a result the shielding constant becomes the sum of a contribution due to the surrounding medium ($\sigma_{solvent}$) plus that inherent in the molecule itself (σ_{mol}). Hence,

$$\sigma = \sigma_{solvent} + \sigma_{mol} \qquad (2)$$

This solvent contribution to the shielding of the nucleus makes it difficult to obtain absolute chemical shifts characteristic of the isolated molecule.

An early study was made by Schaefer et al[1,2,3] on solvent effects and in their paper with Buckingham[1] it was considered that there were four terms contributing to $\sigma_{solvent}$.

$$\sigma_{solvent} = \sigma_b + \sigma_a + \sigma_w + \sigma_E \qquad (3)$$

When hydrogen bonding, or other solvents which give rise to specific solute solvent interactions are used, another term, σ_H, needs to be added to (3) resulting in the five term expression

$$\sigma_{solvent} = \sigma_b + \sigma_a + \sigma_w + \sigma_E + \sigma_H \qquad (4)$$

When such solvents are employed the term σ_H becomes the most dominant of the contributions to $\sigma_{solvent}$ because it arises as a result of direct interaction between solute and solvent molecules and cannot be eliminated by the use of an internal reference.

The term σ_b represents the bulk magnetic susceptibility of the dissolving medium and can be corrected for when using an external reference but becomes zero when an internal reference is used.

When an aromatic solvent is used the term σ_a is particularly important. It is a measure of the effect of the magnetic anisotropy existing in the solvent molecule and arises as a result of the non-zero averaging of this anisotropy with respect to the solute molecules. Except in cases where there are specific associations (as in the benzene chloroform system) this term may be eliminated by the use of an internal reference.

Weak Van der Waals forces between solute and solvent molecules are represented by the term σ_w. These molecular interactions which occur on the change from gas to liquid distort the electronic distribution in the molecule thus altering the screening constant of a particular nucleus. The magnitude of σ_w has been shown to be about 0.1 ppm[5]. It may also be disregarded if an internal reference is used.

The term σ_E, investigated at length by Buckingham[1,4], is known as the reaction field term. The reaction field arises when a polar solute is dissolved in a polar or polarizable solvent. The permanent dipole of the solute molecule polarises the surrounding medium and a secondary electric field is set up which then affects the electron distribution in the solute molecule which will alter the magnetic shielding constant, σ, for a particular proton in the molecule. Generally, σ, is reduced resulting in a shift to low field which increases with increasing dielectric constant (ε) of the solvent.

There is an approximately linear relationship between the solvent shifts in solvents of different dielectric constants and the expression $\frac{(\varepsilon - 1)}{(\varepsilon + 1)}$[1,4].

Aromatic Solvent Induced Shifts (ASIS)

1) Aliphatic Solutes

The pronounced effects on the PMR spectra of many solutes on changing from an inert solvent, such as n-hexane, to benzene or another aromatic solvent[2,3,6-15] were first observed in 1956[6,7]. It has been established that these effects are the consequence of the particular stereochemistry and electron distribution within the aromatic molecule.

The cause of the pronounced shift is the ring current effect[9,16,17]. Consider Fig.2.1 which represents a benzene ring with its loosely bound

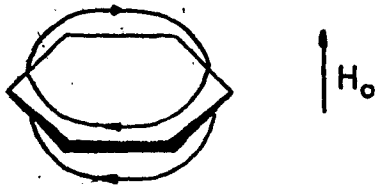


Fig.2.1

π-electron system above and below the plane of the ring. When the benzene molecule is placed in an external magnetic field, H_o, perpendicular to the plane of the ring, the mobile π-electrons are caused to precess around the ring. This precession may be considered as a super-conducting ring current and will generate its own secondary magnetic field, (represented in Pople's mathematical treatment as a dipole placed at the centre of the ring), which is such that it reinforces the applied field experienced by those solute molecule protons which lie in the plane of the benzene ring (thus causing them to resonate at lower applied field). Also it follows that solute molecule protons which are positioned above or below the plane of the ring will be in a region where the secondary

field will oppose the applied field and will thus resonate at a field value higher than H_o.

If there were no specific solute-solvent interactions, the effect due to an aromatic solvent on the chemical shifts of solute protons could be expressed by the term σ_a in equation 4 and could then be disregarded when using an internal reference. However, the π-electron clouds above and below the plane of such aromatic molecules provide a region of quite exposed negative charge and the molecule will tend to form associations (by acting as a π-electron donor) with other molecules in which there is a deficiency of electronic charge at certain sites. This kind of association implies that the solute and solvent molecules have a specific orientation with respect to each other (as indicated by Bothner-By and Glick[6] and thus ASIS are more correctly linked with the term σ_H;

There is currently some disagreement as to the exact nature of the solute-solvent interaction. Some authors favour the idea of a definite 1:1 collision complex between the solute and solvent molecules and the majority of experimental results to date have been interpreted employing this theory. Ledaal[18] described the complex as having the dipole axis of the solute molecule located along the six-fold axis of a benzene nucleus with the positive end of the dipole nearest, and the negative end farthest away from the axis.

Later workers[60 - 67] have cast doubts upon the validity of the idea of a 1:1 complex and have proposed instead a more general solvation theory.

Whatever the mode of interaction it is almost certainly much weaker than that between groups of polar molecules. In spite of this the chemical

shift changes experienced by solute protons in going from an inert solvent to benzene are frequently quite large, sometimes as much as 200 Hz. The shift in resonance position of a particular solute proton relative to its value in the non-solvated solute molecule (measured either in the gas phase or in an inert solvent) may be either to high or low field depending on the stereochemistry of the associated solute-benzene species, because this will determine whether or not the proton concerned is shielded or deshielded by the benzene ring.

Pople[22,23] was one of the first to treat mathematically the problem of shielding due to an aromatic ring although later treatments by Johnson and Bovey[16] and Waugh and Fessenden[24] are now considered to be more successful.

From their calculations Johnson and Bovey[16] produced the contour diagram shown below.

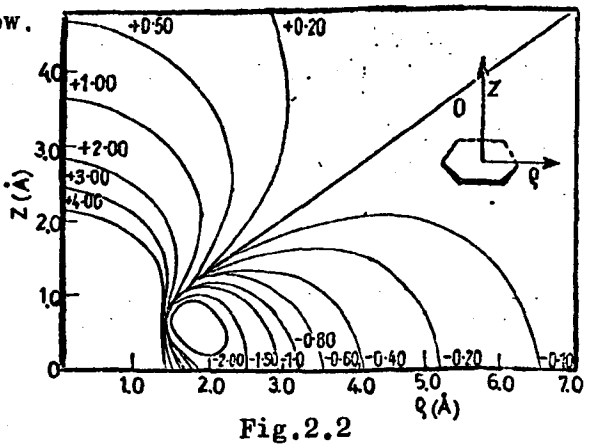


Fig.2.2

This gives an indication of the various regions adjacent to the benzene ring in which a proton would be expected to be shielded or deshielded.

Although the diamagnetic shift due to benzene solvation can be quite large it decreases inversely with the third power of the separation R of the solute and the centre of the aromatic ring.

The benzene-chloroform system[9,14] provides a good example of the

shielding effect of the benzene ring. On going from pure chloroform to a benzene solution of chloroform, the chloroform proton resonance experiences a considerable shift upfield which has been attributed to the chloroform molecule taking up, as shown, below a preferred orientation with respect to the benzene molecule.

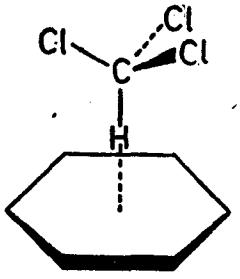


Fig.2.3

The interaction between the benzene π-electrons and the chloroform proton draws the solute molecule close to the benzene ring and into its region of maximum shielding.

Abraham's work[25] on methyl halides and Pajak's work [26] on chloroform-heterocyclic systems supports this model.

Hatton & Richards[11] investigated the spectra of dimethylformamide and dimethylacetamide dissolved in various solvents. They found that aliphatic solvents and water produced only small solvent effects whereas dissolution in an aromatic solvent changed the spectrum considerably, the resonances of both N-methyl groups being shifted to higher field, one much more than the other.

From their results they concluded that this differential methyl shift was a result of a stereospecific association between the amide and the

aromatic ring. (Fig.2.4).

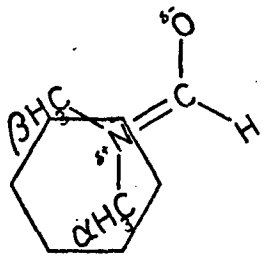


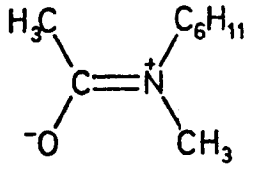
Fig.2.4

In this case the slightly positively charged nitrogen atom is situated above the plane of the benzene ring (i.e. in the region of exposed negative charge) and the negatively charged carbonyl oxygen is as far away as possible from the aromatic π-electrons. As a consequence of this arrangement the α-methyl group is more affected by the aromatic ring current than the β-methyl group which does not lie directly over the ring. A similar stereospecific association was suggested by Moriarty and Kliegman[12] from the results of their work on N-methyl lactams in benzene solution.

Hatton and Richards[11] found that when naphthalene derivatives were used as solvents the observed solvent shifts were greater than were observed in benzene. Such an observation was also made by Schneider[9] during an investigation of acetonitrile. The reason for this increased ASIS is considered to be the mutual reinforcement of ring currents in naphthalene.

Further work on N-methylamides was carried out by Moriarty[27] who also suggested the existence of a stereospecific solute-solvent complex. He concluded that N-methylcyclohexyl acetamide (I) formed different stereospecific solute-solvent complexes with benzene and pyridine. He

observed that both the N-CH_3 and C-CH_3 peaks moved, in benzene solution,



(I)

to higher fields (i.e. both shielded) leading him to propose an association of the type shown in Fig.2.5.

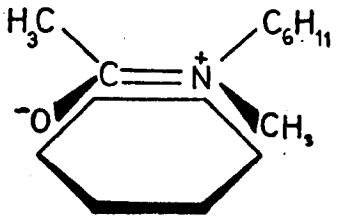


Fig.2.5

When N-methylcyclohexyl acetamide was dissolved in pyridine[27] the general direction of shift was downfield which suggested the formation of the complex shown in Fig.2.6.

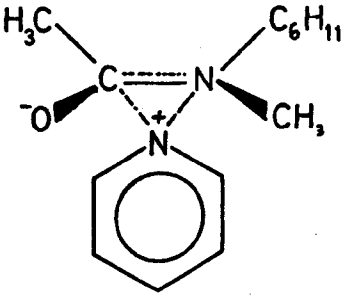


Fig.2.6

In this complex the interaction involves the lone pair of electrons of the nitrogen atom in pyridine. In such an arrangement the plane of the pyridine ring is at right-angles to the plane of the acetamide molecule and the methyl groups are well away from the shielding regions above and below the plane of the ring and may well come within the cone-shaped deshielding region (approximately in the plane of the ring) thus accounting for the observed downfield shift.

La Planche and Rogers[28] investigated the configurations of a number of N-monosubstituted amides and used again the idea of a specific association with benzene to confirm previous conclusions about the stereochemistry of rotational isomers.

In some early work Hatton and Richards[29] measured the chemical shift of the acetylenic proton in a number of substituted acetylenes in various solvents. They found that benzene caused a shift to higher field presumably due to an association between solute and solvent similar to that in the benzene-chloroform system[9,14].

Ledaal[18] investigated the benzene solvent effect for a number of solutes and found the shielding to be parallel to the acidic and electrophilic character of the solute protons but could find no simple correlation with dipole moments.

Solvent shifts of acetonitrile in benzene were investigated by Schneider[9] who proposed a dipole-induced dipole interaction between solute and solvent to account for the large upfield shift of the methyl resonance compared with its shift in neopentane solution. He envisaged an interaction (Fig.2.7) with the negative end of the cyano group dipole

repelled by the π-electron cloud to a position above and well away

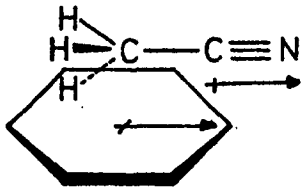


Fig.2.7

from the benzene ring. As a result of the dipole induced in benzene (by the polar acetonitrile molecule) the methyl protons are situated directly above the ring where there is maximum ring current shielding.

In an earlier paper Abraham[25] has proposed a specific acetonitrile-benzene association, but in this case one (similar to the chloroform-benzene association) in which the axis of the acetonitrile molecule is perpendicular to the plane of the aromatic ring. In view of the much larger dipole moment of acetonitrile (3.92 D compared to 1.01 for chloroform) and the ease with which the π-electrons of benzene may be polarised the dipol-induced dipole model seems the more likely one.

Buckingham[30] also observed a large upfield shift for the methyl protons in acetonitrile on changing the solvent to benzene but did not venture to postulate a definite association.

Schneider[9] interpreted his results on the solvent effects in substituted vinyl compounds in terms of a preferred mutual orientation of solute and solvent molecules. He proposed an association (Fig.2.8) in which the solvent and solute molecular planes were parallel, with the

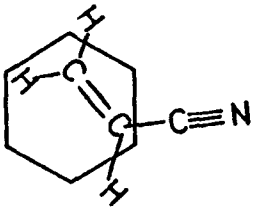


Fig.2.8

result that the polar group in the vinyl compound tends to lie off the benzene ring. The interaction is presumably of the dipole-induced dipole type he proposed for acetonitrile. In the case of acetonitrile there is no need to think that the assumption about the planes of the solute and solvent molecules being parallel is wrong. However, in the present case there will be a repulsive interaction between the π-electrons of the benzene ring and ethylenic double bond which may result in a non-parallel orientation of the molecules.

Variable temperature work by Hatton and Schneider[31] and Whittaker and Siegel[32,33] has provided supplementary evidence for the possible existence of specific solvent-solute complexes in solution.

Whittaker and Siegel investigated by PMR the effects of solvents on the hindered internal rotation in dimethyl formamide[32] and some higher alkyl amides. They used the solvents carbon tetrachloride, acetone, fluorotrichloromethane and hexamethyl disiloxane and observed that the chemical shifts of the methyl protons were both solvent - and temperature - dependent whereas that of the formyl proton was independent of both. From this they concluded that although there appeared to be dipolar association between solute and solvent the formyl proton took no part in this.

Klinck and Stothers[13] also concluded that the temperature dependence of the solvent shifts of various protons in some aromatic aldehydes was evidence for the existence of stereospecific solute-solvent interactions.

For compounds containing one or more carbonyl groups, solvent shifts may often be predicted quite accurately. It has been found[34] that the point of association with the solvating benzene molecule is the carbonyl carbon atom. The interaction is such that protons on the oxygen side of a perpendicular plane drawn through the carbonyl carbon and at right angles to the carbonyl bond (Fig.2.9)move downfield and

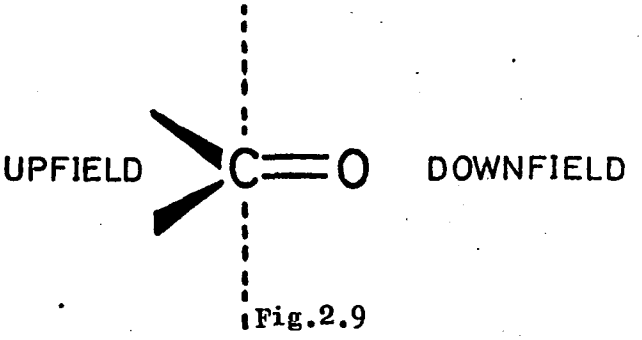
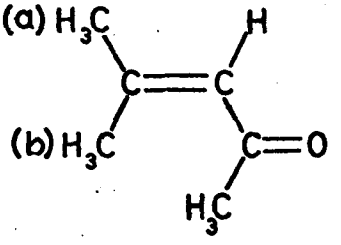


Fig.2.9

those on the other side move upfield[34-36]. For example, in the case of mesityl oxide[15](II) the order of upfield shifts resulting from the



(II)

addition of benzene was CH_3(b) > $COCH_3$ > CH_3(a). These shifts were explained by Hatton and Richards[15] in terms of the association shown below (Fig.2.10)in which the benzene ring interacts with the carbonyl

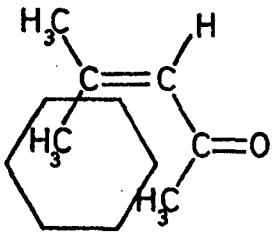
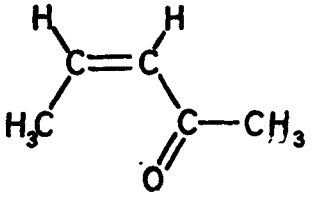
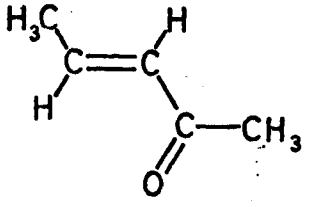


Fig. 2.10

carbon (carrying a partial positive charge) whilst trying to keep as far away as possible from the partial negative charge of the oxygen atom. Obviously this interpretation relies on the correct assignment of resonances to start with and Baldwin has provided evidence[37], from work on cis-3-penten-2-one (III) and trans-3-penten-2-one (IV) that the



(III)



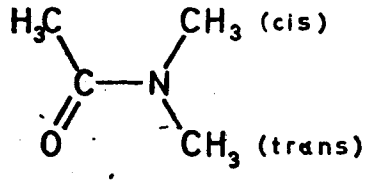
(IV)

original assignments of Hatton and Richards[15] were incorrect.

The idea of the reference plane discussed above has proved very useful in the investigation of steroid conformations and considerable interest has been shown in this field[38-40].

Yonezawa and co-workers[41,42] have investigated the effect produced by the addition of a protic substance (trifluoroacetic acid or methanol) to the benzene solution of a polar compound such as an amide, nitrosamine or azabenzene. They found that in general the shift resulting from this

addition was upfield and greatest for those protons situated closest to the proton-accepting centre. For example, in the case of dimethyl acetamide[42] (V) the cis methyl group was found to exhibit a much



(V)

larger upfield shift than either of the other two methyl groups (the opposite of what was observed when changing the solvent from carbon tetrachloride to benzene). They postulated the sequence of events shown in Fig. 2.11 to account for the observed shifts.

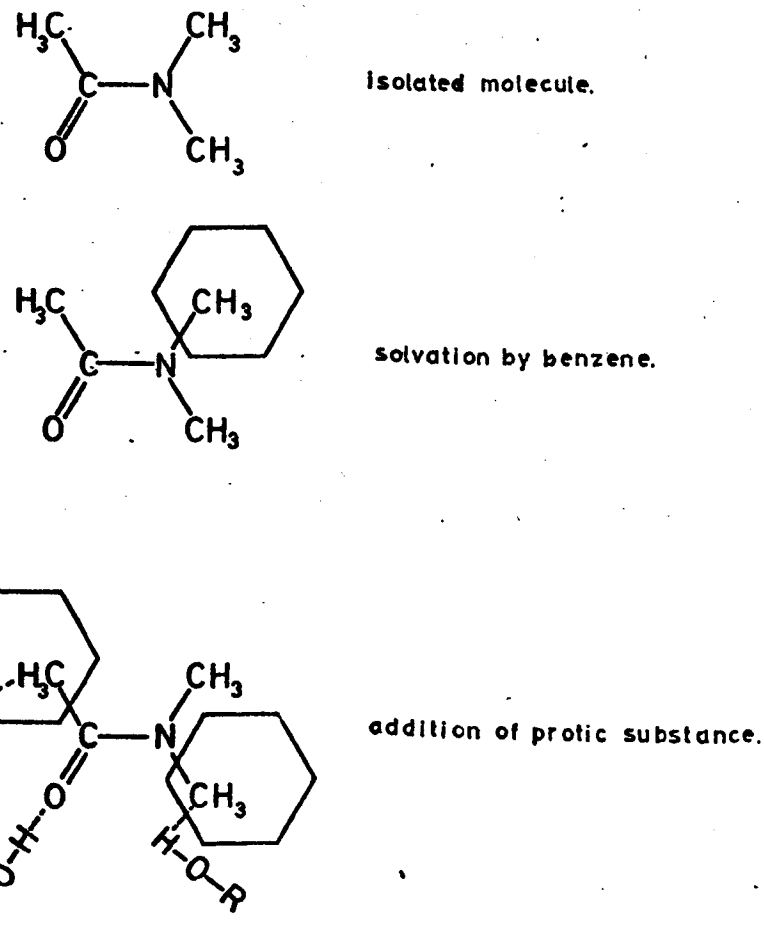
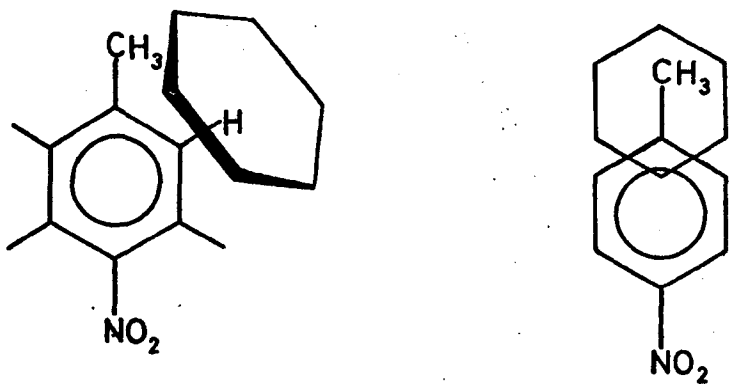


Fig.2.11

The authors showed[41] that a benzene solvent molecule is repelled by the nitrogen lone pair of electrons and thus the protons some distance from the lone pair were markedly more affected by benzene solvation. On the addition of a protic substance those protons in the vicinity of the nitrogen lone pair suffered the greatest upfield shift.

Aromatic and Heteroaromatic Solutes

Schaefer and Schneider[2,3] together with Buckingham[1] investigated solvent effects on the spectra of a number of aromatic and heteroaromatic compounds using the solvents n-hexane, acetone and benzene. From the general upfield shift of aromatic ring protons observed in p-methyl nitrobenzene when changing the solvent from n-hexane to benzene, they concluded that some form of specific solute-solvent complex existed in the benzene solution. At the same time they suggested that because the solvent shift for the protons ortho to the methyl group was greatest the interaction was probably of the form Fig.2.12a. Here the solvent interaction is with a specific proton which is especially prone to



(a) (b)

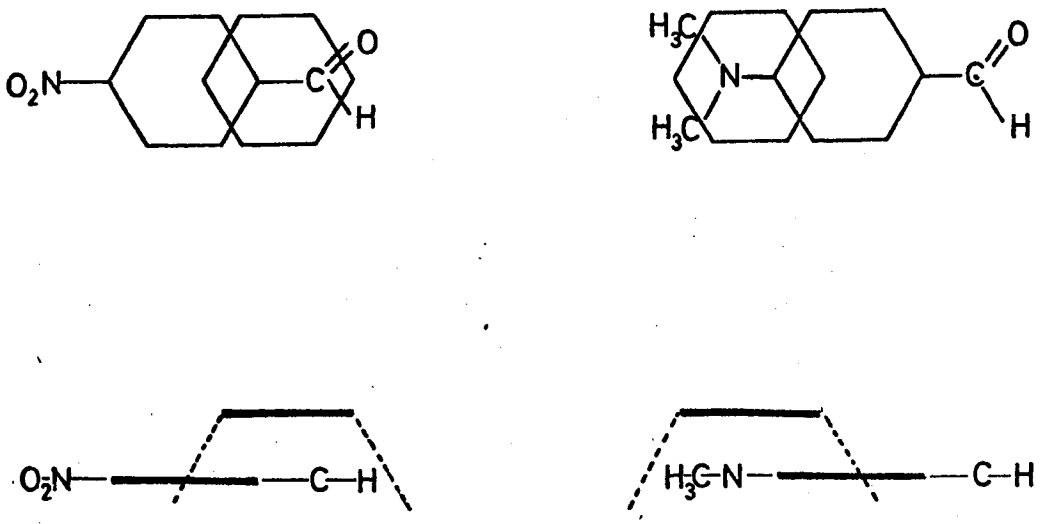
Fig.2.12

hydrogen bonding because the C-H bond at this position has been polarised by the electronegative substituent.

Schaefer and Schneider found[2] that when the electropositive $-N(CH_3)_2$ group was substituted into the ring in place of the nitro group the protons meta to the methyl substituent moved upfield by a greater

amount than the ortho protons. This they attributed to a reversal of the polarising field. In view of later work the form of association with benzene proposed by Schaefer and Schneider appears unlikely and their results may be explained in terms of solvation by the benzene ring of the electron deficient region of the molecule as shown in Fig.2.12(b) for p-methyl nitrobenzene. Such a mode of solvation has been postulated by Klinck and Stothers[43] to account for solvent shifts in dimethyl amino benzaldehyde.

Klinck and Stothers[43] observed the effect on the PMR spectra of a number of aromatic aldehydes of changing the solvent. They used carbon tetrachloride as their inert solvent and found that, relative to its position in carbon tetrachloride, the formyl proton signal moved to lower field in acetone and higher field in benzene. Also, the benzene solvent shift was found to be very dependent on the nature of the substituent in the aromatic aldehyde ring. They came to the conclusion that aldehyde solute and benzene solvent molecules were forming complexes of specific stereochemistry and that the interaction between them involved the π-electron system of the benzene ring acting as an electron donor to an electron deficient site within the aldehyde molecule. For example in the case of p-nitrobenzaldehyde, the experimental results could be explained by invoking an association involving the carbon atom of the formyl group (Fig.2.13a) which tends to have a positive charge as a result of the group being in a para position to an electron withdrawing substituent.



(a) (b)

Fig.2.13

In the case of the substituent being electron releasing (as in the dimethyl amino derivative) the point of association appeared to be this substituent itself (Fig.2.13b.).

In a later paper[13] Klinck and Stothers extended their survey by considering the chemical shifts of all solute protons. Their hypothesis that those protons in closest proximity to the solvating molecule would show the greatest solvent shift was supported by their experimental results. They analysed graphically the chemical shift of methyl and aldehyde group protons as a function of benzene concentration for benzene solutions of dimethyl aminobenzaldehyde and p-nitrobenzaldehyde. They found that the N-methyl protons in dimethyl aminobenzaldehyde and the formyl proton in p-nitro benzaldehyde exhibit very similar upfield shifts with increasing benzene concentration. The reason for this can be seen from Fig.2.13, (a) and (b). In the nitro derivative the solvating molecule lies close to

the aldehyde group and thus the formyl proton is in the shielding region resulting from the aromatic ring current. Similarly in the dimethyl amino derivative, where the benzene ring is located approximately over the substituent group, the N-methyl protons will lie on the shielding region and the formyl proton will be sufficiently far removed to be little affected. This explains the rather small dependence on concentration of this proton.

Hatton and Richards[15] observed that when γ-picoline was diluted with carbon tetrachloride a downfield shift was shown by the methyl resonance. They explained this by proposing that in the pure compound γ-picoline molecules are associated in the manner shown in Fig.2.14.

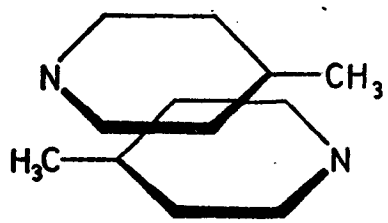


Fig.2.14

In both molecules the methyl protons and those ortho to the methyl group would be shielded by the aromatic ring current of the neighbouring molecule. On dilution with an inert solvent, the extent of this type of interaction would decrease, and hence the methyl and ortho proton resonance values approach those of the isolated molecule, i.e. they move downfield.

A consequence of increasing the concentration of γ-picoline in

carbon tetrachloride was an increase in the internal chemical shift of the ortho and meta protons. A similar increase in internal shift was observed when the solvent was changed from carbon tetrachloride to benzene. This was also observed in earlier work by Schneider[3]. The cause of this increase is probably an association between the γ-picoline and benzene molecules (Fig. 2.15).

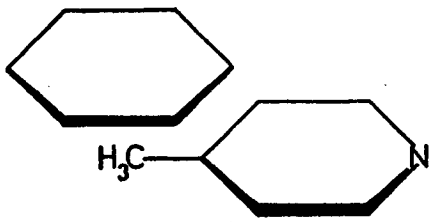


Fig.2.15

Gil and Murrell studied the effect of solvent on the spectra of azabenzenes[44] and azabiphenyls[45] and concluded that the dominant effect influencing the azabenzene chemical shift was not the reaction field proposed by Buckingham[1,4] but the formation of a specific solute-solvent complex as proposed by Schaefer and Schneider[2], Klinck and Stothers[42,43] and Hatton and Richards[15].

In the case of diazines they proposed an association arising from the high charge polarisation of the molecules. (Fig.2.16).

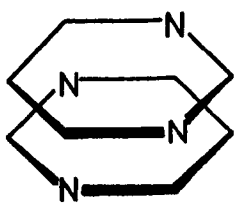


Fig.2.16

McDonald et al[46,47] have investigated the effect on the spectrum of pyridine of changing from carbon tetrachloride to an aromatic solvent. They observed a diamagnetic shift for all protons except for that α to the nitrogen atom. This was observed earlier by Ronayne and Williams[48] during an extensive study of solvent effects in PMR[48-59]. From this study it was proposed that the solvating benzene ring need not necessarily be co-planar with the solute molecule but can be orientated at an angle to the solute molecule so that it is as far away as possible from the negative end of the dipole. For example, in dimethyl aniline originally investigated by Schneider[9] the proposed association is that shown in Fig.2.17. This would explain the order of downfield shifts for the ring

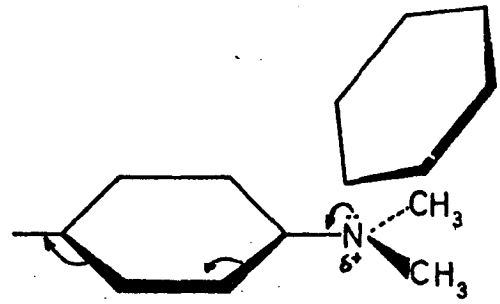


Fig.2.17

protons - o > m > p - and the appreciable upfield shift of the N-methyl protons. The situation was reversed when nitrobenzene, which has a dipole in the opposite direction to dimethyl aniline, was the solute. Now the solvating benzene molecule tends to lie over the solute ring (Fig.2.18)

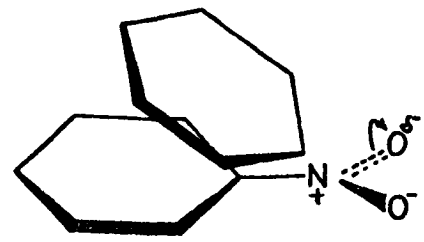


Fig.2.18

shielding the para and meta protons to a greater extent than the ortho.

Alternative Model for Aromatic Solvent Induced Shifts (ASIS)

Some workers have expressed doubts about the validity of the 1:1 solute-solvent complex theory described in the preceding section. During their investigation of solvent effects (using benzene and methyl substituted benzenes) on the PMR spectra of organo-methyl compounds Brown and Stark[60] concluded that "The hypothesis that hydrogen bonding (i.e. the formation of specific 1:1 complexes) plays a major role in producing large diamagnetic shifts in any solute is open to serious question". They proposed instead a more general solvation model in which dipole-induced dipole interactions played a major role and correlated solute dipole moment with solvent shift.

Diehl[63] investigated ASIS in the spectra of substituted benzenes and found the 1:1 complex theory untenable and proposed that there was a general ordering of benzene solvent molecules in a particular region of the dipolar solute molecules.

Matsuo investigated ASIS[61,62] and pointed out that the interaction energy of the postulated 1:1 complexes would only be a few kilocalories per mole[61] which at room temperature is close to the translational energy of molecules. He also suggested that the observed solvent shifts were too large to be explained satisfactorily by 1:1 complex formation. Some are as large as 2 ppm and this (according to Johnson and Borey[16] would mean the solute protons being about 2.6Å directly above or below the plane of the benzene ring, a condition not necessarily fulfilled in a 1:1 association complex in which the planes of the solute and solvent molecules are parallel and certainly not in the non-parallel arrangement proposed by Ronayne and Williams.[48,56,59]. Matsuo proposed instead[61] a model in

which the observed solvent shift was in fact due to the cumulative effect of the Van der Waals forces of a number of solvent molecules clustering around a particular site in the solute molecules.

Fort and Lindstrom[64] investigated the effect of solvent on the spectra of t.-butyl and adamantyl halides. No evidence for the existence of a 1:1 solute-solvent could be obtained from freezing-point experiments.

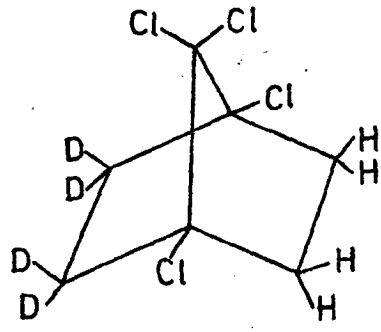
They proposed a model where a weak ordering of solvent molecules occurred in a particular region of the solute, as a result of the solute dipole interacting with the solvent. They suggested this ordering was geometrically, but not thermodynamically, equivalent to a complex.

Engler et al[65,66] have investigated ASIS and pointed out the weakness of the concept of specific 1:1 interactions. They proposed the shifts might be a combination of two contributing factors, a site factor and a solvent factor. The former simply takes into account the position of a particular proton in the solute molecule relative to the polar functional group and the latter term takes into account those effects which are responsible for the degree of solute-solvent interaction such as size of solvent molecule and the magnitude of the ring current. Thus the ASIS may be expressed by the equation below[66].

$$(\text{ASIS}) = (\text{site factor})(\text{solvent factor})$$

Engler and Laszlo also support the general solvation theory in which ASIS arise as a result of solvent molecules clustering around a particular site in the solute molecule.

Recent work by Marchand and Weimar[67] on 1,4,7,7-tetrachloro-



(VI)

2,2,3,3-tetradeuterionorbornane(VI) in 2-substituted m-xylene solvents supports the ideas of Engler and Laszlo[66].

Solvents Effects Induced by Non-Aromatic Solvents

Compared with aromatic solvents there has been little interest shown in solvent effects due to dimethyl sulphoxide and acetone. Unlike benzene which acts as a π-electron donor solvent both acetone and dimethyl sulphoxide can act as n-type donor solvents because of the lone-pair electrons on the oxygen atom in each molecule. It is generally accepted that solute solvent interactions in these solvents involve these electrons.

Schaefer and Schneider[2] studied substituted benzenes in acetone and compared their spectra with those of solutions in n-hexane in which it was assumed that solute-solvent interactions were negligible. The observed solvent shift in acetone was downfield and this was attributed to a hydrogen bonding interaction of the type shown (Fig.2.19).

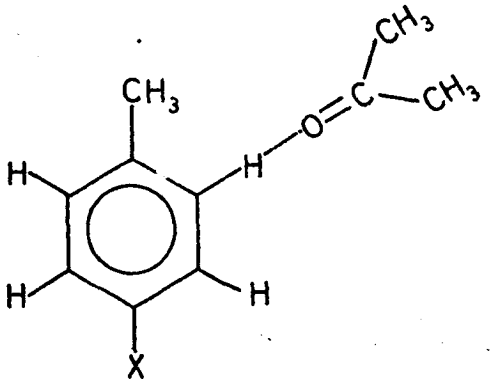


Fig.2.19

The resonance position of a hydrogen bonded proton is known to occur at lower field compared with its free state value[69]. Additional deshielding may result, when dimethyl sulphoxide and acetone solvents are used, from the magnetic anisotropy of the $\geq$S=0 and $\geq$C=0 double bonds which produces a deshielding region along the axis of the bonds.[69,85]

Drinkard and Kivelson[70] investigated the variation, with concentration, of chemical shift of the -OH proton in both water and methanol in dimethyl sulphoxide and acetone solutions. As the mole fraction of solvent (either dimethyl sulphoxide or acetone) was increased the -OH resonance was shifted to higher field, thus indicating that hydrogen bonding between water molecules is stronger than that between water and dimethyl sulphoxide (or acetone) molecules. They suggested the order for increasing hydrogen bond strength was

$$CO\text{----}HO \quad < \quad SO\text{----}HO \quad < \quad HO\text{----}HO$$

Porter and Brey[71] investigated hydrogen bonding in the pyrrole-dimethyl sulphoxide system (Fig.2.20) observing that the NH resonance was both temperature and concentration dependent

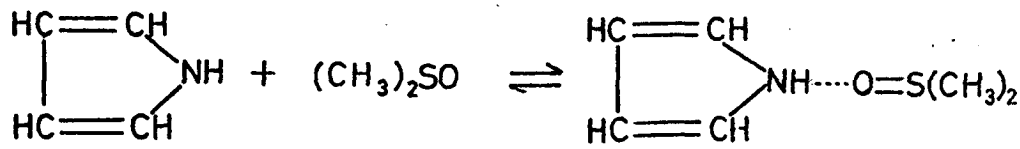
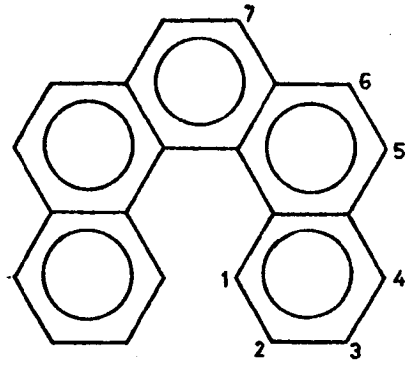


Fig.2.20

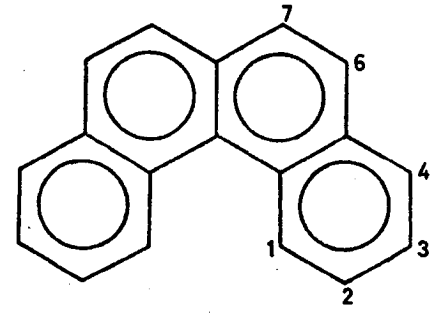
They suggested that the interaction was of the n-donor type similar to that proposed by Schaefer and Schneider[2] for solutes in acetone solution. Increasing the temperature caused an upfield shift as did an increase in concentration of pyrrole. The direction of shift indicates

a decrease in this type of interaction. Similar effects were observed by these authors for the succinimide–dimethyl sulphoxide system[72].

The downfield solvent shift due to dimethyl sulphoxide has been observed with other kinds of organic molecules by Matthews et al[73]. They studied polycyclic compounds (VII) and (VIII) in dimethyl sulphoxide



(VII)



(VIII)

and proposed that the interaction between these and the dimethyl sulphoxide molecule was via the positive end of the solvent molecule dipole and the π-electrons of the ring system leading to enhanced ring current effects causing a downfield shift.

In (VII) H_1 does not exhibit a large downfield shift. This was attributed to the non-planarity of the molecule causing H_1 to be out of the field of effect of the enhanced ring currents. In view of the fact that dimethyl sulphoxide causes downfield shifts of protons in non-aromatic solutes by hydrogen bonding interactions of the type[69] shown in Fig.2.21.

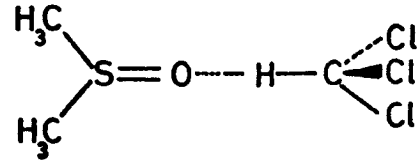
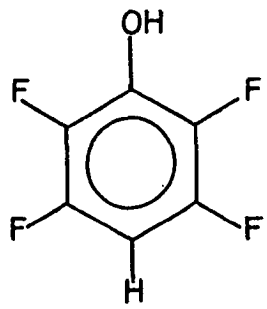


Fig.2.21

it seems that a more likely explanation is that dimethyl sulphoxide interacts with aromatic protons in a similar way except where the interaction is limited or is not possible for steric reasons. This would explain why H_1 does not show the downfield shift exhibited by other protons in (VII) and (VIII) for this is the proton least accessible sterically to solvent molecules. Furthermore if the interaction suggested by Matthews et al did exist, with the positive end of the solvent dipole interacting with the solute molecule π-electrons, the methyl groups of the solvent molecules would be in the shielding region above the plane of the aromatic ring (cf. chloroform-benzene and acetonitrile-benzene systems) and their resonance should exhibit an upfield shift compared with the value in neat dimethyl sulphoxide. This argument was tested experimentally using phenanthrene and dimethyl sulphoxide. No change of shift of the solvent resonance was observed when phenanthrene was added, indicating that the dipole- π-electron interaction is insignificant.

The spectrum of bipyridyl in a number of solvents was measured by Spotswood and Tanzer[74]. Changing the solvent from carbon tetrachloride to acetone caused a downfield shift for all protons. The proton resonance much less affected by solvent change was that of the 3(3')-proton. The reason for this may be similar to that suggested above for the 1-protons in dibenzo phenanthrene.

Dale[75] observed an increasing downfield shift, with increasing electron donor ability of the solvent, for the para-proton in tetrafluorophenol (IX) and reasoned that this was a result of increased



(IX)

direct interaction (hydrogen bonding) between the para proton and the electron donor solvent molecules.

Spotswood and Tanzer have investigated solvent effects on the spectra of pyridine and its derivatives[76,77]. They concluded that change in chemical shift with solvent was a result of interaction of the hydrogen bonding solvent with the nitrogen lone-pair and a resultant reduction in the electrostatic field associated with this lone pair. The reaction field was not considered to be the dominant effect.

Using solvents such as benzene, pyridine, dimethyl sulphoxide and acetone, Karabatsos et al[78-90] have investigated the spectra of some phenylhydrazones. They proposed not only an interaction between phenylhydrazone and solvent molecules but also self-association between the phenylhydrazone molecules. Their conclusions are of particular relevance to this work and will be discussed at greater length in the Discussion of this chapter.

Choice of Solvents

Dimethyl sulphoxide was chosen as the solvent for most of the compounds in this work as it was the only commonly available deuterated solvent which would dissolve both the organic ligands and the metal complexes sufficiently for PMR purposes. It was realised that because of the polar nature of the solvent the observed chemical shifts of the compounds would not be those of the isolated molecules.

In an attempt to gain some insight into the extent of the solvent effect spectra of E and Z-PAPHY in carbon tetrachloride and benzene were measured. The latter solvent was unsatisfactory with regard to obtaining reference chemical shifts because of the existence of aromatic solvent induced shifts (ASIS) which are described elsewhere. Dilution studies indicated that the solute-solvent interaction in carbon tetrachloride was relatively small and therefore that solvent was chosen as the inert reference solvent.

Ideally cyclohexane or n-hexane should be used but even at elevated temperatures these solvents failed to dissolve a sufficient quantity of any of the compounds of interest. The fluorocarbon solvent FC78(3M Co.Ltd.) was tried but this failed to dissolve the compounds investigated.

Fort and Lindstrom[64] have previously used carbon tetrachloride as an inert solvent for PMR studies and considered it satisfactory although Dixon[83] showed that there was some interaction between methanol and carbon tetrachloride which appeared to be of the hydrogen bonding type.

It has been proposed by Ladd and Jones[81] and Sharpe and Walker[84]

that there is a weak interaction between carbon tetrachloride and pyridine (Fig.2.19) of the type which occurs with chloroform involving

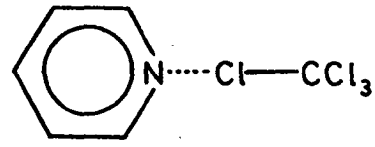


Fig. 2.19

the nitrogen lone-pair but the effect on the PMR spectrum is considered to be unimportant.

Engler and Laszlo[66] concluded that if solvent shifts are sufficiently large then the choice of inert reference solvent (carbon tetrachloride, cyclohexane or fluorocarbon solvent FC75) has little effect on the results.

Discussion and Results

2.1 · The Origin of Shifts Induced by Non-Aromatic Solvents

Before discussing the nature of the solvent induced shifts observed in the course of this work it is necessary to consider their origin.

It has been suggested[45,81] that the chemical shift changes occurring with change in solvent (e.g. carbon tetrachloride to methanol) are predominantly due to the solvents having different dielectric constants which in turn affects the reaction field surrounding the solute molecule. It is considered that results from this work, together with the results of Spotswood and Tanzer[76,77] show that this may not be the case and the solvent shifts are largely a result of solute-solvent interactions.

Dilution studies, in dimethyl sulphoxide, on the resonance position of the methyl group proton in some methyl substituted PAPHY's show that there is no observable dilution shift. This implies that hydrogen bonding between these protons and the solvent molecules is very small or non-existent. Spotswood and Tanzer[76] also found a negligible solvent dependence for the methyl protons resonance in γ-picoline. Also the resonance position of the methyl group in Z-2'-Me-PAPHY is the same (230 Hz) in both carbon tetrachloride and dimethyl sulphoxide. This is further evidence for the lack of methyl group-solvent interaction. If the reaction field was dominant in determining solvent shifts in this case one would expect some change in the methyl group resonance position on changing the solvent from carbon tetrachloride to dimethyl sulphoxide which has a much higher dielectric constant.

It is predicted in Buckingham's reaction field theory[4] that an increase in the dielectric constant of the solvent will result in a deshielding of the β and γ-protons, in pyridine, with respect to the α-proton. This means that the internal shifts $\nu_\alpha - \nu_\beta$ and $\nu_\alpha - \nu_\gamma$, should become less positive. Table.2.1 lists values of these internal shifts, for PAPHY, 2,2'-bipyridyl and 1,10-phenanthroline, obtained in solvents of different dielectric constant. It may be seen that although there are one or two inconsistencies the general trend is a decrease in internal shift with increase in solvent dielectric constant. At first sight this would appear to support the reaction field theory. However, it has been shown[82] that the low shielding of the α-proton relative to the β and γ-protons is a result of the anisotropy of the nitrogen atom and the local dipole dipole moment associated with the nitrogen lone-pair. Spotswood and Tanzer[76] calculated values for the contribution to the chemical shift of the pyridine ring protons from the effects associated with the lone-pair. Their values were (α) 0.43 ppm, (β) 0.20 ppm, (γ) 0.15 ppm.

It is clear that any interaction with the solvent involving the lone-pair* will have a greater shielding effect on the α-proton than on the β and γ-protons.

The reaction field theory also predicts[4] that the relationship

---

* The chloroform proton resonance signal occurs at 728.3Hz in the neat liquid and 801Hz in an approximately 50-50 (by volume) mixture of chloroform and pyridine. This downfield shift implies interaction with the nitrogen lone pair rather than with the aromatic π-electrons as is the case with benzene

Table 2.1. Variation of internal chemical shifts with solvent for bipyridyl, PAPHY, and 1,10-phenanthroline.

Bipyridyl[a]

Solvent	$\frac{\varepsilon-1}{\varepsilon+1}$	$\nu_\alpha - \nu_\beta$ (Hz)	$\nu_\alpha - \nu_\gamma$ (Hz)
CCl_4	0.344	140.3	0.860
$CDCl_3$	0.655	139.3	88.0
CH_2Cl_2	0.802	135.4	84.2
CH_3I	0.750	134.2	81.5
Me_2CO	0.908	127.5	76.2
MeOH	0.941	122.5	72.3
D_2O	0.973	112.2	66.4

PAPHY

CCL_4[b]	-	142.2(140.9)*	91.90(60.05)
$CDCl_3$[d]	-	139.71(143.10)	91.65(63.38)
d_6DMSO[b]	-	124.40(133.22)	73.87(46.6)

1,10-phenanthroline[c]

CCl_4	-	150.0	97.50
$CDCl_3$	-	161.70	100.0
CH_2CL_2	-	151.3	82.83

* Figures in brackets refer to the hydrazine ring of PAPHY

(a) Ref. 77.

(b) This work

(c) R.M. Carmen and J.R. Hall, Aust. J. Chem., 17, 1354, (1964). E.V. Donckt, R.H. Martin, and F. Geerts-Evrard, Tetrahedron, 20, 1495, (1964) and D.J. Blears and S.S. Danyluk, ibid., 23, 2927, (1967)

(d) M.K. Cooper, B.G. McGrath, and S. Sternhell, Aust.J.Chem., 22, 1549, (1969)

between $\frac{(\varepsilon-1)}{(\varepsilon+1)}$ and the solvent shift is approximately linear; therefore plots of $\nu_\alpha - \nu_\beta$ and $\nu_\alpha - \nu_\gamma$ against $\frac{(\varepsilon-1)}{(\varepsilon+1)}$ should also be linear. This has been done for bipyridyl using the spectral data of Spotswood and Tanzer[77]. The plots, (Fig.2.22) are not linear and this could be a result of the presence of specific solute-solvent interactions. It is of interest to note that the last three points on the graph (representing the solvents acetone, methanol and deuterium oxide) indicate a relatively large variation of internal shift for a small variation in $\frac{(\varepsilon-1)}{(\varepsilon+1)}$. This may be a result of the ability of these solvents to engage in hydrogen bonding with ring protons.

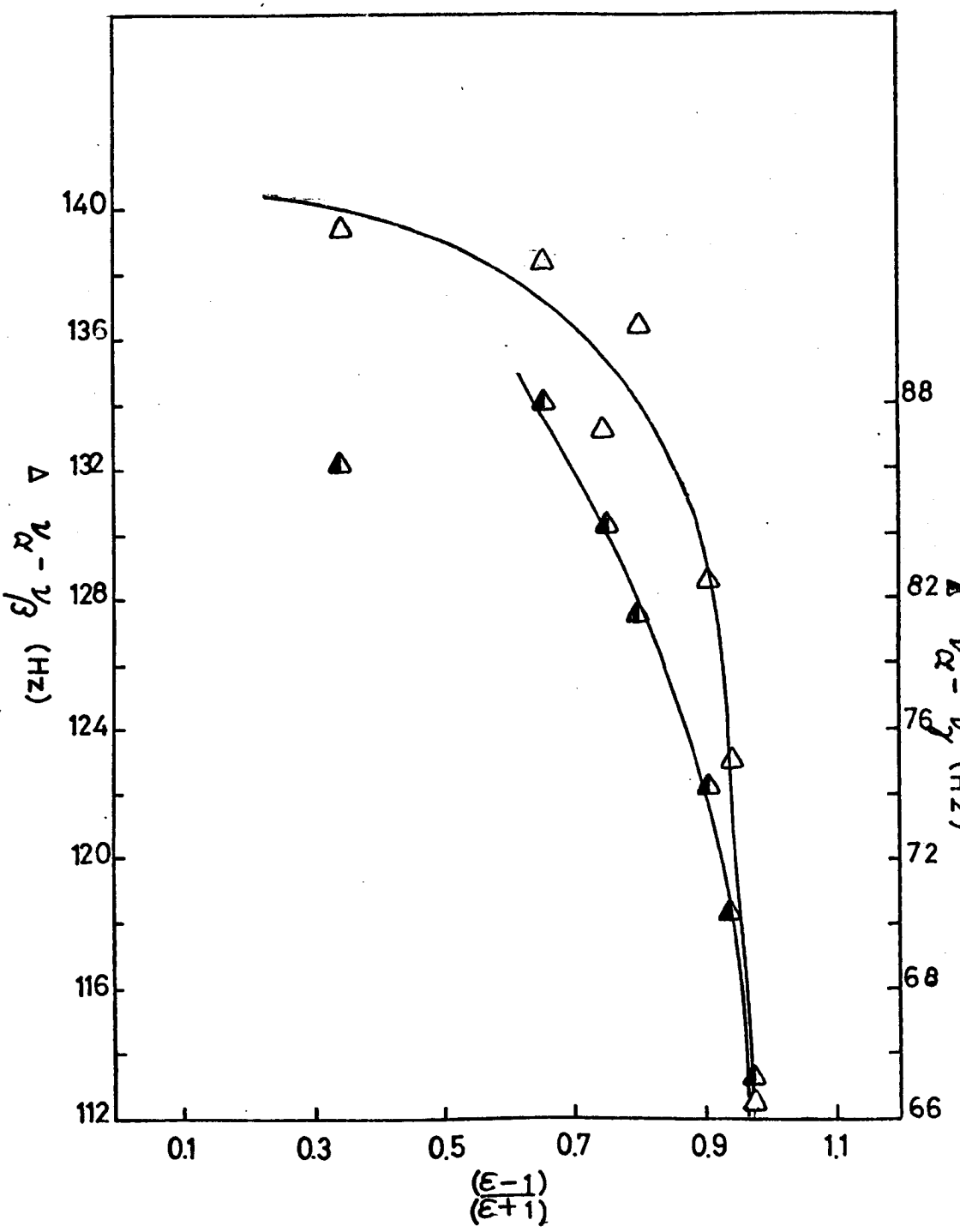

140
136
132
128
124
120
116
112
88
82
76
72
68
66
0.1
0.3
0.5
0.7
0.9
1.1
(ε−1)/(ε+1)
(zH) ν₂ − ν₁
(zH) ν₂ − ν₁

Fig.2.22

2.2. E-PAPHY in carbon Tetrachloride

The spectrum of E-PAPHY in carbon tetrachloride (S.2.2) shows no overlapping of resonances except for those of H_2 and H_2'. Splitting of the H_2 resonance by the formyl proton can be observed.

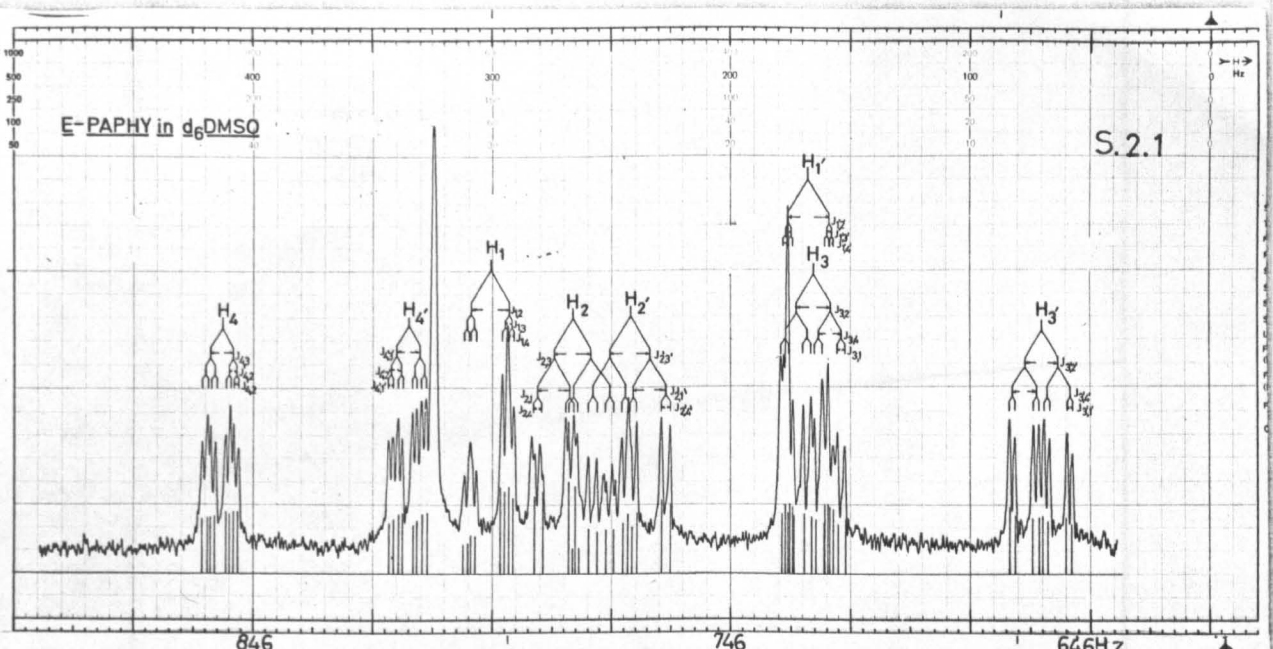
The dilution curves for E-PAPHY in carbon tetrachloride are shown in Fig.2.23,(a), (b) and (c). Over the concentration range studied the chemical shift variation with concentration was quite small except for the formyl and imino protons. Apart from H_2 the shift was positive with increased concentration.

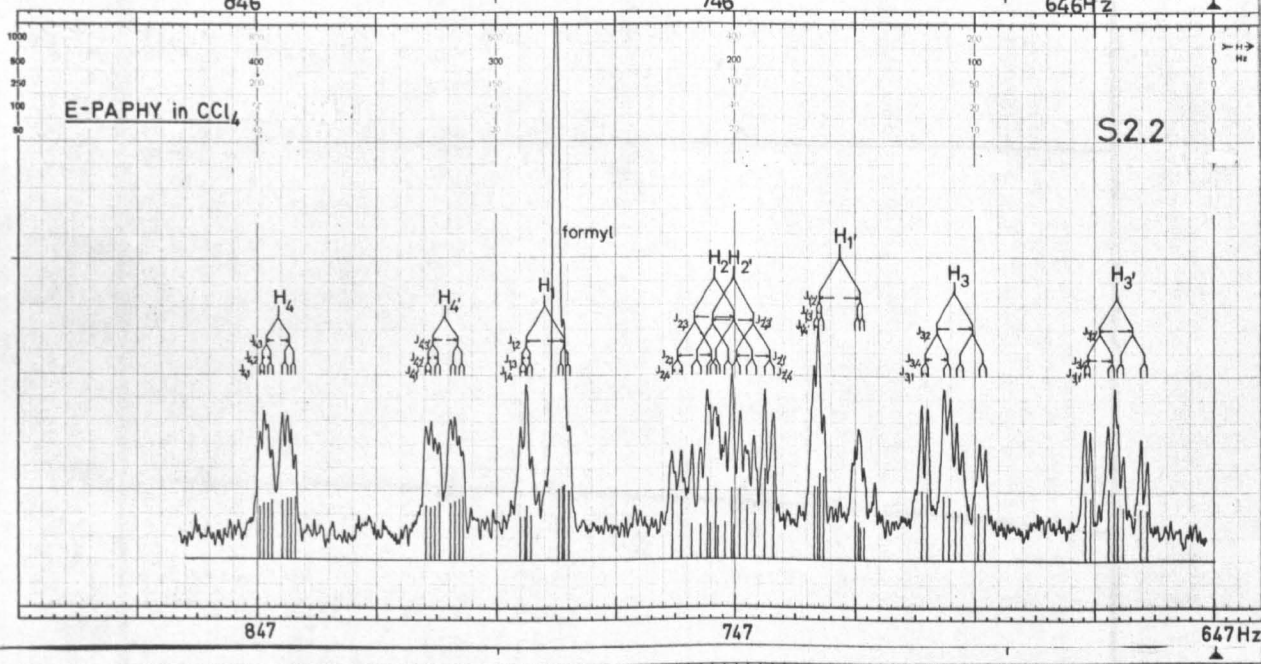
The increase in chemical shift may be attributed to some form of solute-solvent interaction which has a deshielding effect on the ring protons. There are three possible types of interaction

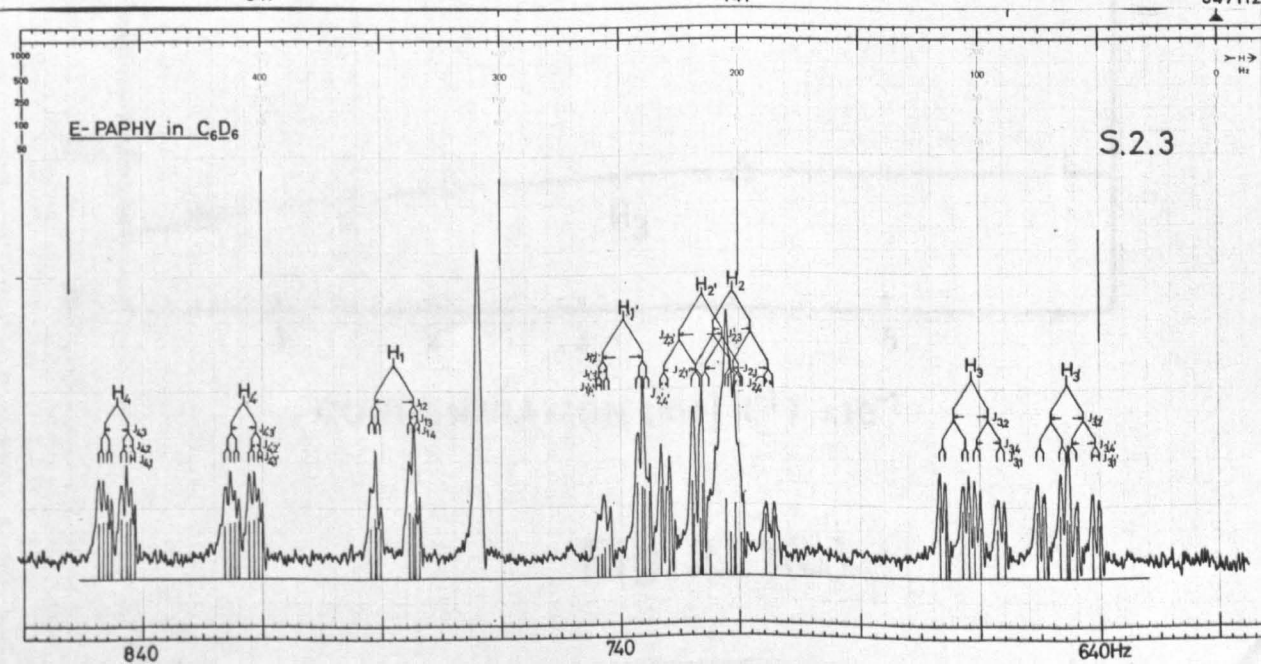
(I) Hydrogen bonding between the imino proton of one PAPHY molecule and the nitrogen lone pair of one of the ring nitrogens of another PAPHY (and possibly the nitrogen atom of the $\rangle C = N-$ linkage). (Fig.2.24a)

(II) Hydrogen bonding between the lone-pair of either ring nitrogen (and again possibly the nitrogen of the $\rangle C = N-$ linkage) and the ring protons of another PAPHY molecule (Fig.2.24b)

(III) Intermolecular (dipole-dipole) interaction.


E-PAPHY in d6DMSO
S.2.1
H4
H4'
H1
H2
H2'
H1'
H3
H3'
846
746
646Hz


E-PAPHY in CCl4
S.2.2
formyl
H4
H4'
H1
H2 H2'
H1'
H3
H3'
847
747
647Hz


E-PAPHY in C6D6
S.2.3
H4
H4'
H1
H1'
H2' H2
H3
H3'
840
740
640Hz

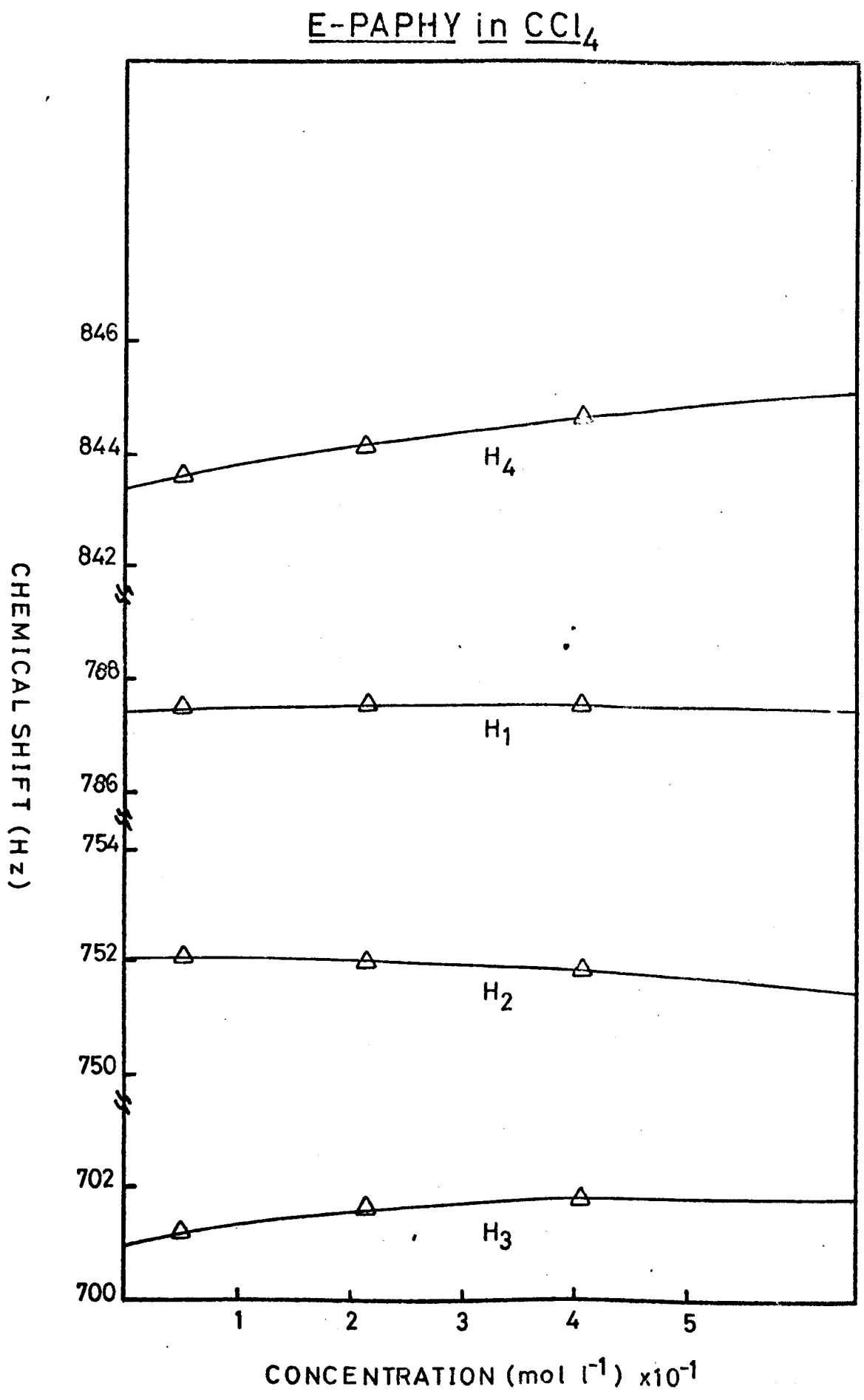

E-PAPHY in CCl_4
846
844
842
788
786
754
752
750
702
700
H_4
H_1
H_2
H_3
1
2
3
4
5
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l^{-1}) $x10^{-1}$

Fig. 2.23(a)

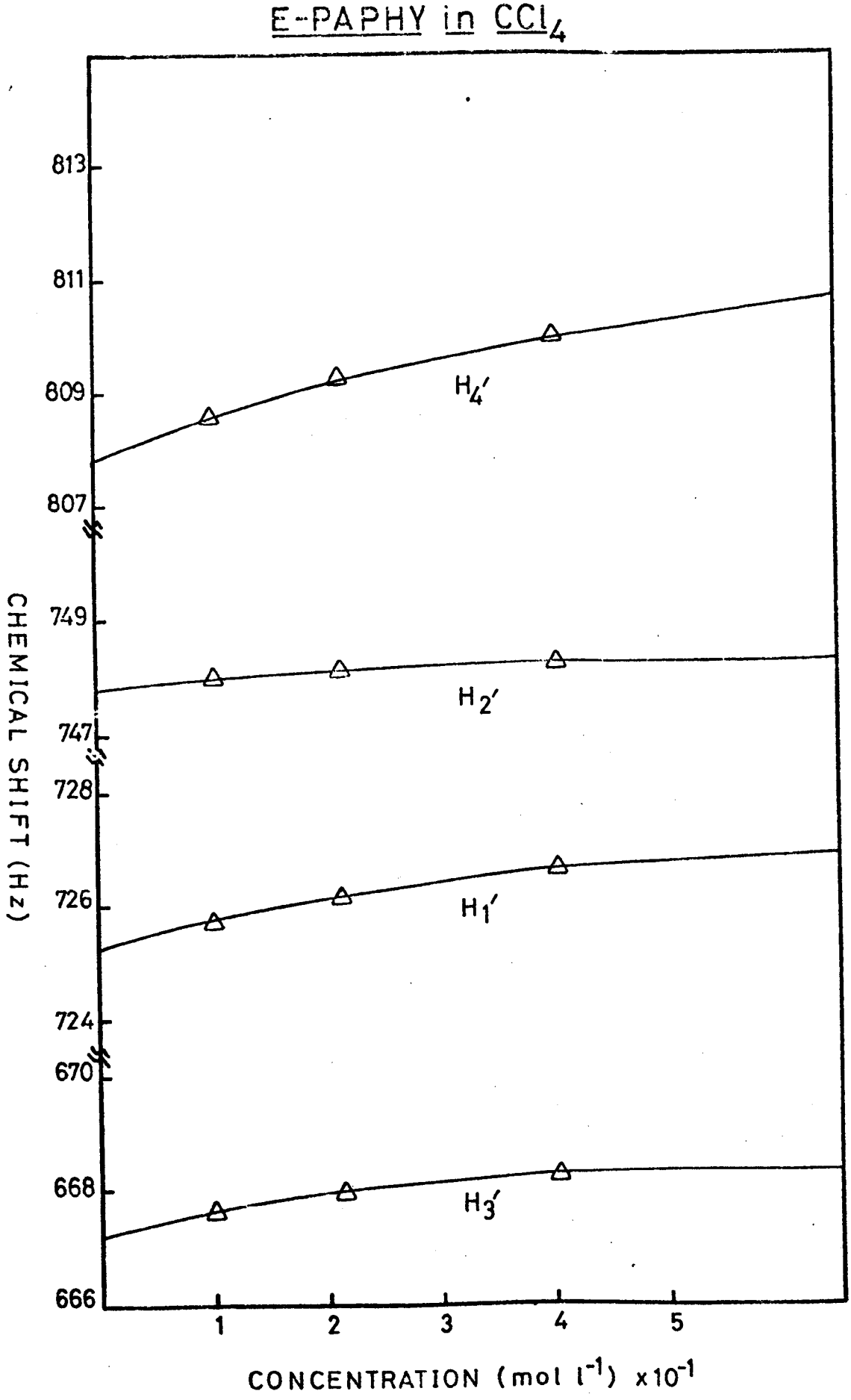

E-PAPHY in CCl4
813
811
809
807
749
747
728
726
724
670
668
666
H4′
H2′
H1′
H3′
CHEMICAL SHIFT (Hz)
1
2
3
4
5
CONCENTRATION (mol l-1) x10-1

Fig.2.23(b)

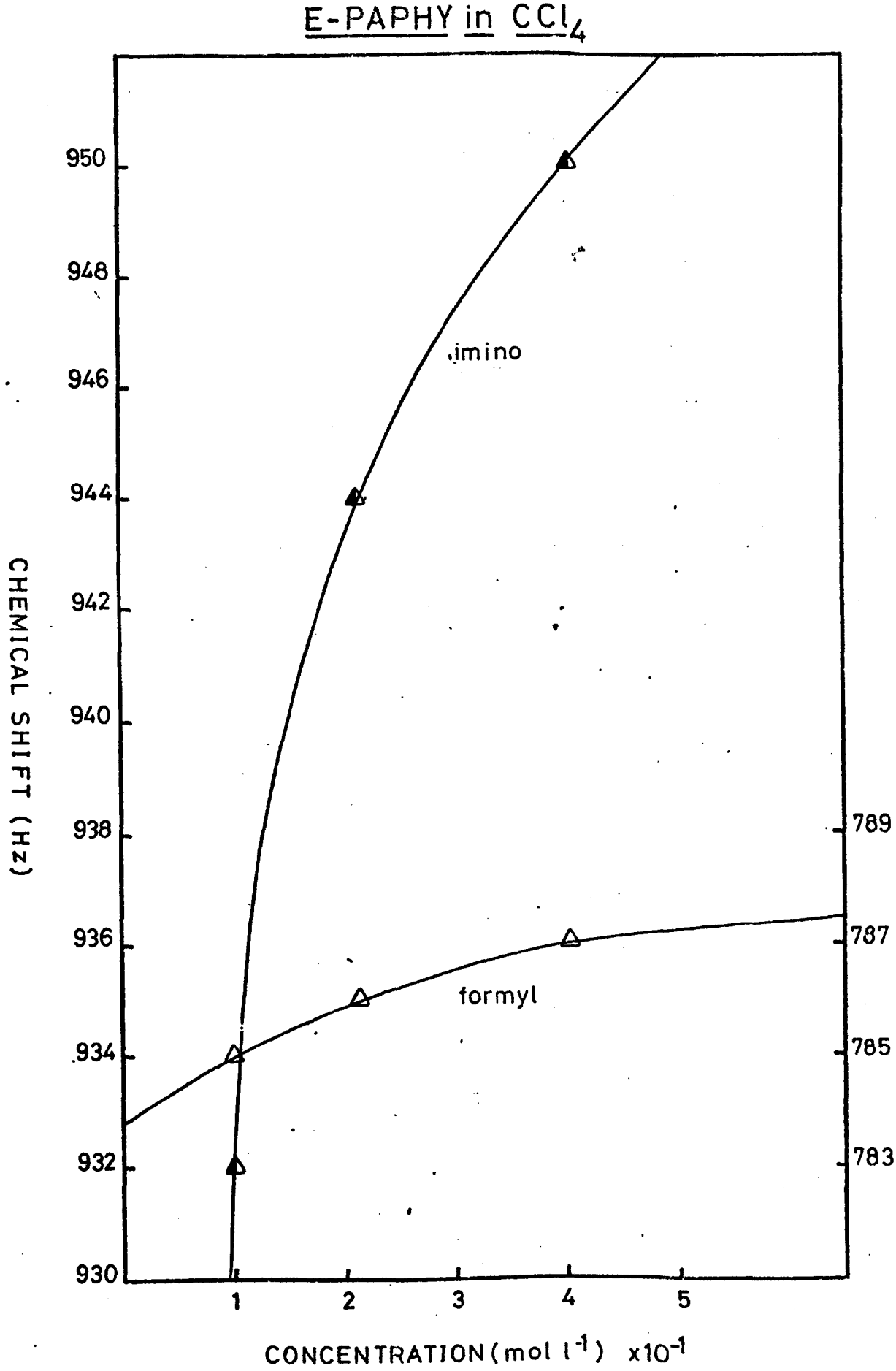
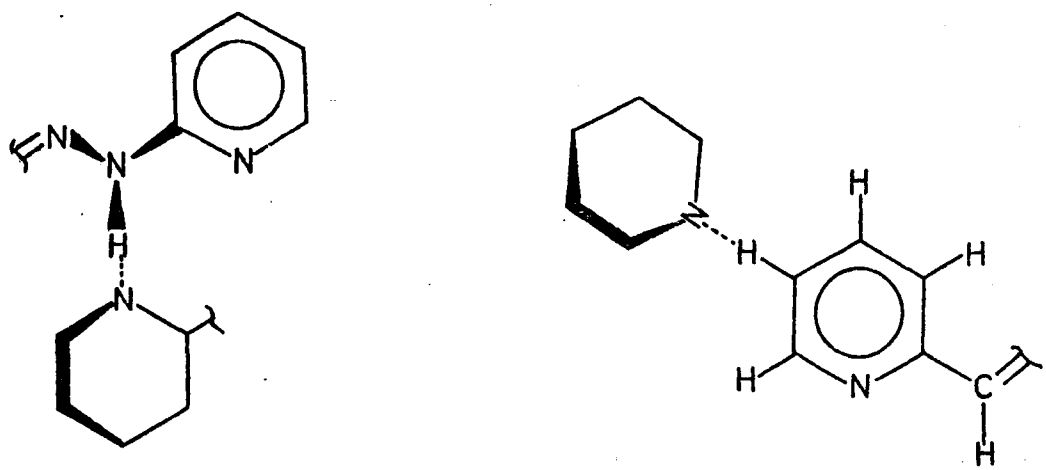

E-PAPHY in CCl_4
950
948
946
944
942
940
938
936
934
932
930
789
787
785
783
imino
formyl
CHEMICAL SHIFT (Hz)
1
2
3
4
5
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig.223(c)



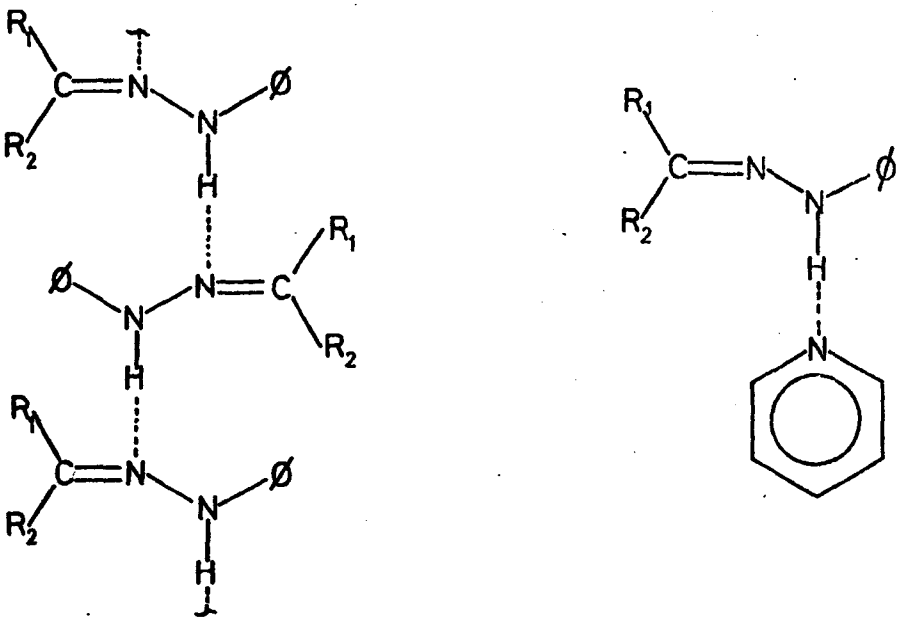
(a) (b)

Fig.2.24

Both types of hydrogen bonding would have the effect of deshielding the ring protons, type (I) simply by withdrawal of electronic charge via the nitrogen atom (cf. protonation in trifluoroacetic acid) and type (II) by virtue of the hydrogen bonding of the ring protons with the nitrogen of another PAPHY molecule. The latter effect will also result in a deshielding of the protons of the ring which contains the associating nitrogen atom.

The dipole-dipole interaction would presumably lead to a parallel alignment of the heterocyclic rings and hence a shielding of at least some ring protons as observed by Gill and Murrell[37] for diazine association. Experimental evidence is that this type of interaction is not significant.

The imino proton shift shows a very large concentration dependence indicating that it is involved in hydrogen bonding of the type (I). A similar interaction (Fig.2.25a) has been proposed by Karabatsos and Taller[78] for phenlyhydrazones. They proposed phenylhydrazone self-association (Fig.2.25a) in carbon tetrachloride and phenylhydrazone-pyridine



(a) (b)

Fig.25

association (Fig.2.25b) in pyridine.

It is reasonable to assume that the type (II) interaction described above is also present and that both contribute to the shape of the dilution curves.

As the solute concentration decreases there is the possibility of

another type of interaction in which the lone pair of the ring nitrogen interacts weakly with the solvent molecules (Fig.2.19) as discussed in the Introduction. This could account for the fact that the shifts of H_4 and $H_{4'}$ are more concentration dependent than the other protons and are deshielded relative to them with decreasing solute concentration. As the solute-solute interaction decreases (i.e. both type (I) and (II)) the solvent interaction with the nitrogen lone-pair will increase. It was shown in the Introduction that such an interaction shields the proton α to the nitrogen relative to the β and γ-protons. Of course, interactions (I) and (II) both involve ring nitrogen lone-pairs but the shielding of the α-proton relative to the β and γ protons is probably to a great extent masked by the hydrogen bonding of the ring protons having a deshielding effect.

2.3 E-PAPHY in Dimethyl Sulphoxide

On changing the solvent from carbon tetrachloride to dimethyl sulphoxide which is highly polar and an n-type donor the spectrum of E-PAPHY changes considerably (S.2.1). All proton shifts move downfield Fig.2.26 gives values of $\Delta^{DMSO}_{CCl_4}$ (= ν_{CCl_4} - ν_{DMSO}). A positive

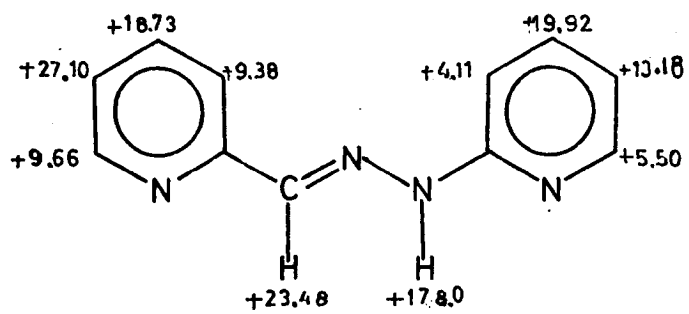


Fig.2.26

sign indicates a downfield shift.

The deshielding is greatest for $H_{2(2')}$ and $H_{3(3')}$ and less for $H_{1(1')}$ and $H_{4(4')}$. For the 1-protons the small $\Delta^{DMSO}_{CCl_4}$ values may be a result of them being ortho to another substituent group in the ring thus making them less sterically accessible to dimethyl sulphoxide molecules. From the dilution curves in carbon tetrachloride (Fig.2.22) it may be seen that the solute solute interactions had a greater deshielding effect on H_4 and H_4'. However, dissolution in dimethyl sulphoxide which is a hydrogen bonding solvent would considerably reduce the solute-solute interaction and in turn the deshielding effect it had on H_4 and H_4'. Karabatsos and Taller[78] also found that hydrogen bonding between dimethyl sulphoxide and phenylhydrazone is stronger than phenylhydrazone self-association

and phenylhydrazone-pyridine association. Phenylhydrazone-carbon tetrachloride association is weakest of all.

The values of $\Delta^{DMSO}_{CCl_4}$ in the aldehyde ring are larger than those observed for the hydrazine ring and this may be a result of the electron withdrawing formyl substituent making the ring proton more susceptible to solvent attack. The imino proton exhibits the largest value of $\Delta^{DMSO}_{CCl_4}$ which is not surprising when one considers its quite acidic nature.

The general downfield shift of resonances in dimethyl sulphoxide may be attributed to hydrogen bond formation between the oxygen lone-pair electrons of the solvent molecule and the solute protons similar to that proposed by Schaefer and Schneider[37] for substituted benzenes in acetone solution.

Comparison of the dilution curves in dimethyl sulphoxide (Fig.2.27c) and carbon tetrachloride (Fig.2.23c) show that in the former case the concentration dependence of the imino proton is less. This may be because over the concentration range studied it is likely that the acidic amino protons of almost all solute molecules are solvated by dimethyl sulphoxide molecules and thus would show less concentration dependence.

In the absence of any intermolecular (solute-solute) interactions the dilution curves in dimethyl sulphoxide would be expected to show a decrease in shift with increase in concentration. This is because the observed chemical shift of a proton is the time-weighted average of the shift of that proton in the isolated molecule and its shift in the solvated molecule. Thus as the solute concentration increases the time that the solute

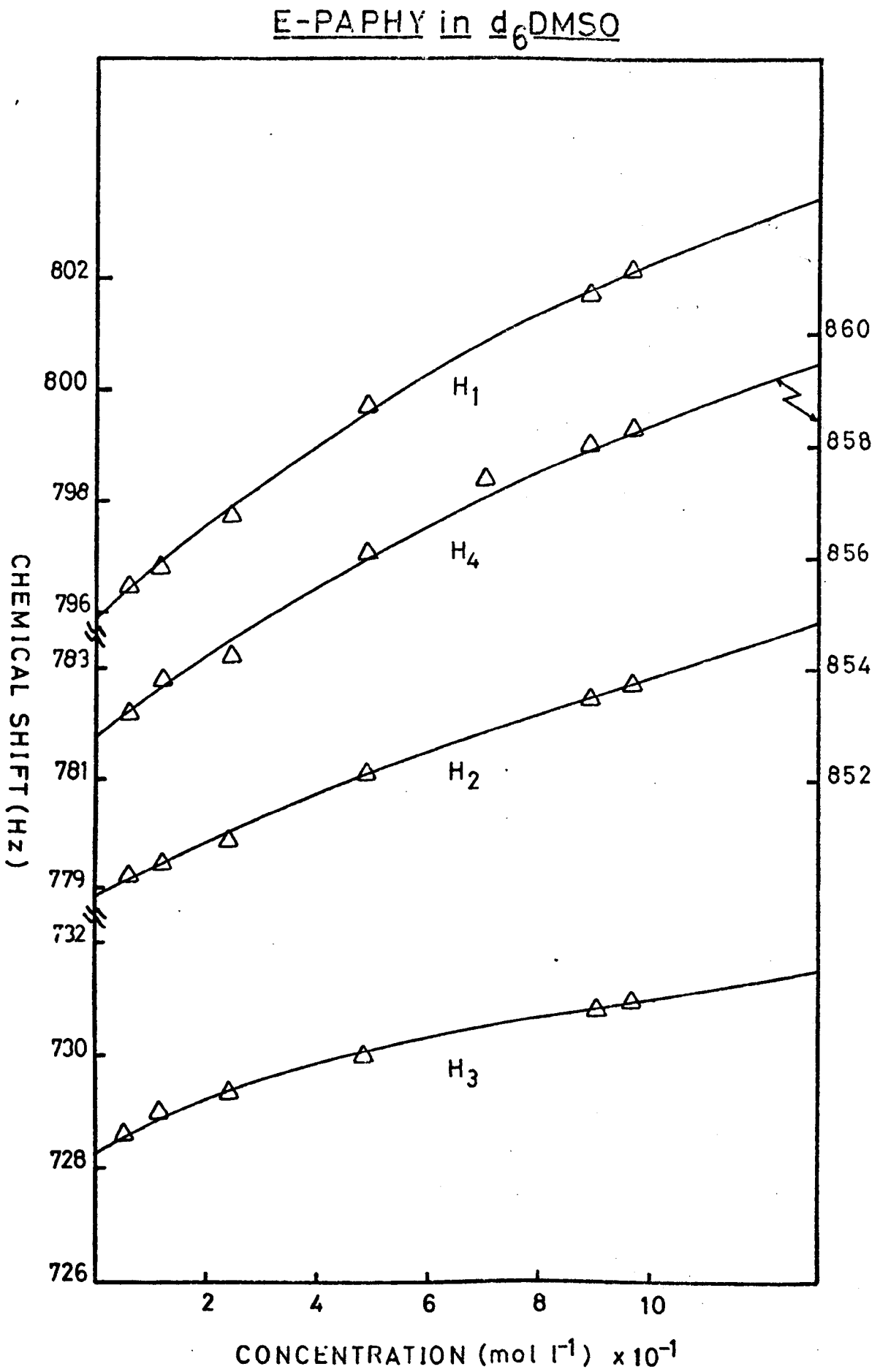

E-PAPHY in d6DMSO
802
800
798
796
783
781
779
732
730
728
726
860
858
856
854
852
H1
H4
H2
H3
2
4
6
8
10
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l-1) x 10-1

Fig. 2.27(a)

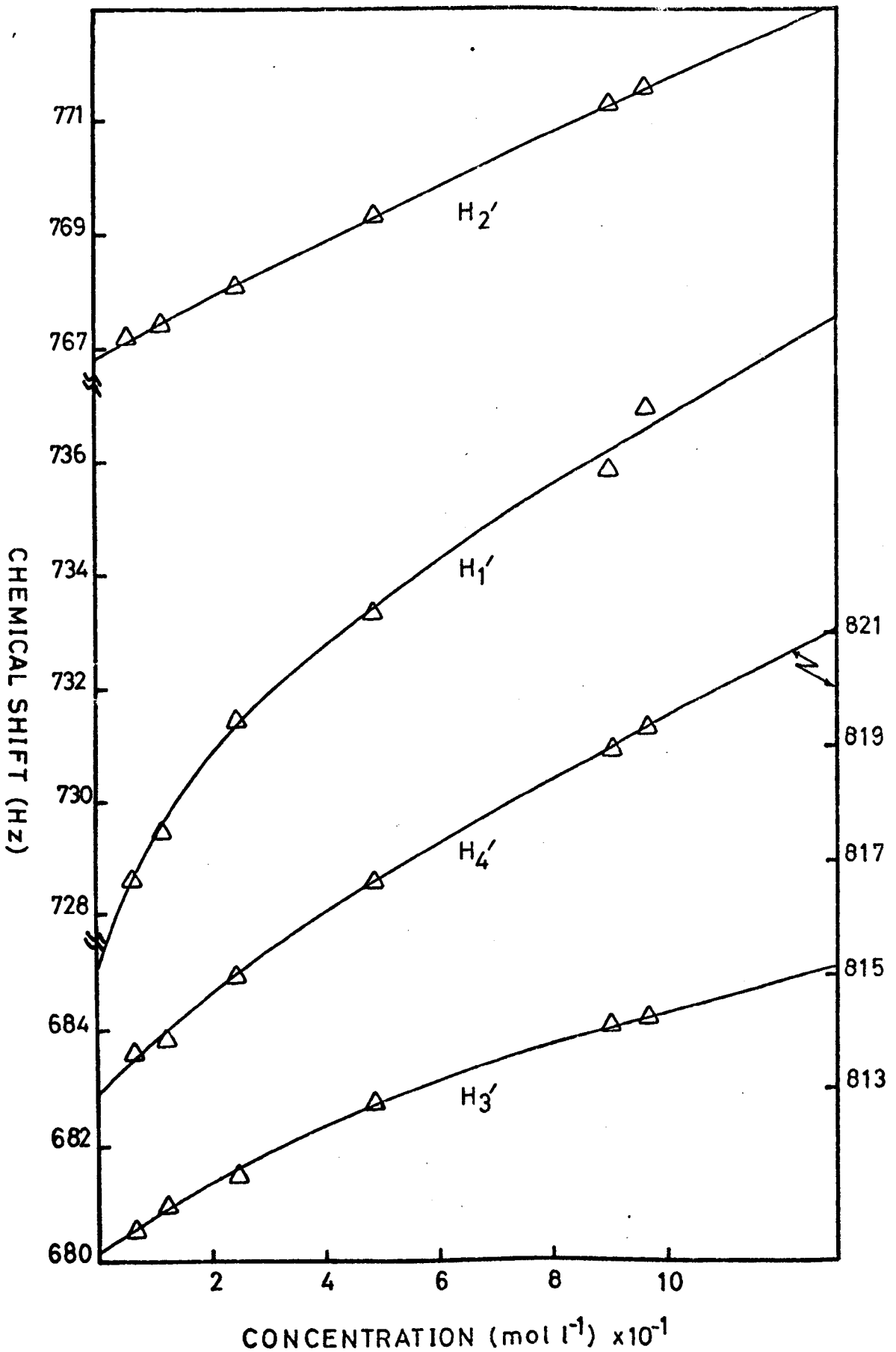

E-PAPHY in d_6DMSO
771
769
767
736
734
732
730
728
684
682
680
821
819
817
815
813
$H_{2'}$
$H_{1'}$
$H_{4'}$
$H_{3'}$
2
4
6
8
10
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig.2.27(b)

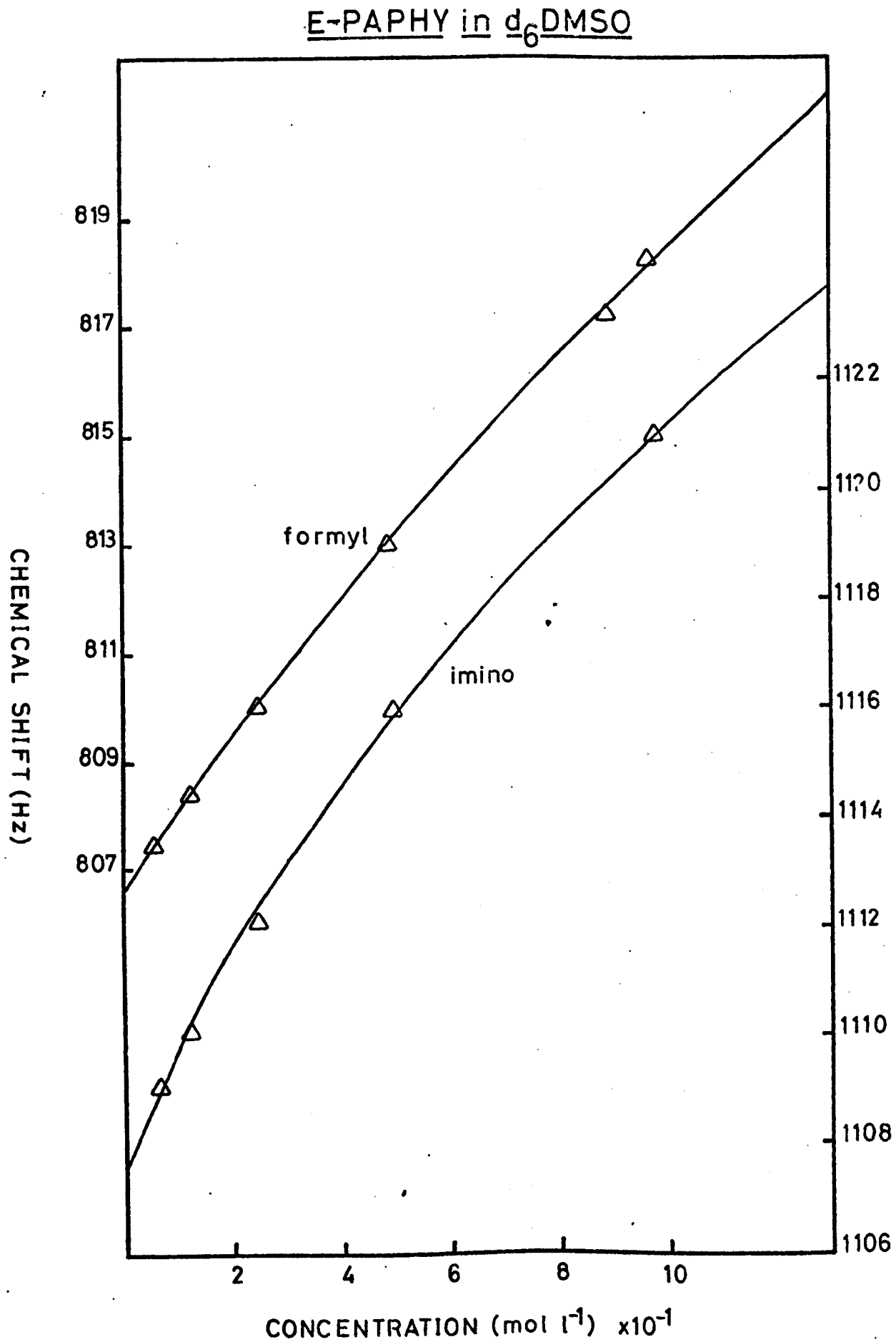

E-PAPHY in d_6DMSO
819
817
815
813
811
809
807
1122
1120
1118
1116
1114
1112
1110
1108
1106
formyl
imino
2
4
6
8
10
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig. 227(c)

molecule spends in the associated state with solvent molecules will decrease, and as the association has the effect of increasing the chemical shift, a nett decrease in shift should be observed for all protons. The fact that this is not observed may possibly be attributed to the solute-solute interactions described previously although the following evidence is against this argument.

(I) The combined effect of solute-solute and solute-solvent interactions would be expected to produce dilution curves shallower than those obtained in carbon tetrachloride. This would arise because solute-solute hydrogen bonding decreases with dilution in dimethyl sulphoxide (thus decreasing the chemical shift) and solute-solvent hydrogen bonding increases (thus increasing the chemical shift). The chemical shifts will therefore appear to be less sensitive to concentration changes.

(II) Dilution curves for the protons in the hydrazine ring in Z-PAPHY (Fig.2.36) are very similar to those obtained for corresponding protons in E-PAPHY. This appears to indicate that the type (I) interaction involving the imino protons (which is not possible in the Z-isomer) has little effect on the chemical shifts of the hydrazine ring protons, although the hydrazine ring proton shifts in E-PAPHY do appear to show a greater dependence on concentration in E-PAPHY than in Z-PAPHY.

(III) Dilution curves for some metal complexes in dimethyl

sulphoxide (Figs.2.28 and 2.29) show the same general shape as for PAPHY. Solute-solute interactions of the type discussed are not expected to be present in the metal complex case.

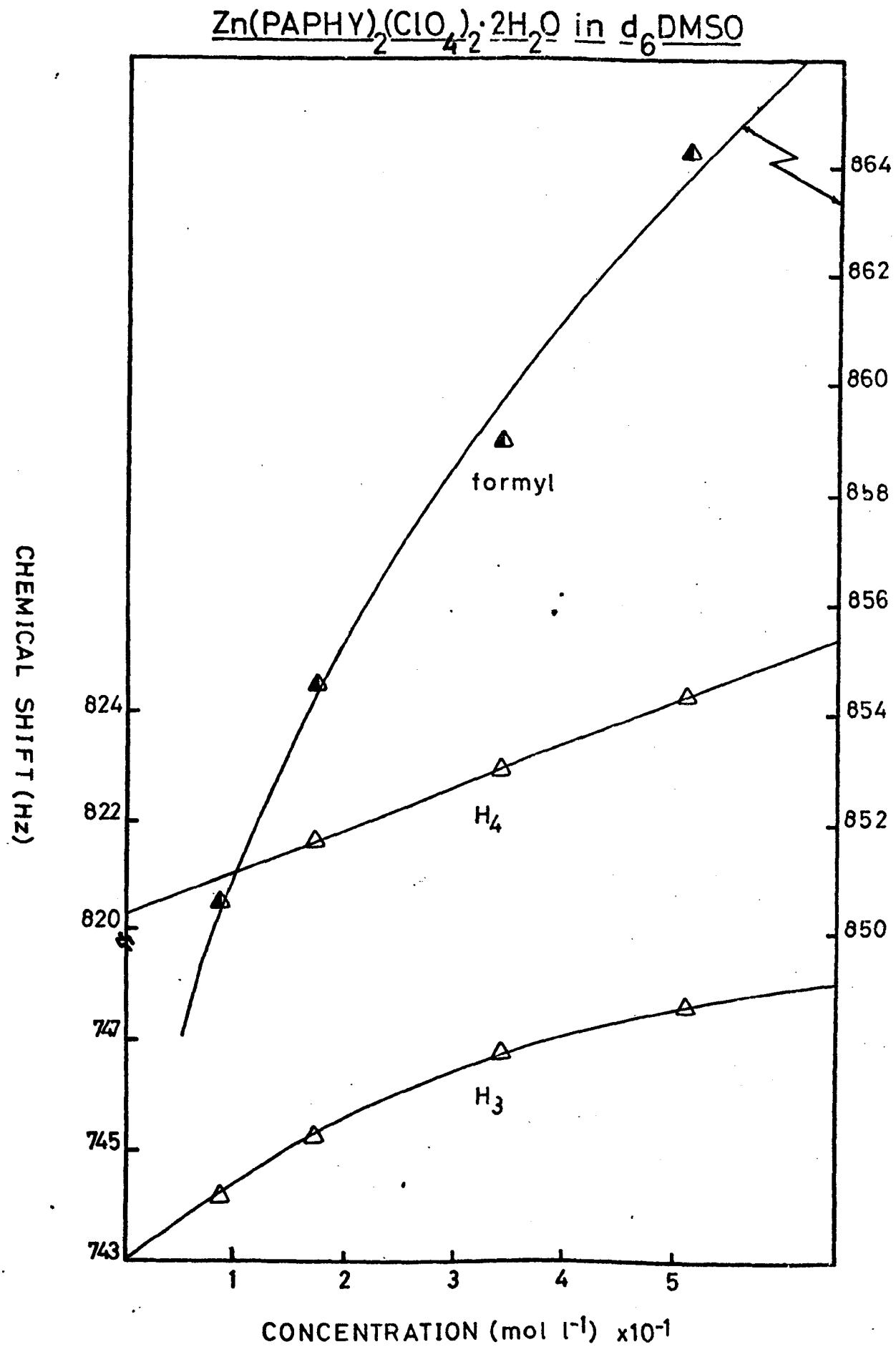

Zn(PAPHY)2(ClO4)2·2H2O in d6DMSO
CHEMICAL SHIFT (Hz)
824
822
820
747
745
743
864
862
860
858
856
854
852
850
formyl
H4
H3
1
2
3
4
5
CONCENTRATION (mol l-1) x10-1

Fig.2.28(a)

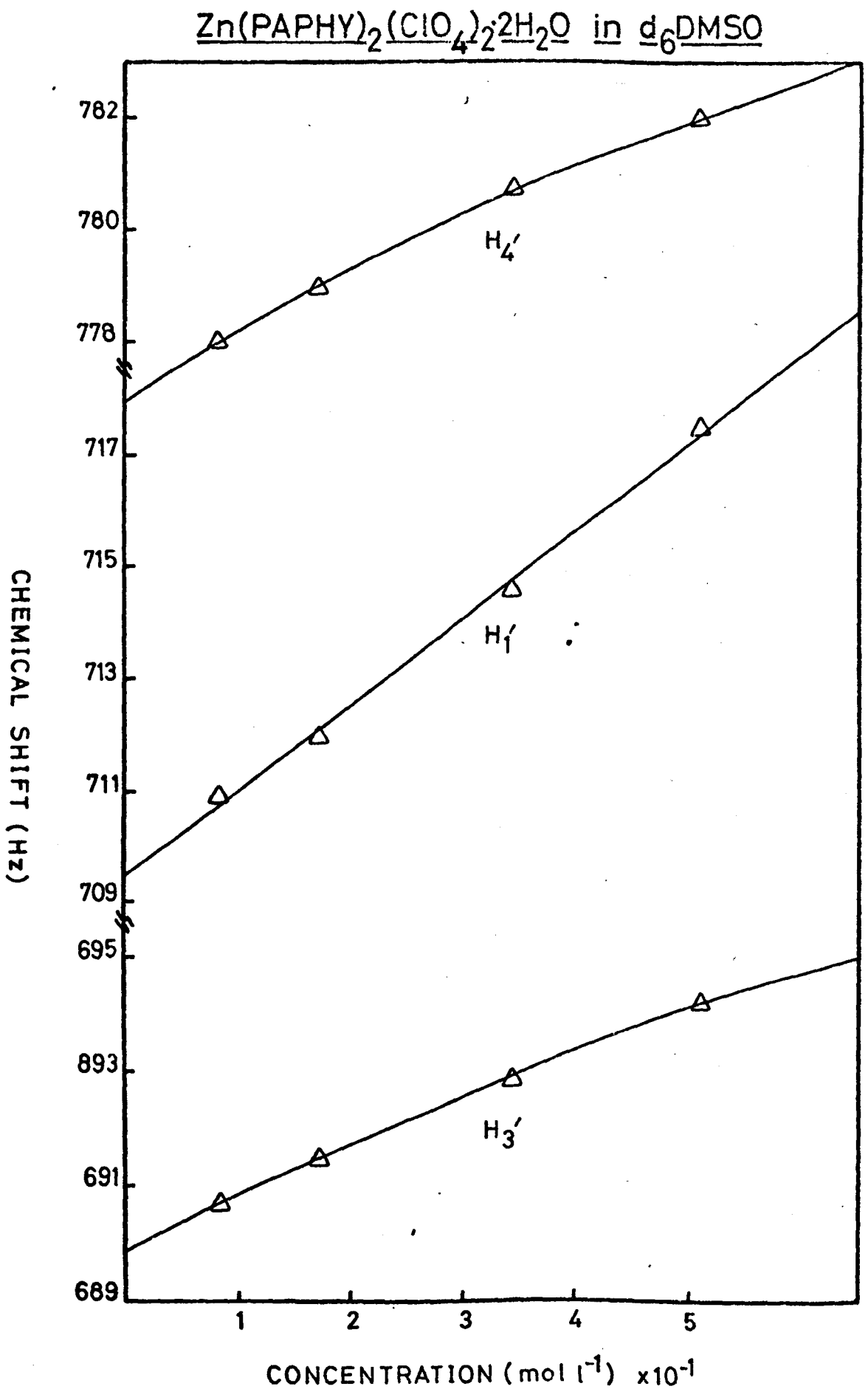

Zn(PAPHY)2(ClO4)2·2H2O in d6DMSO
782
780
778
717
715
713
711
709
695
893
691
689
H4′
H1′
H3′
CHEMICAL SHIFT (Hz)
1
2
3
4
5
CONCENTRATION (mol l-1) x10-1

Fig.2.28(b)

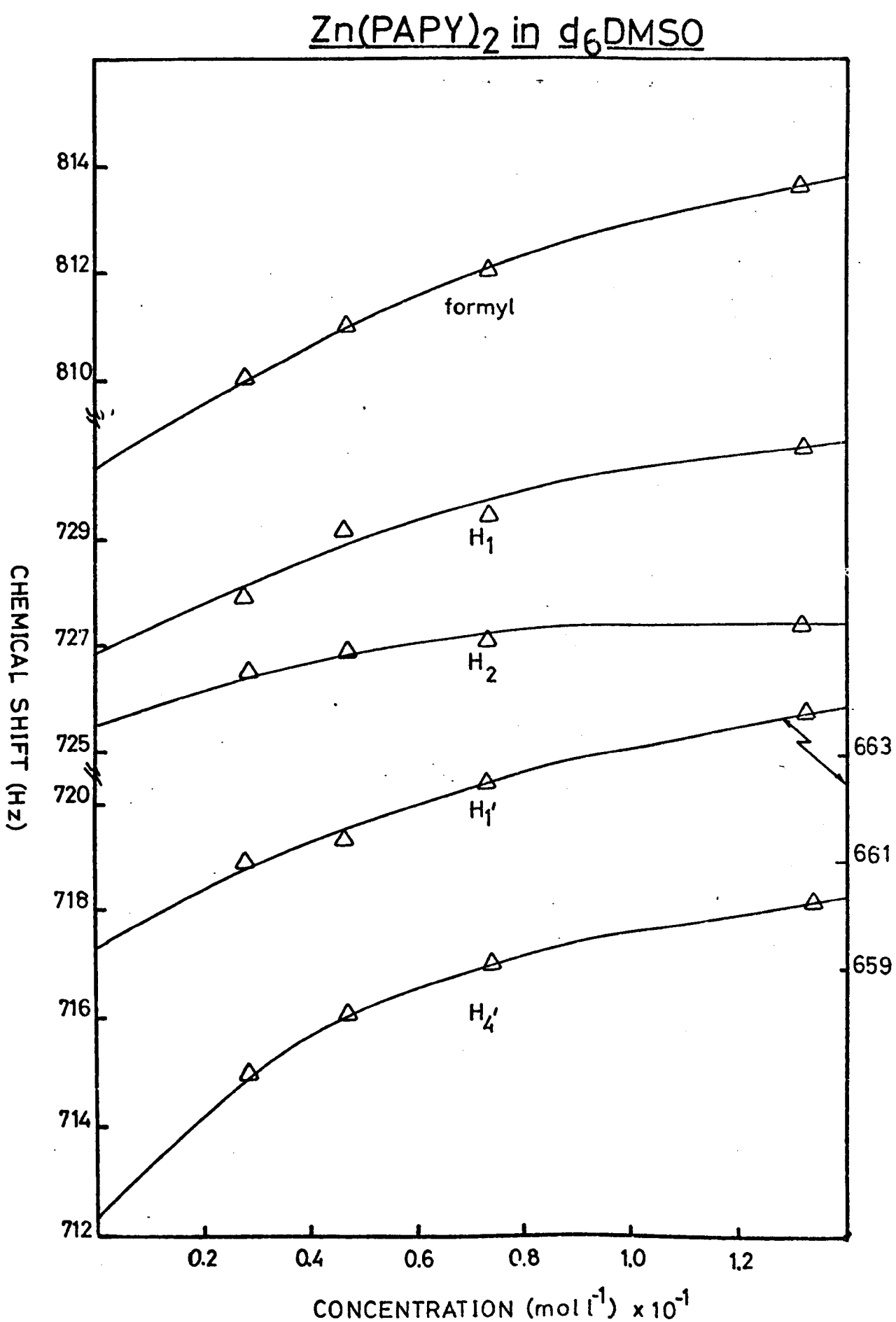

Zn(PAPY)2 in d6DMSO
814
812
810
729
727
725
720
718
716
714
712
663
661
659
formyl
H1
H2
H1'
H4'
0.2
0.4
0.6
0.8
1.0
1.2
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l-1) x 10-1

Fig. 2.29.

2.4 E-PAPHY in Benzene

Changing the solvent from carbon tetrachloride to benzene alters the spectrum of E-PAPHY (S.2.3) in a complex manner as shown by the values of $\Delta^{C_6D_6}_{CCl_4}$ in Fig.2.30 below.

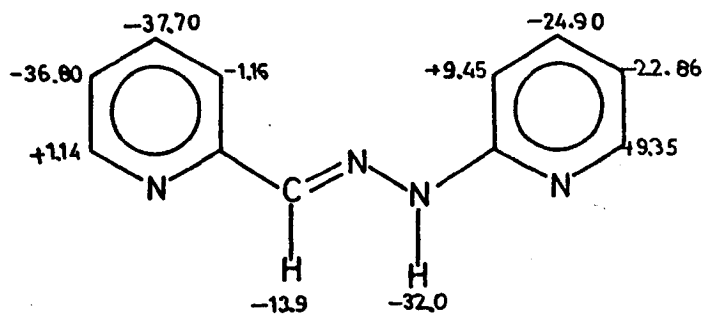


Fig.2.30

In the Introduction to this chapter the various postulated modes of solvation by benzene were described. The one proposed here is one in which there is a higher concentration of solvent molecules in the region of the positive end of the pyridine ring dipole than anywhere else in the solute molecule. A transient association is formed between the positive end of the dipole of the pyridine rings and the π-electrons of one particular solvent molecule. During the existence of this association, which will be short as it is only a very weak association, the protons in the pyridine ring will experience a shielding or deshielding depending on their position relative to the benzene molecule. Dissociation occurs and the pyridine ring protons experience a change in shielding again. Thus the observed chemical shift values for the pyridine ring protons will be time averaged values of the shifts in the associated and

unassociated states. The smaller the concentration of solute the more rapidly will the dissociating benzene molecule be replaced by another associating with the pyridine ring. Consequently if a proton is shielded by this association then as its shift is a time averaged value a gradual upfield shift will be observed as the concentration of solute decreases as the solute will spend a greater proportion of its time in the associated state.* The reverse applies if a proton is deshielded by the association.

Shown in Fig.2.31 is the proposed mode of benzene solvation. The asterisks indicate a region shielded by the anisotropy of the solvating benzene molecule.

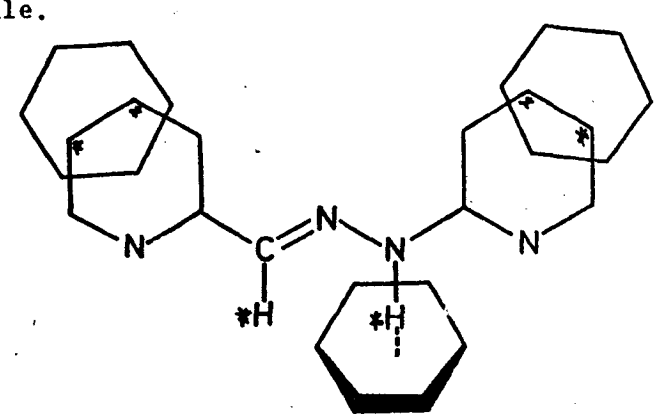


Fig.2.31

From the $\Delta^{C_6D_6}_{CCl_4}$ values (Fig.2.30) it may be seen that the 1 and 4-protons in each ring are generally affected very little by benzene solvation. This is probably a result of these protons lying in or near the deshielding cone of the benzene ring (cf. Fig.2.13).

---

* The duration of the association does not necessarily increase but the time between associations decreases.

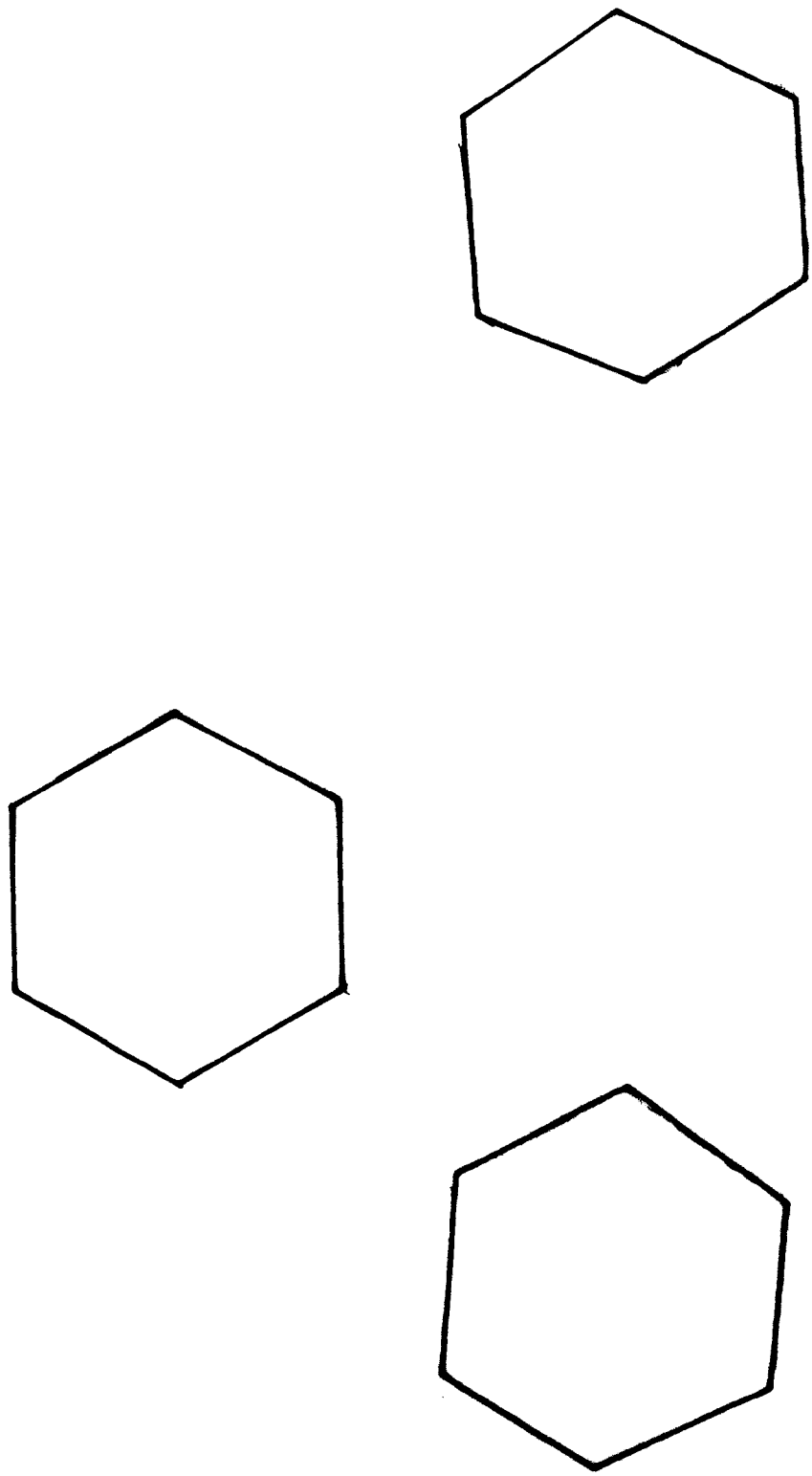
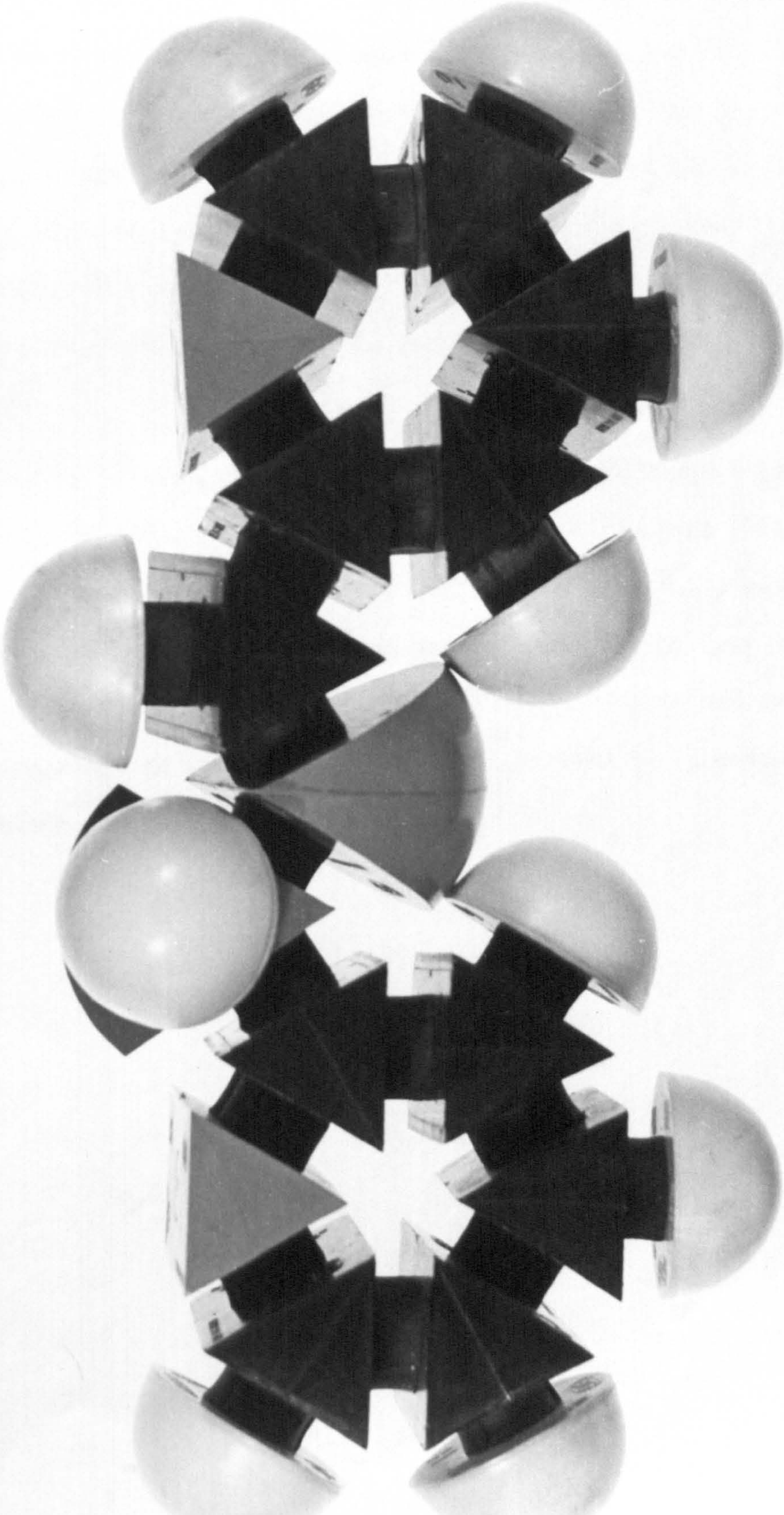


Fig. 231. Solvation by benzene.



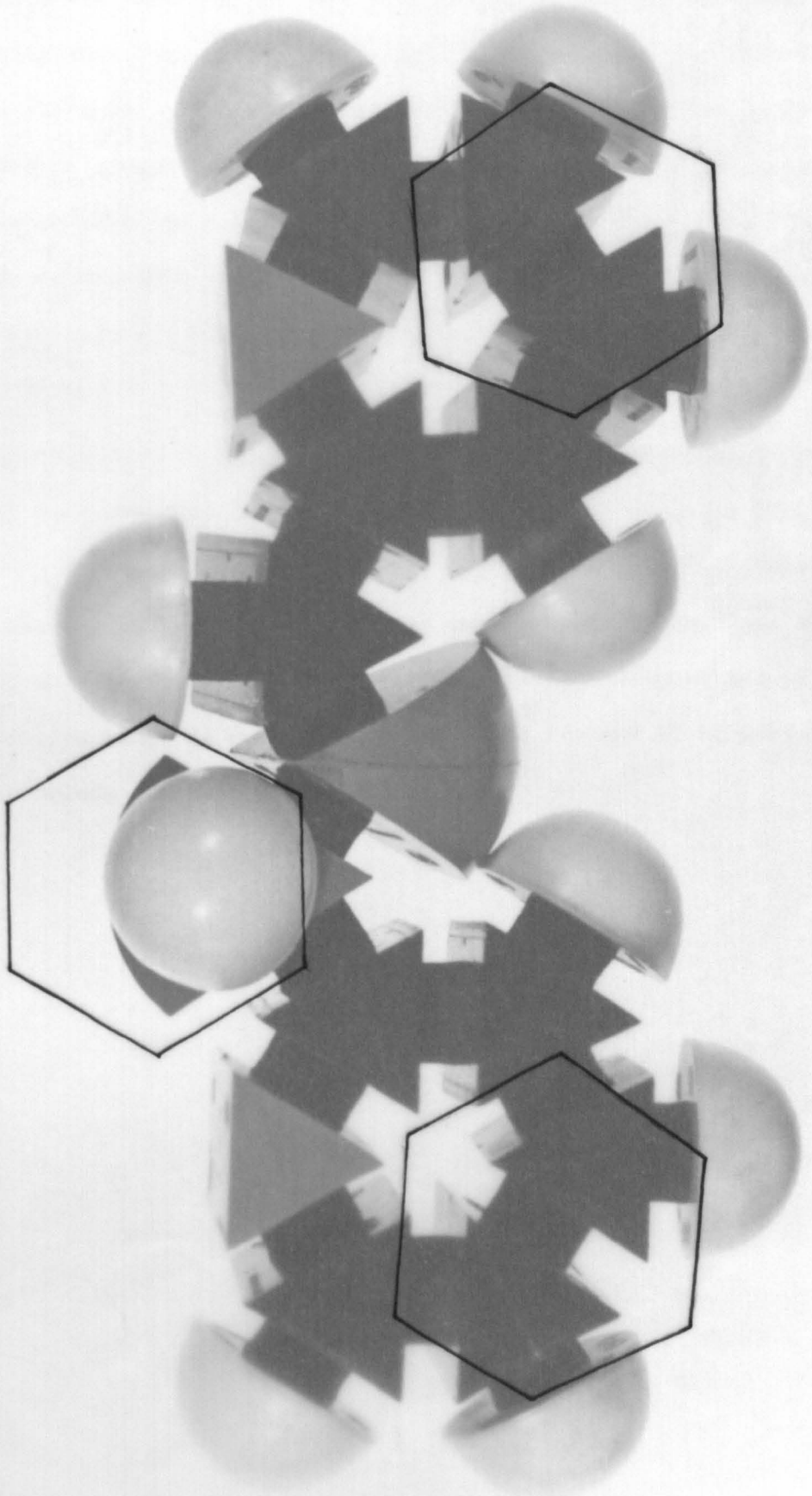


Fig. 231. Solvation by benzene.

The 2 and 3 protons in each ring are quite heavily shielded indicating that this is the region most closely associated with the benzene molecule. It would appear that substitution of the hydrazine and aldehyde groups into the pyridine rings has affected the dipole of the ring so that its positive end now lies between $H_{2(2')}$ and $H_{3(3')}$.

The appreciable negative $\Delta^{C_6D_6}_{CCl_4}$ value observed for the imino proton could result from solvation by benzene which may also affect the formyl proton.

Dilution curves have been obtained for E-PAPHY in benzene (Fig.2.32). Contrary to expectation all resonances show an upfield shift with increasing solute concentration. However, extreme difficulty was experienced in making up the solutions used because of the poor solubility of PAPHY in benzene which makes the concentrations suspect and so the concentration range is very small. For these reasons it is unwise to try to conclude too much from these curves.

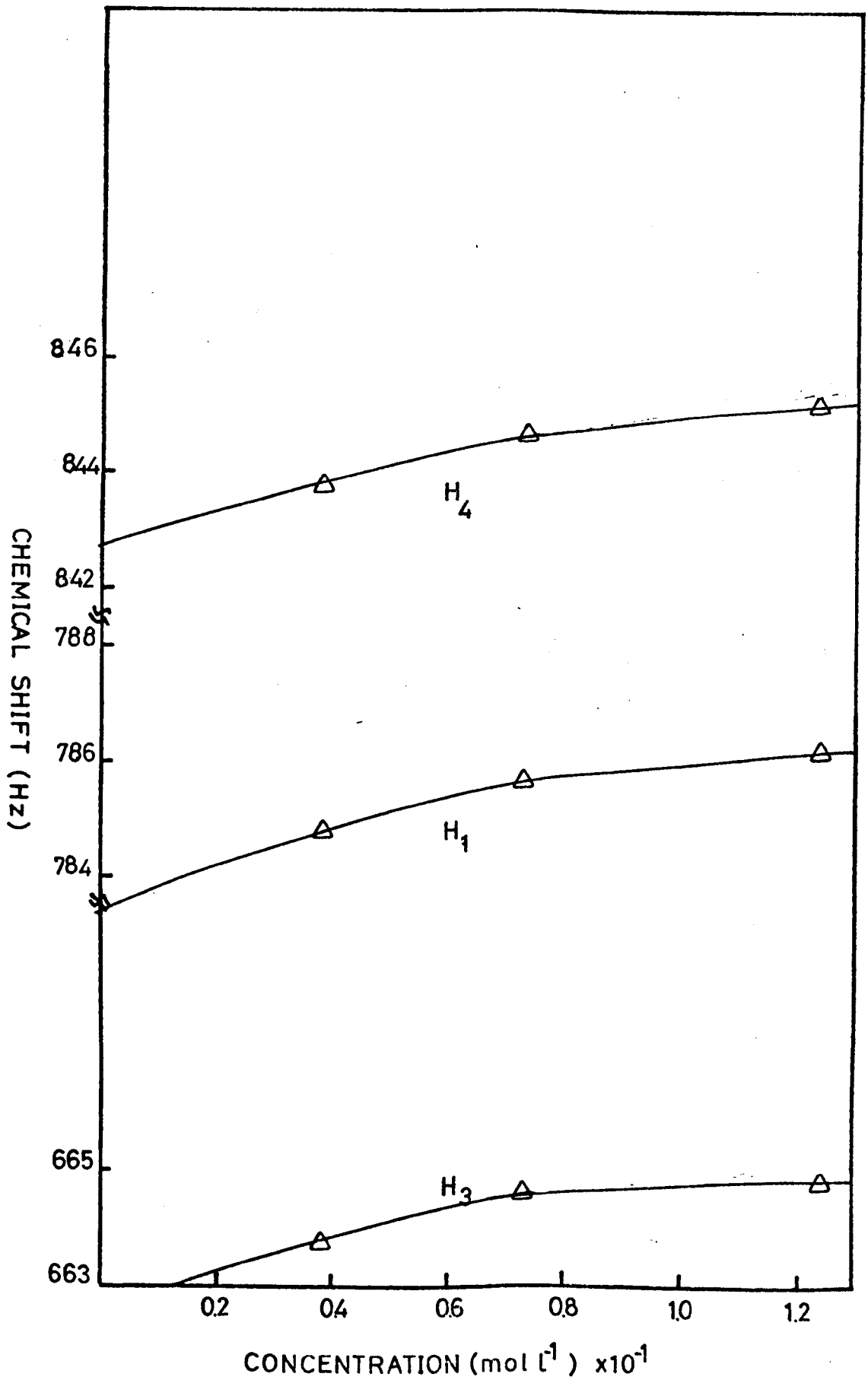

E- PAPHY in C6D6
846
844
842
788
786
784
665
663
H4
H1
H3
CHEMICAL SHIFT (Hz)
0.2
0.4
0.6
0.8
1.0
1.2
CONCENTRATION (mol l-1) x10-1

Fig. 2 32(a)

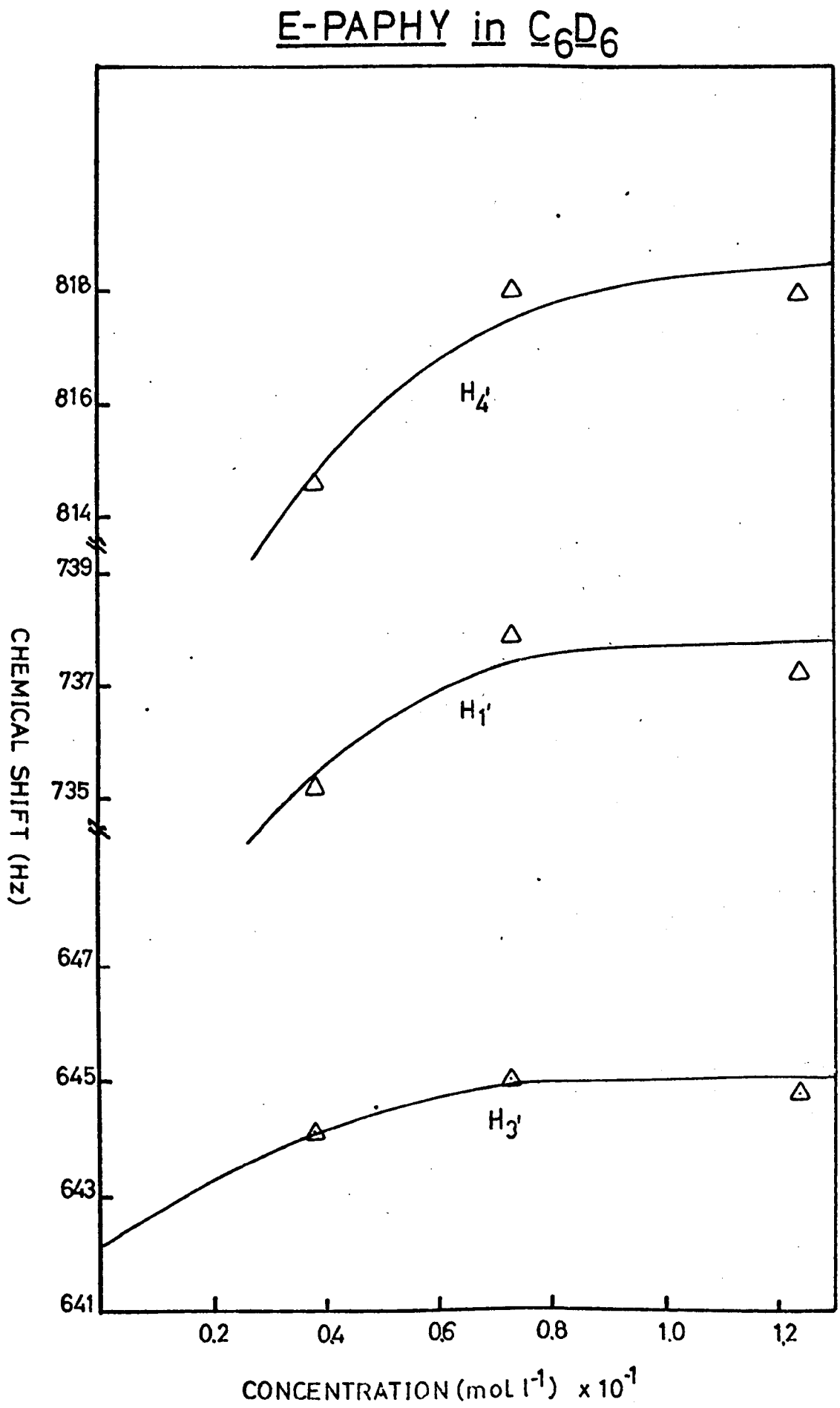

E-PAPHY in C_6D_6
818
816
814
739
737
735
647
645
643
641
H_4'
H_1'
H_3'
CHEMICAL SHIFT (Hz)
0.2
0.4
0.6
0.8
1.0
1.2
CONCENTRATION (mol l^{-1}) x 10^{-1}

Fig. 2.32(b)

2.5 Z-PAPHY in Carbon Tetrachloride

The changes in chemical shift on isomerisation of E-PAPHY to Z-PAPHY in both carbon tetrachloride and dimethyl sulphoxide have been discussed in Chapter 1.

The dilution curves for Z-PAPHY in carbon tetrachloride (Fig.2.33) exhibit a number of obvious differences when compared with those obtained for E-PAPHY in the same solvent. The slopes of the plots for the hydrazine ring protons (Fig.2.33b) are less steep than those obtained for the corresponding protons in E-PAPHY. This may be a result of reduced solute-solute interaction because of the hydrogen bonded nature of the imino proton in the Z-isomer. The 4' proton still exhibits the greatest concentration dependence (Fig.2.33b). The imino proton resonance position did not show much variation with concentration (perhaps 3Hz over the concentration range studied) but the broadness of the peak and the poor signal to noise ratio of the spectra of the lower concentration solutions prevented accurate measurement. This vastly reduced concentration dependence (compared with the E-isomer case) is to be expected as the type(I) solute-solute interaction (Fig.2.23) is no longer possible.

The curves for the aldehyde ring protons differ considerably from their E-isomer counterparts (Fig.2.23). They exhibit a very marked downfield shift with decreasing solute concentration. This applies also to a much lesser extent to the formyl proton plot (Fig.2.33c).

The most likely explanation for the form of the dilution curves is

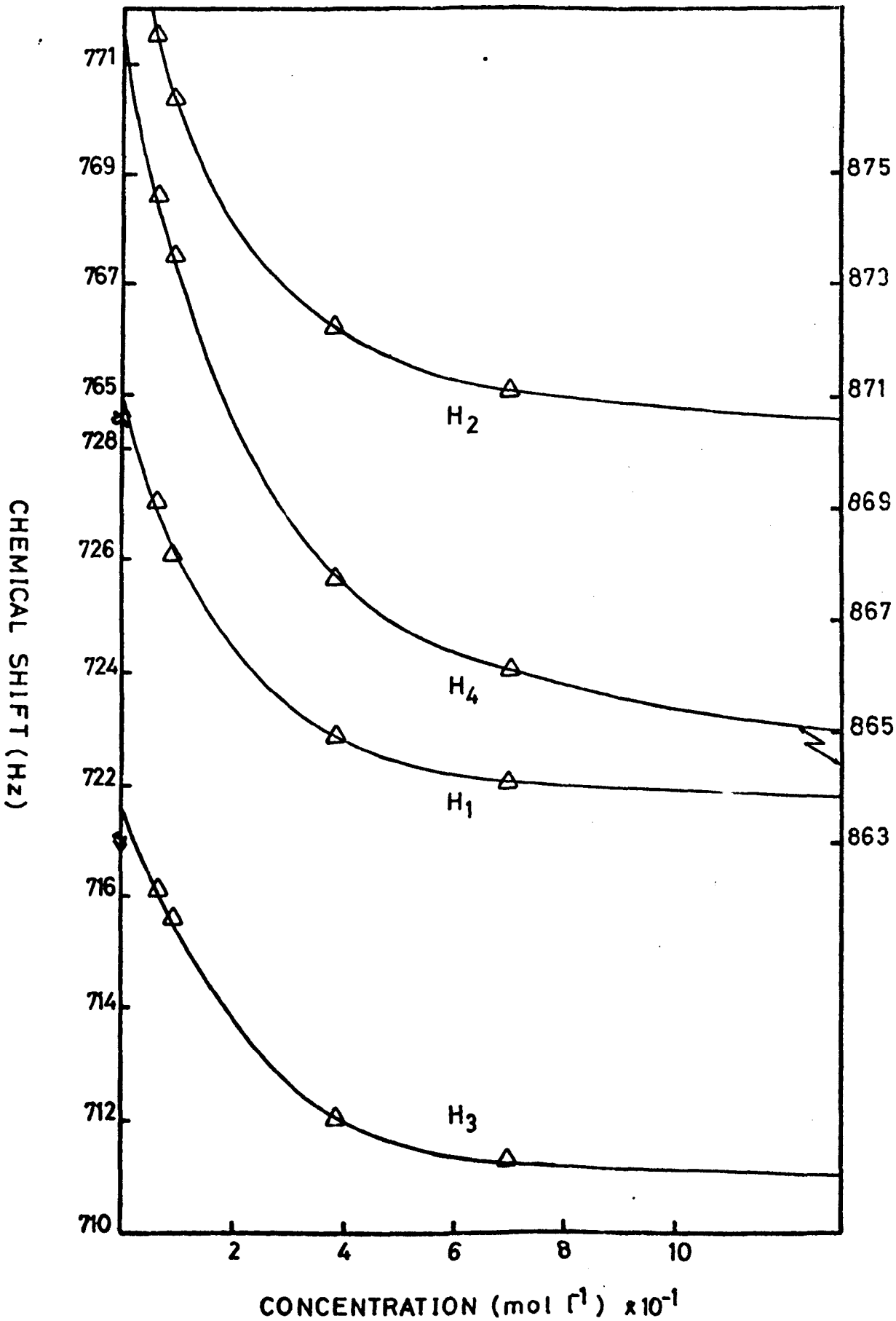

Z-PAPHY in CCl_4
771
769
767
765
728
726
724
722
716
714
712
710
875
873
871
869
867
865
863
H_2
H_4
H_1
H_3
2
4
6
8
10
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig. 2.33(a)

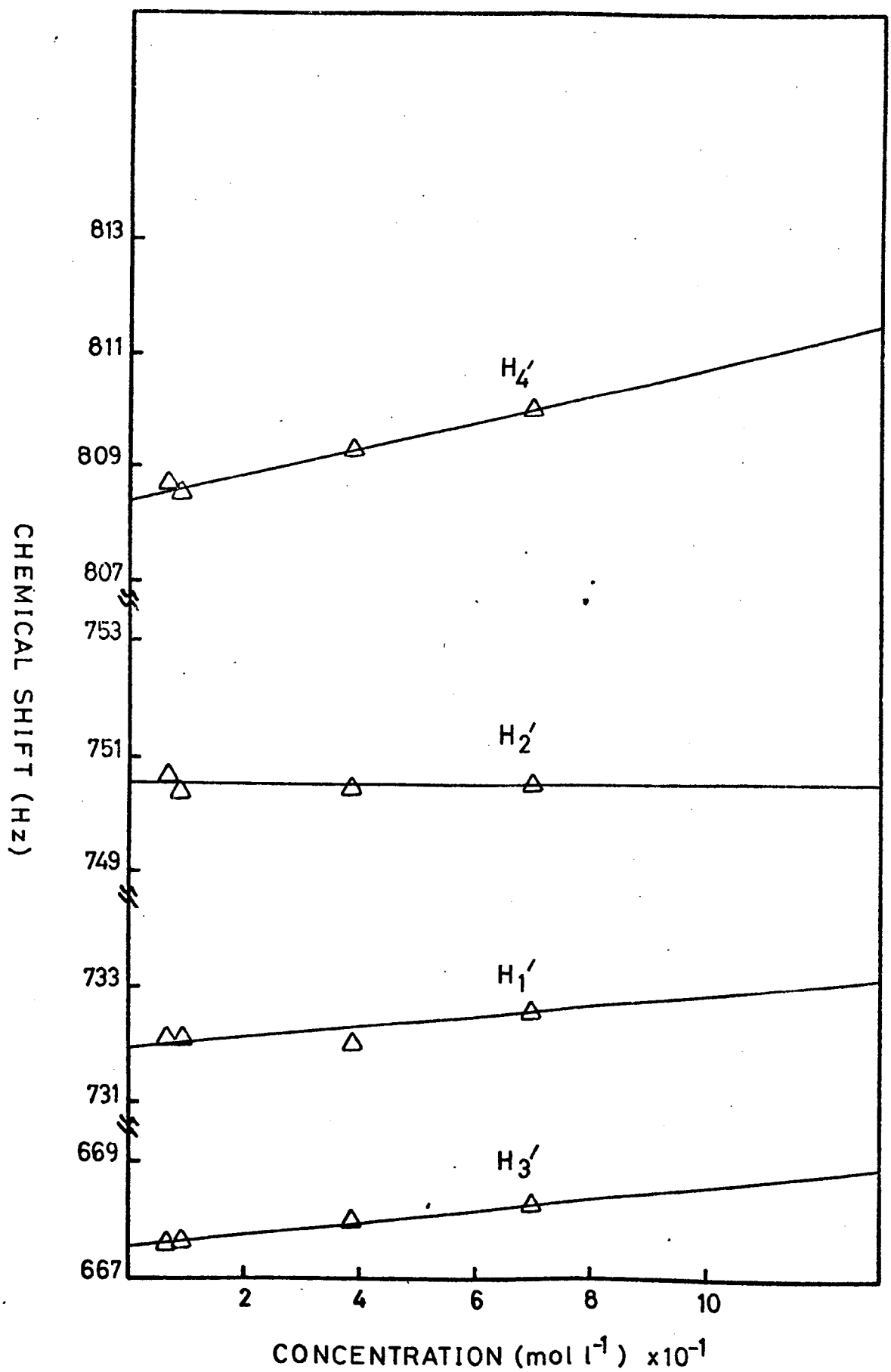

Z-PAPHY in CCl4
813
811
809
807
753
751
749
733
731
669
667
H4′
H2′
H1′
H3′
2
4
6
8
10
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l-1) x10-1

Fig.2.33(b)

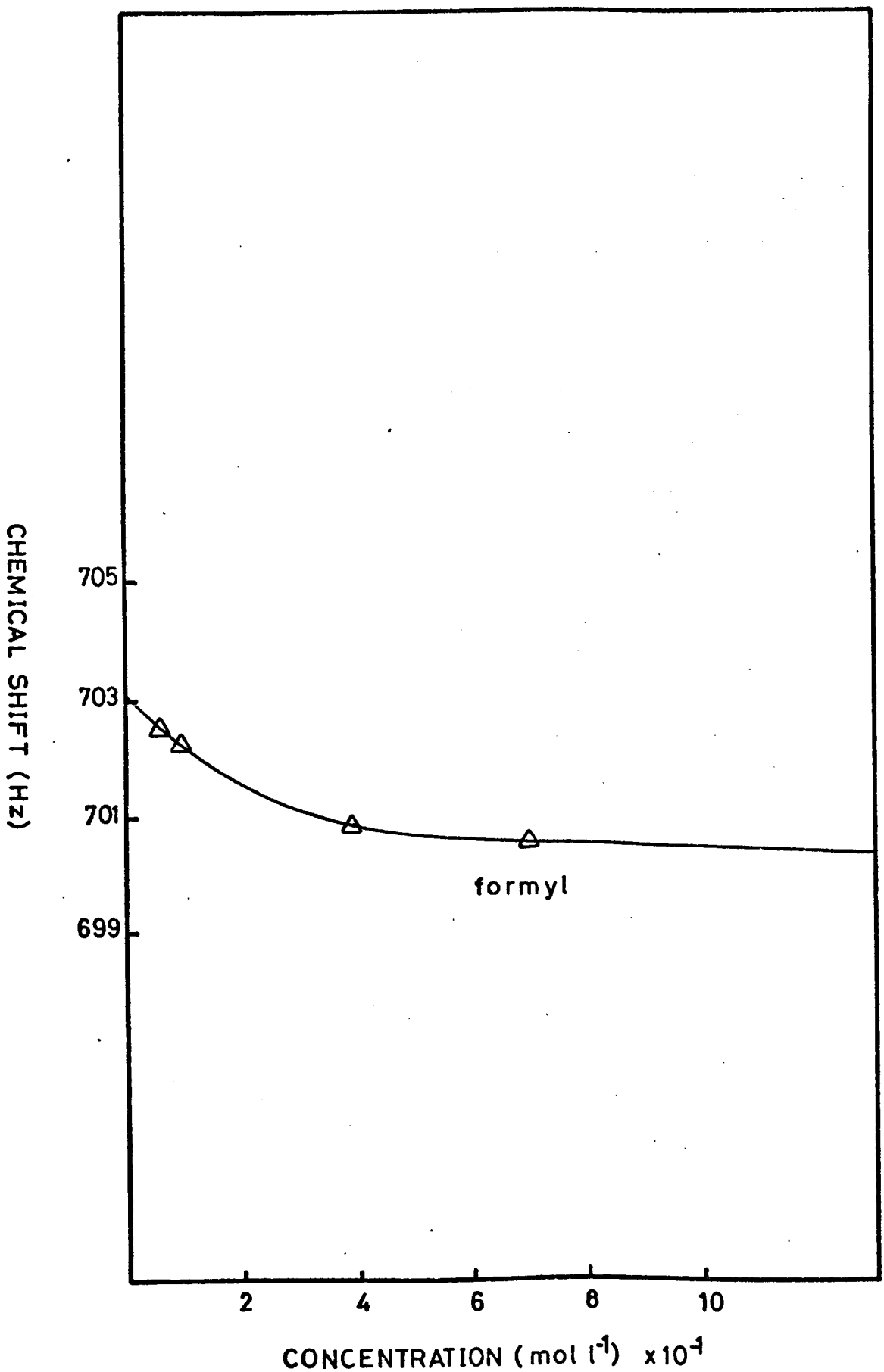

Z-PAPHY in CCl4
CHEMICAL SHIFT (Hz)
705
703
701
699
formyl
2
4
6
8
10
CONCENTRATION (mol l-1) x10-4

Fig. 2.33(c)

that there exists a dipolar solute-solute interaction involving the aldehyde rings of different solute molecules (Fig.2.34). Mutual shielding of the ring protons of the two interacting rings would take

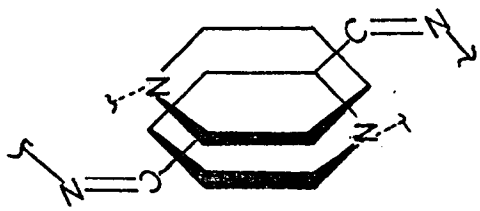
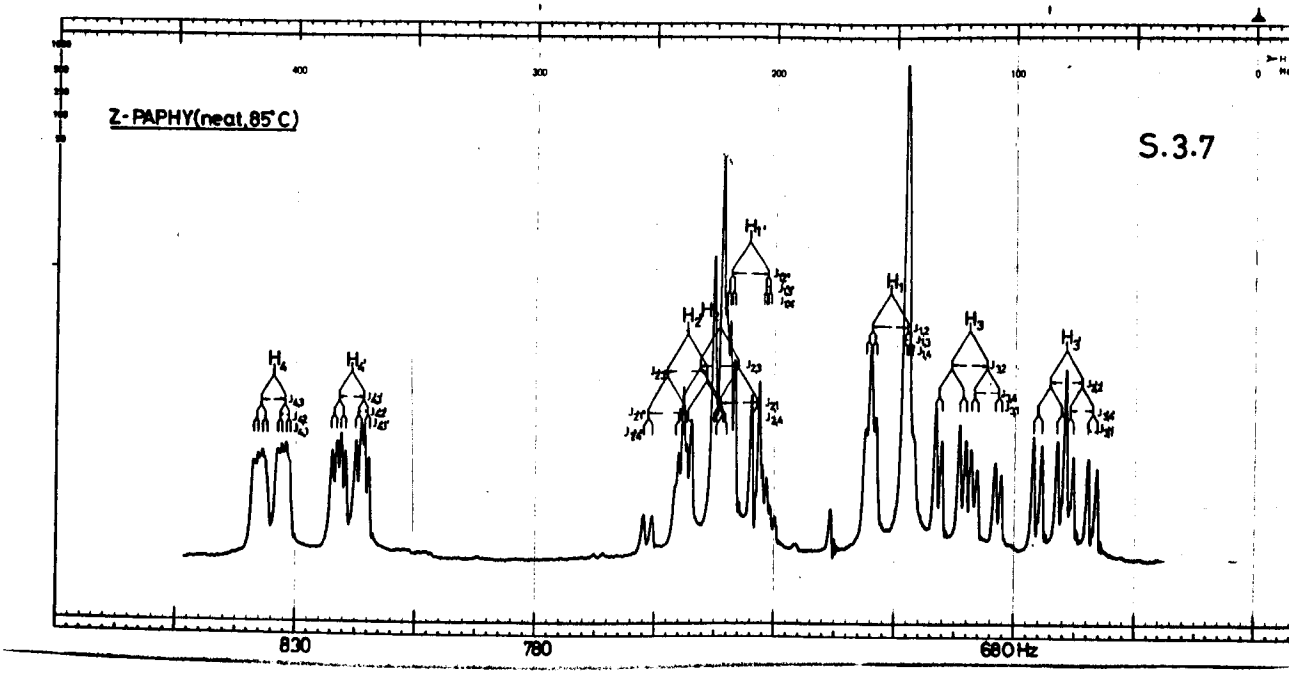
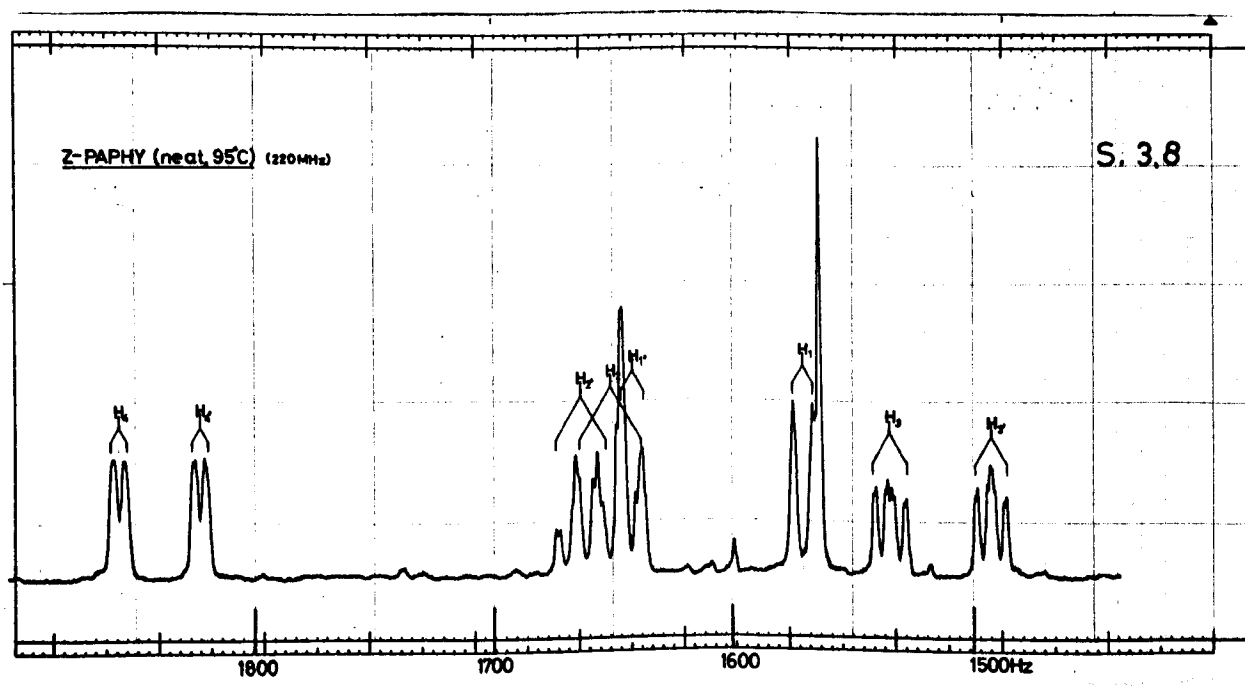


Fig.2.34

place (a result of the pyridine ring current). That the effect appears to be nearly the same for all ring protons implies that one ring is located almost directly above the other. As the concentration of the solute increases the degree of this interaction would increase and be manifested as a decrease in chemical shift.

In order to test this theory it was decided to observe the spectrum of Z-PAPHY in the liquid state at 85°C (S.2.7 and S.2.8). Chemical shifts obtained at 100MHz and 220MHz are compared with those obtained from the dilution curves (at 1 mol l^{-1}) in Table 2.2. From the data in this table it may be seen that the aldehyde ring protons exhibit appreciable negative $\Delta^{neat}_{CCl_4}$ values. That is they become more shielded when the sample is in the liquid state. This is to be expected as the proposed interaction (Fig.2.34) would be stronger in the neat liquid. The hydrazine ring protons are further deshielded, as would be expected from their dilution curves. This is probably a result of an increase in the type II interaction described previously (Fig.2.2)


Z-PAPHY(neat,85°C)
S.3.7
400
300
200
100
830
780
680Hz


Z-PAPHY (neat, 95°C) (220MHz)
S. 3.8
1800
1700
1600
1500Hz

	Chemical Shifts (Hz)			
	CCl_4	neat		$\Delta^{neat}_{CCl_4}$
H_1	722.01	712.43[a]	(718.39)[b]	-10.58
H_2	769.70	747.65	(753.18)	-22.05
H_3	715.91	693.70	(701.86)	-22.21
H_4	873.44	840.40	(847.55)	-33.04
H_1'	732.10	740.73	(750.48)	+8.63
H_2'	750.20	752.40	(761.15)	+2.20
H_3'	667.70	674.70	(682.77)	+7.00
H_4'	808.50	824.03	(832.43)	+15.53

Table.2.2

(a) From uncalibrated 100MHz spectrum (85°C)

(b) From calibrated 220MHz spectrum.(95°C). Data converted to 100MHz. Both sets of data originally obtained referred to HMDS as internal reference. Converted to TMS internal reference by addition of 5.5Hz to original values.

Inspection of the figures in brackets in Table 2.2 which were obtained from a 220MHz spectrum of a sample run at 95°C shows that the aldehyde ring protons are deshielded slightly which is reasonable as increasing the sample temperature would be expected to reduce the dipole-dipole interaction. However the hydrazine ring protons also further deshielded which is not what one would expect.

2.6 Z-PAPHY in Dimethyl Sulphoxide

On changing the solvent from carbon tetrachloride to dimethyl sulphoxide the spectrum of Z-PAPHY (S.2.4.) shows there is a general downfield shift of all proton resonances. Shown in Fig.2.35 are values of $\Delta^{DMSO}_{CCl_4}$. Compared with the value of $\Delta^{DMSO}_{CCl_4}$ for the imino proton in

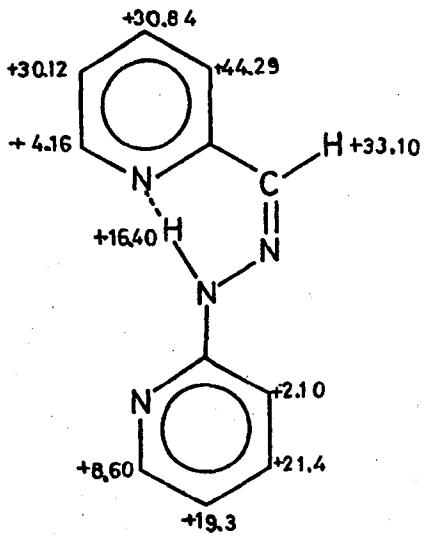
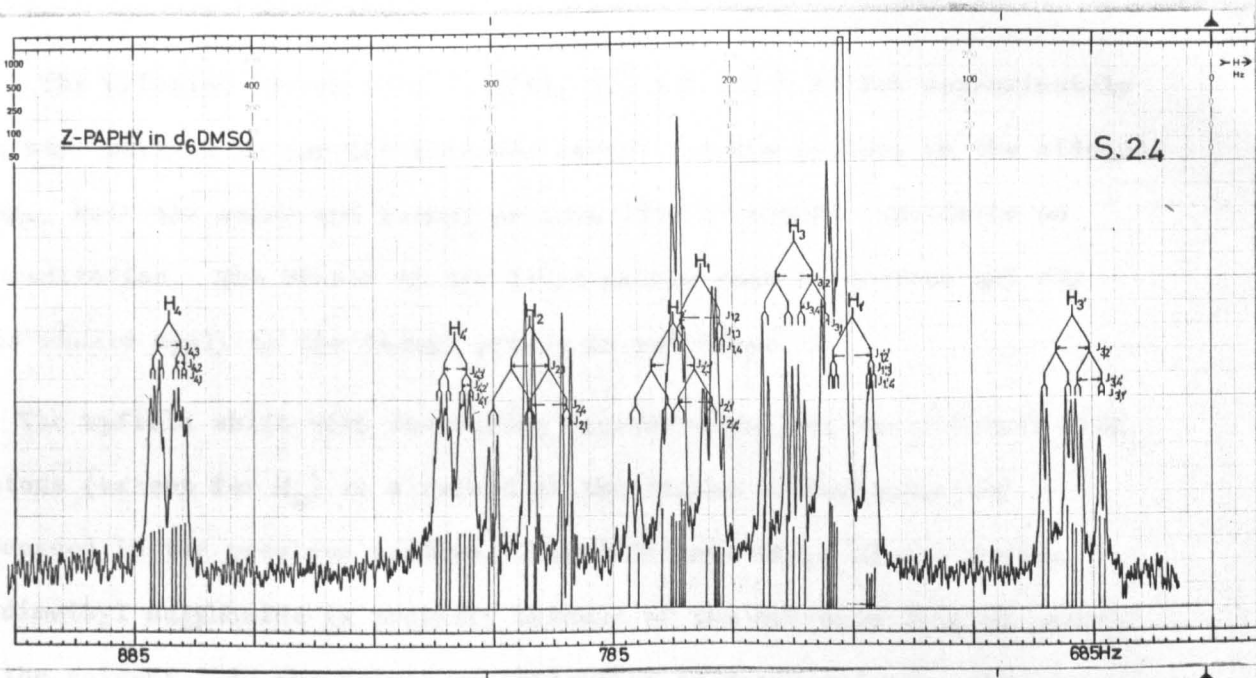
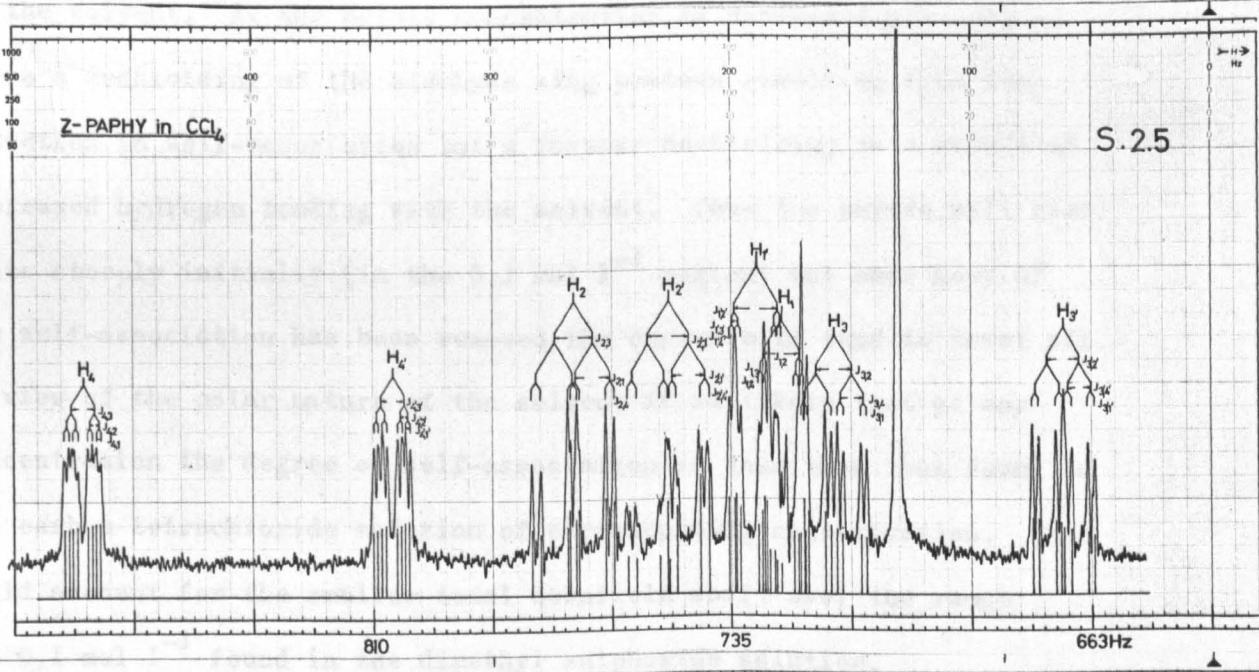
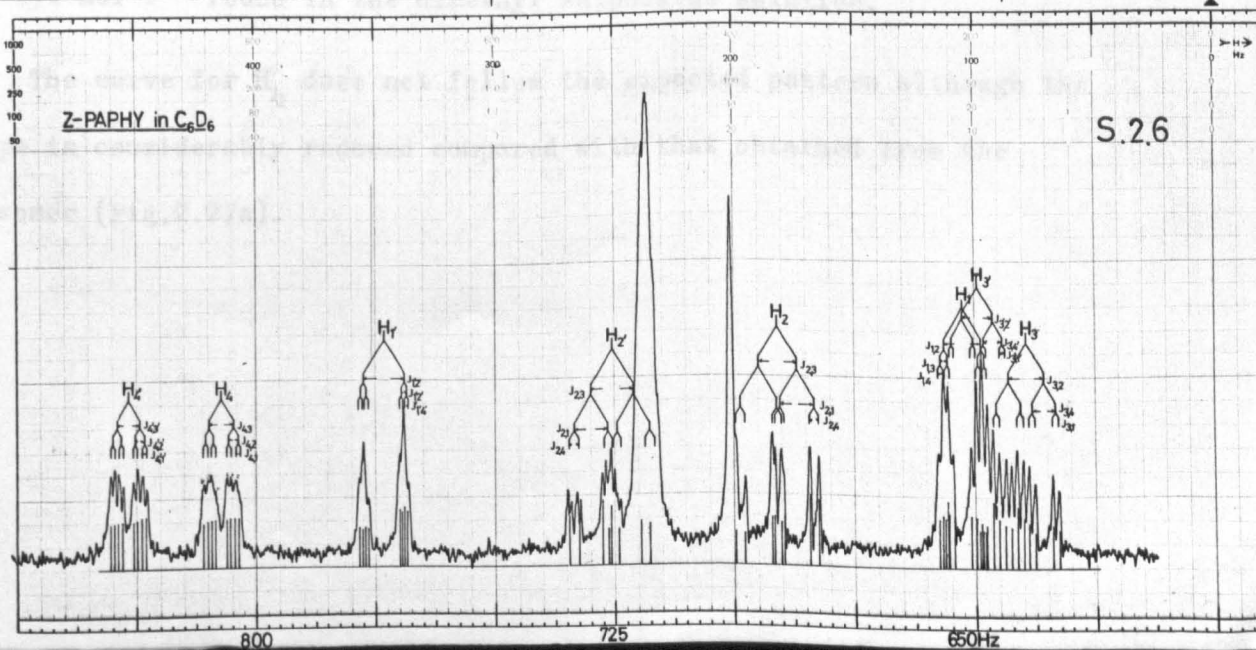


Fig.2.35

the E-isomer (Fig.2.26) there is very little change in the Z-isomer presumably because it is already involved in hydrogen bonding with the ring nitrogen atom and is much less prone to interaction with the dimethyl sulphoxide molecules. Apart from that for H_1 the values of $\Delta^{DMSO}_{CCl_4}$ obtained for the Z-isomer agree well with those from the E-isomer (Fig.2.26). The considerably larger value of $\Delta^{DMSO}_{CCl_4}$ for H_1 in the Z-isomer is attributed to the fact that in this isomer the proton is far more exposed and therefore more readily available for interaction with the solvent molecules. This is more fully discussed in section 2.3.


Z-PAPHY in d_6DMSO
S.2.4
885
785
685Hz


Z-PAPHY in CCl_4
S.2.5
810
735
663Hz


Z-PAPHY in C_6D_6
S.2.6
800
725
650Hz

The dilution curves (Fig.2.36(a), (b) and (c)) follow approximately the same pattern as for the E-isomer except for the protons in the aldehyde ring. Both the imino and formyl protons show a reduced dependence on concentration. The reason in the imino proton case is obvious but why this should apply to the formyl proton is not clear.

The upfield shift with increasing concentration for the aldehyde ring protons (except for H_4) is a result of the ligand self-association discussed in the previous section. The different shape of the curves in dimethyl sulphoxide is probably because of the hydrogen bonding nature of the solvent. As the solute concentration is decreased not only is there a deshielding of the aldehyde ring protons resulting from the reduction in self-association but a further deshielding as a result of increased hydrogen bonding with the solvent. Thus the curves will rise quite steeply initially (in the 0.1 mol l^{-1} region) but once most of the self-association has been removed the curves will tend to level off. In view of the polar nature of the solvent it is likely that at any concentration the degree of self-association is less than that found in the carbon tetrachloride solution of corresponding concentration. This would account for the smaller total downfield shift over the range 0 - 0.1 mol l^{-1} found in the dimethyl sulphoxide solution.

The curve for H_4 does not follow the expected pattern although the slope is considerably reduced compared with that obtained from the E-isomer (Fig.2.27a).

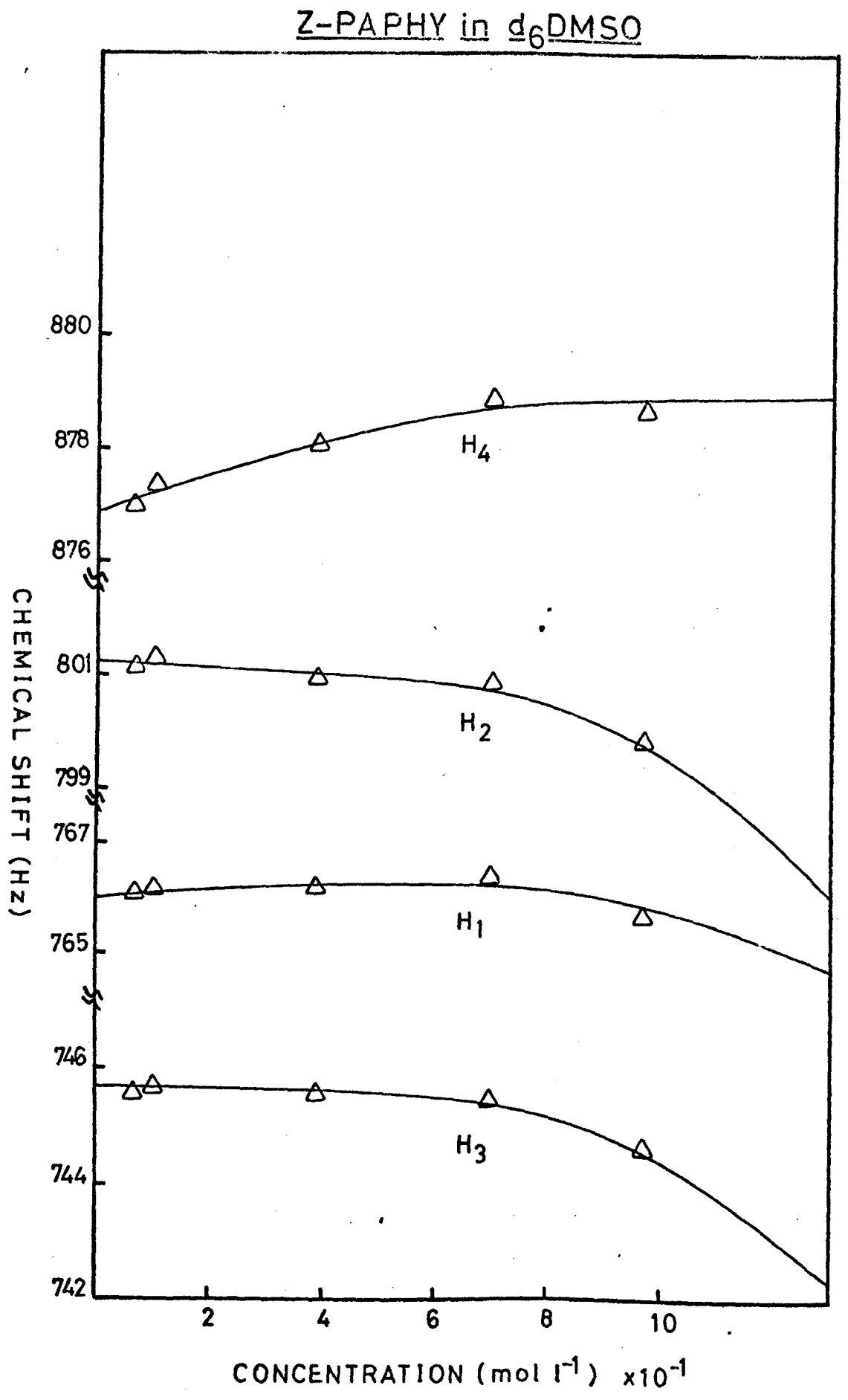

Z-PAPHY in d_6DMSO
880
878
876
801
799
767
765
746
744
742
CHEMICAL SHIFT (Hz)
H_4
H_2
H_1
H_3
2
4
6
8
10
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig. 2.36(a)

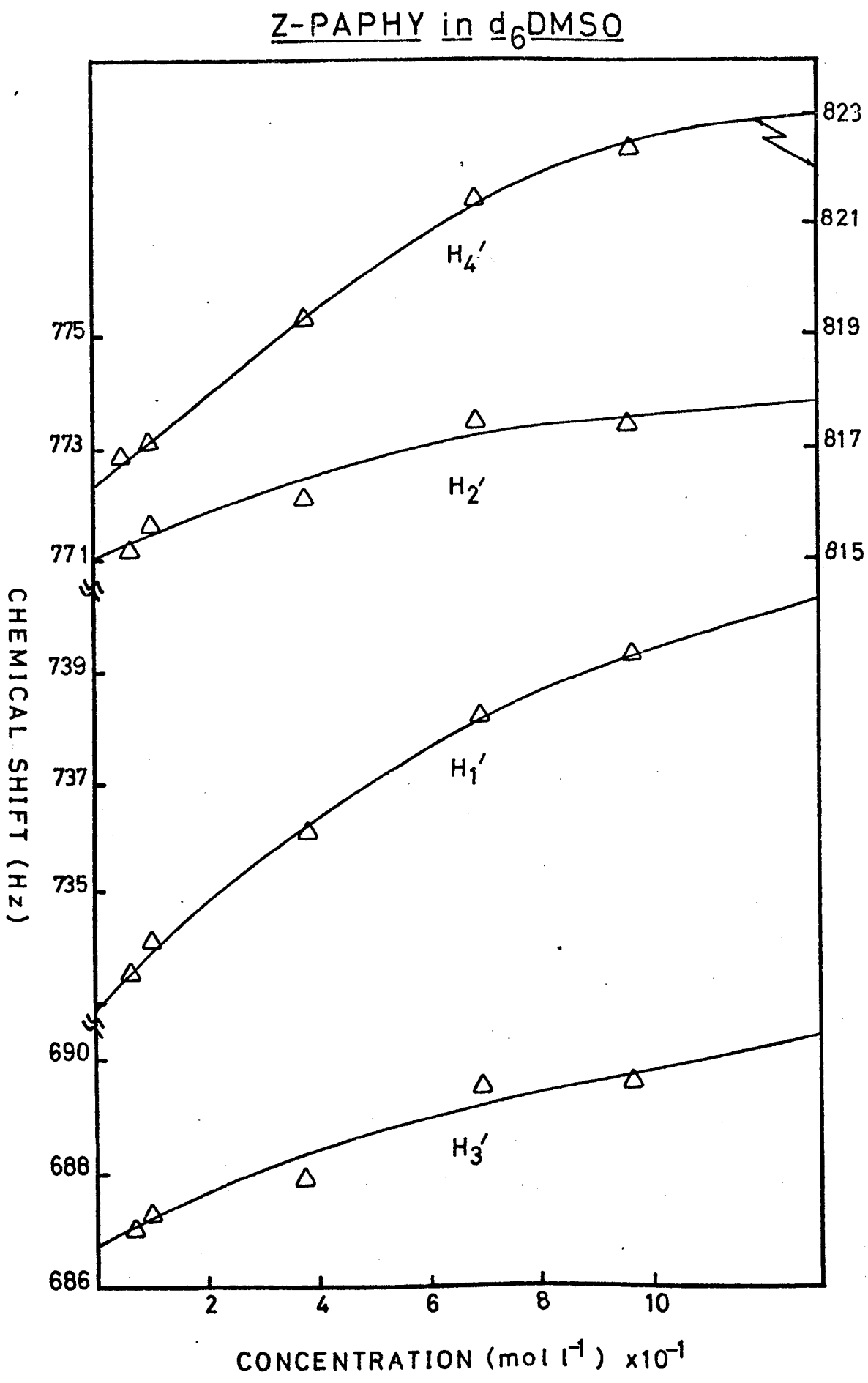

Z-PAPHY in d_6DMSO
823
821
819
817
815
775
773
771
739
737
735
690
686
H_4'
H_2'
H_1'
H_3'
CHEMICAL SHIFT (Hz)
2
4
6
8
10
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig. 236(b)

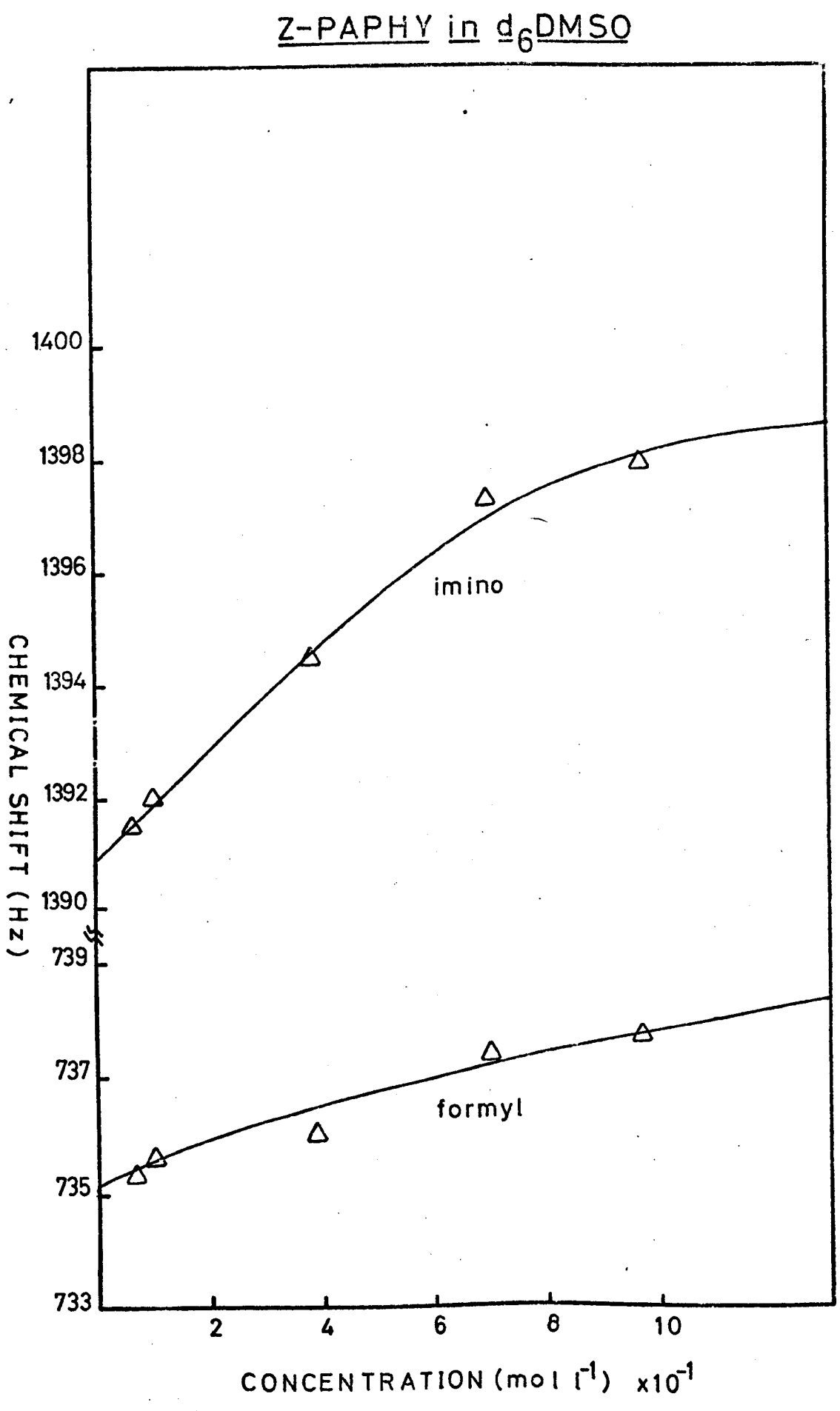

Z-PAPHY in d_6DMSO
1400
1398
1396
1394
1392
1390
739
737
735
733
CHEMICAL SHIFT (Hz)
imino
formyl
2
4
6
8
10
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig.2.36(c)

2.7 Z-PAPHY in Benzene

The effect on the spectrum of Z-PAPHY (S.2.6) of changing the solvent from carbon tetrachloride is quite marked. The $\Delta^{C_6D_6}_{CCl_4}$ values are given in Fig.2.37.

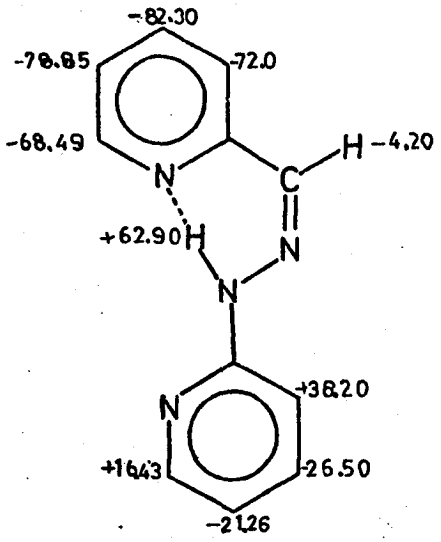


Fig.2.37

The resonance position of the formyl proton is little affected by the solvent change. All the aldehyde ring protons are shielded more extensively by changing the solvent and this implies that the solvating benzene molecule is almost directly over the heterocyclic ring (Fig.2.38)

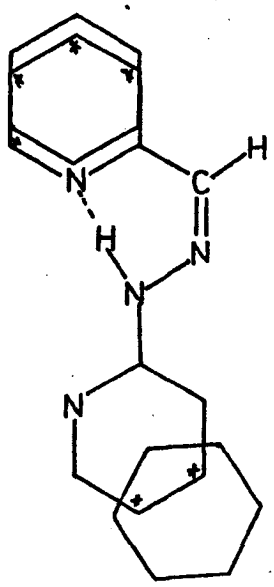


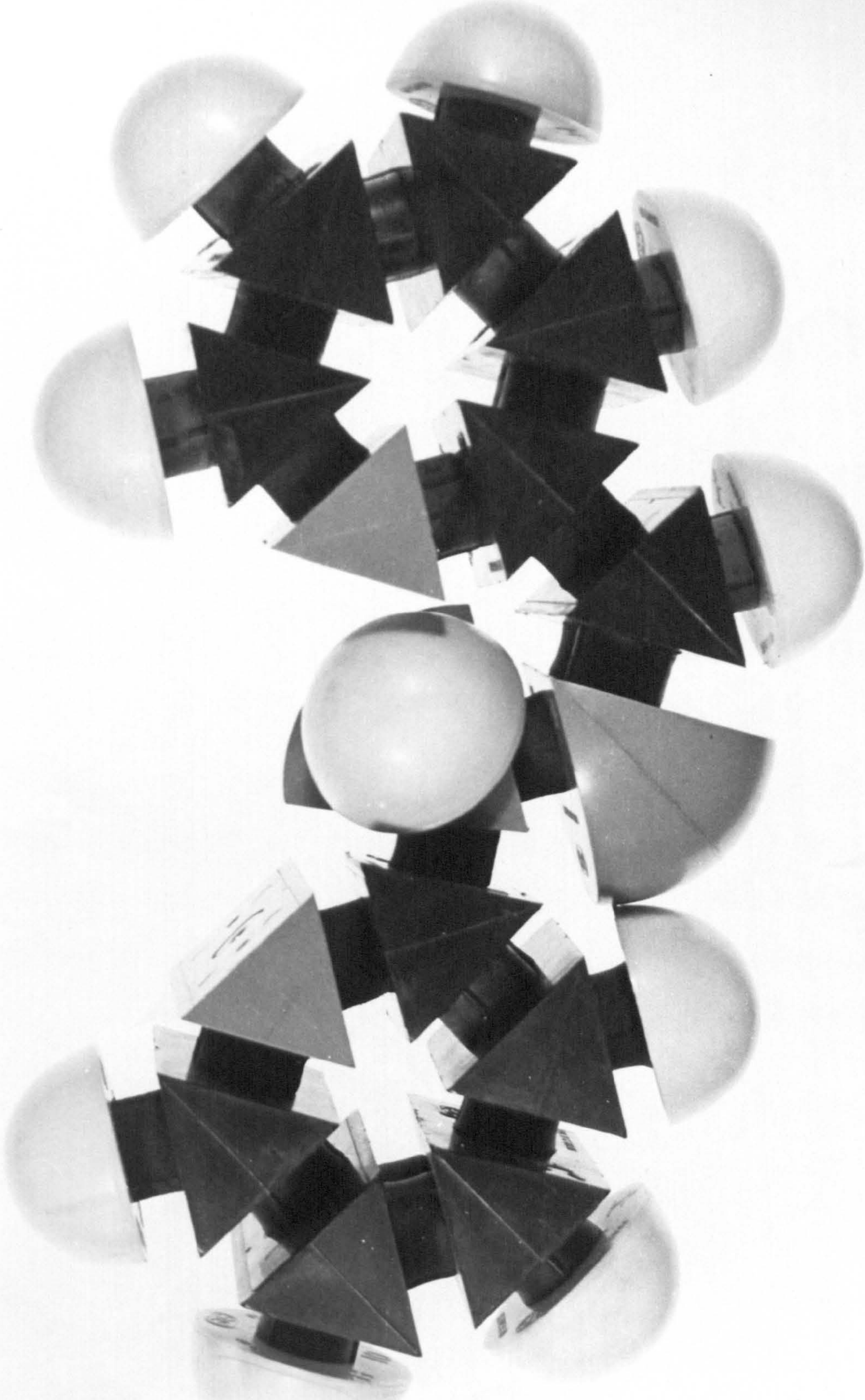
Fig.2.38

This in turn indicates that the positive end of the heterocyclic ring dipole is close to C_2 on line joining C_2 and the nitrogen atom. This would also explain why self-association (which shields all ring protons) occurs (section 2.5).

If the values of $\Delta^{C_6D_6}_{CCl_4}$ for the E-isomer (Fig.2.30) are compared with the corresponding ones for the aldehyde ring in the Z-isomer (Fig.2.37) it is clear that the point of benzene solvation has changed, and there has been a redistribution of charge in the ring. This is a result of the hydrogen bonding interaction between the ring nitrogen atom and the imino proton.

Consider now the Δ^{Z}_{E} values obtained in benzene (Fig.2.39). Comparison with those obtained in carbon tetrachloride (Fig.1.6) which

Fig 2.38. Solvation by benzene.



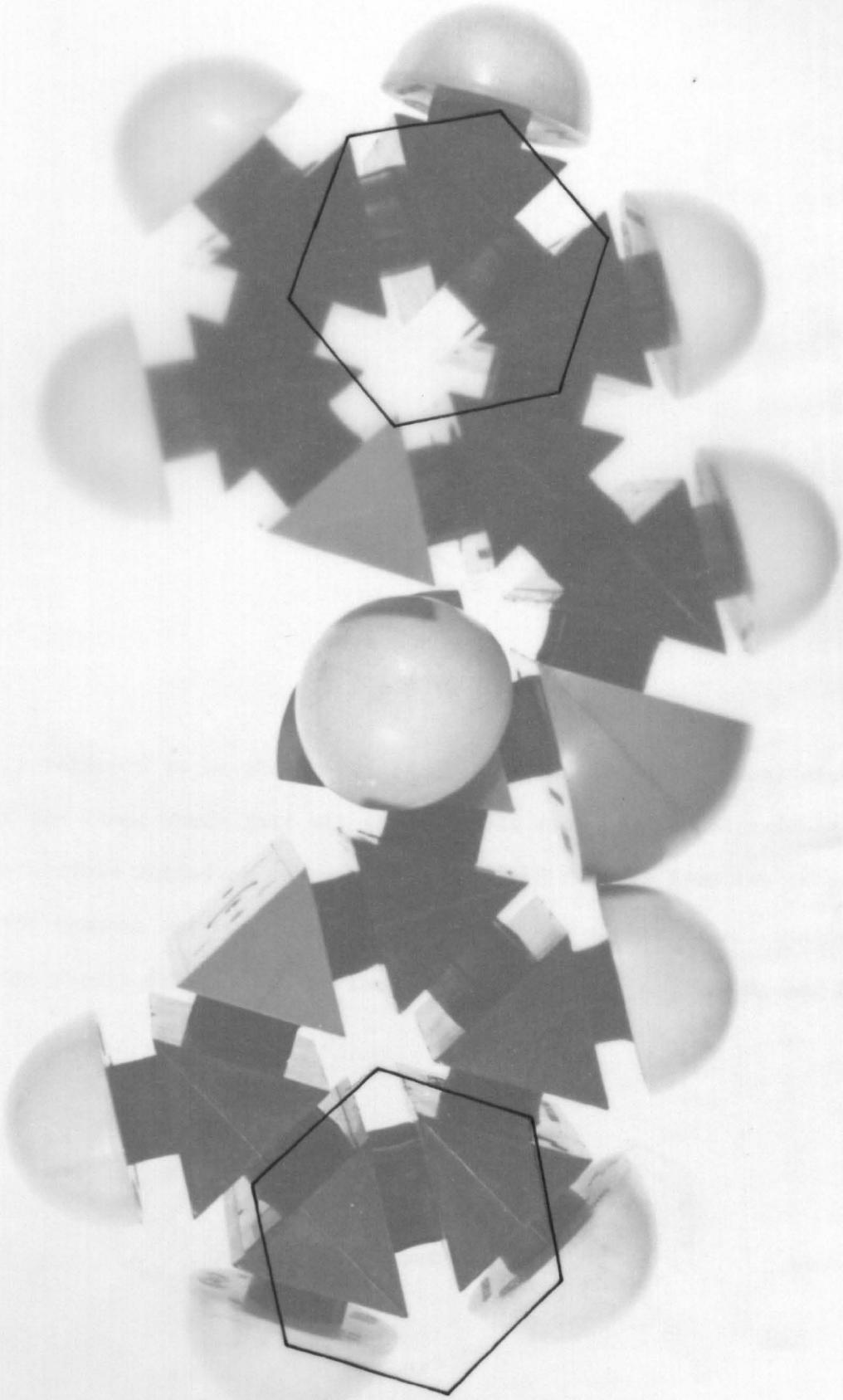


Fig. 2.38. Solvation by benzene.

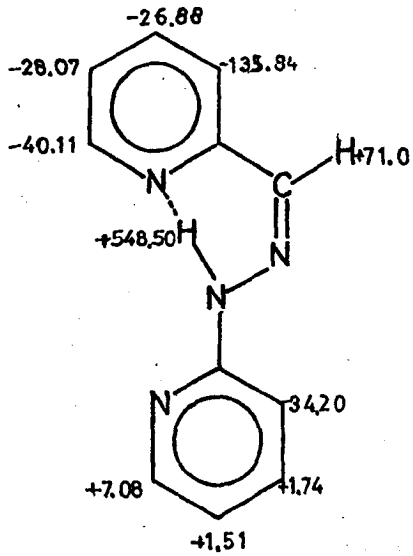


Fig.2.39

are considered to be the shifts resulting only from withdrawal of charge from the ring, shows that all the aldehyde ring protons experience considerable shielding on isomerisation. This results from the re-positioning of the benzene solvent molecule because of the change in orientation of the dipole (Fig.2.40.) Obviously the values of Δ_E^Z for H_2 and H_3 are

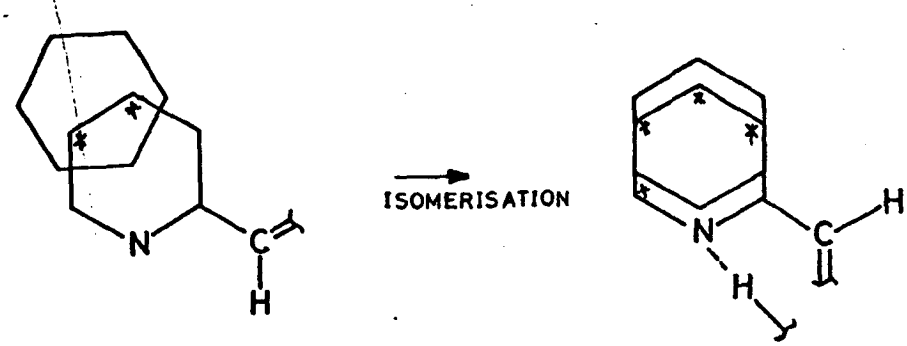


Fig.2.40

going to be considerably less negative because these protons are shielded by benzene solvation in the E-isomer anyway.

The imino proton has a very large positive Δ_E^Z value, larger than that observed in carbon tetrachloride. This probably arises because of the removal of benzene solvation of this proton (section 2.4) in the Z-isomer. Further deshielding may result from the imino proton lying in the deshielding cone of the solvating benzene ring. The dilution curve for this proton supports this idea. The somewhat smaller negative value of Δ_E^Z for the formyl proton probably also arises from the absence of imino proton solvation.

The Δ_E^Z values for the hydrazine ring protons except for H_1, do not differ greatly from those obtained in carbon tetrachloride. It can be seen from Fig.2.39 that H_1, experiences considerable deshielding on isomerisation. It is difficult to say why this should occur unless the benzene molecule solvating the imino proton also has a shielding effect on H_1, which would be removed on isomerisation. The fact that the dilution curve for this proton (Fig.2.39b) indicates a further downfield shift with increasing dilution implies that the deshielding results from benzene solvation of the hydrazine ring (see Fig.2.37).

The dilution curve (Fig.2.41c) for the formyl proton shows only a small concentration dependence which is to be expected from the small $\Delta_{CCl_4}^{C_6D_6}$ value observed for this proton. The imino proton is considerably deshielded with decreasing solute concentration. As pointed out previously this deshielding is probably a result of the proton lying in the deshielding cone of the solvating benzene ring, thus one would expect an increase in shift with decreasing solute concentration because of the time-averaged nature of the shift.

The plots for the aldehyde ring protons all indicate a positive shift with increasing concentration. This is opposite to observations in dimethyl sulphoxide and carbon tetrachloride and is a result of the way in which the benzene molecules solvate. At high solute concentrations there will exist PAPHY self-association (section2.5) which has a shielding effect on ring protons. Dilution with benzene will be quite effective in breaking up this association because of the disc-like shape of the benzene molecule and the PAPHY-PAPHY associations will be replaced by PAPHY-benzene associations (Fig.2.40b). As the $\Delta^{C_6D_6}_{CCl_4}$ values (Fig.2.37) show this solvation has a very strong shielding effect on the ring protons which will increase on further dilution with benzene.

In the hydrazine ring those protons shielded by benzene solvation are further shielded on dilution with benzene and vice versa. The general trend for the curves for both sets of ring protons is the greater the negative $\Delta^{C_6D_6}_{CCl_4}$ value for a proton the steeper the dilution curve.

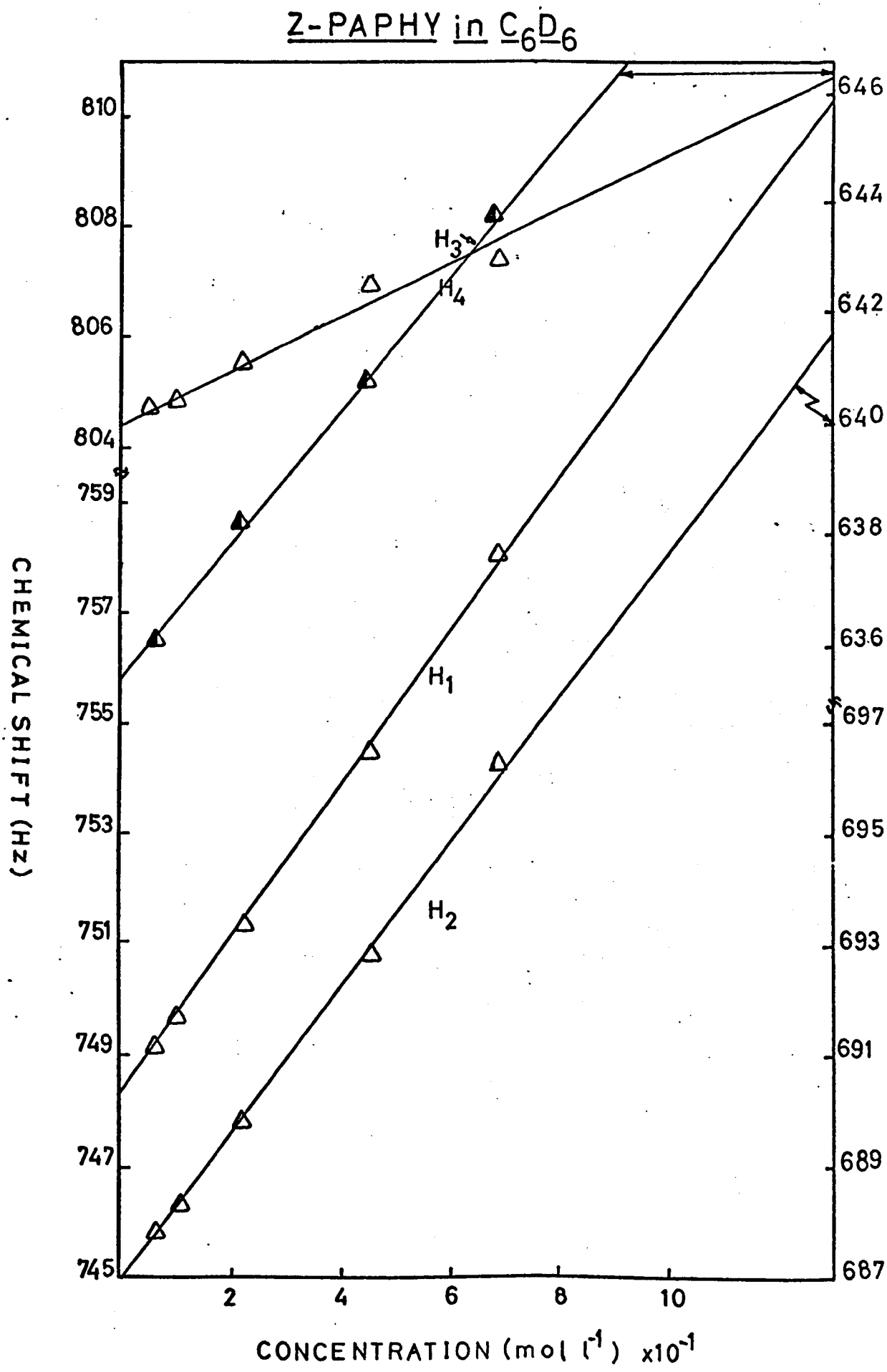

Z-PAPHY in C6D6
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l-1) x10-1
H1
H2
H3
H4
810
808
806
804
759
757
755
753
751
749
747
745
646
644
642
640
638
636
697
695
693
691
689
687
2
4
6
8
10

Fig. 2.41(a)

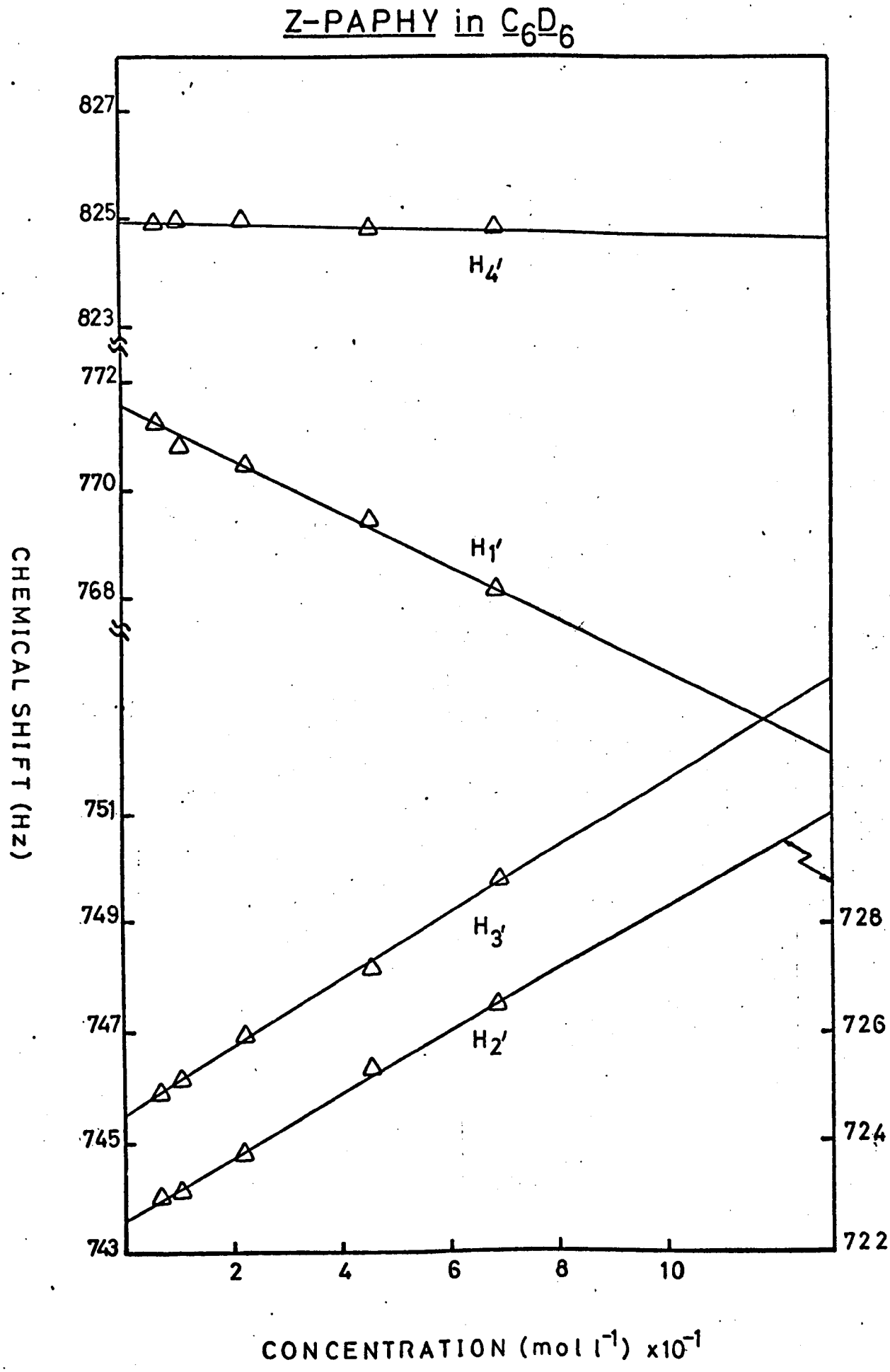

Z-PAPHY in C_6D_6
827
825
823
772
770
768
751
749
747
745
743
728
726
724
722
H_4'
H_1'
H_3'
H_2'
2
4
6
8
10
CHEMICAL SHIFT (Hz)
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig.2.41(b)

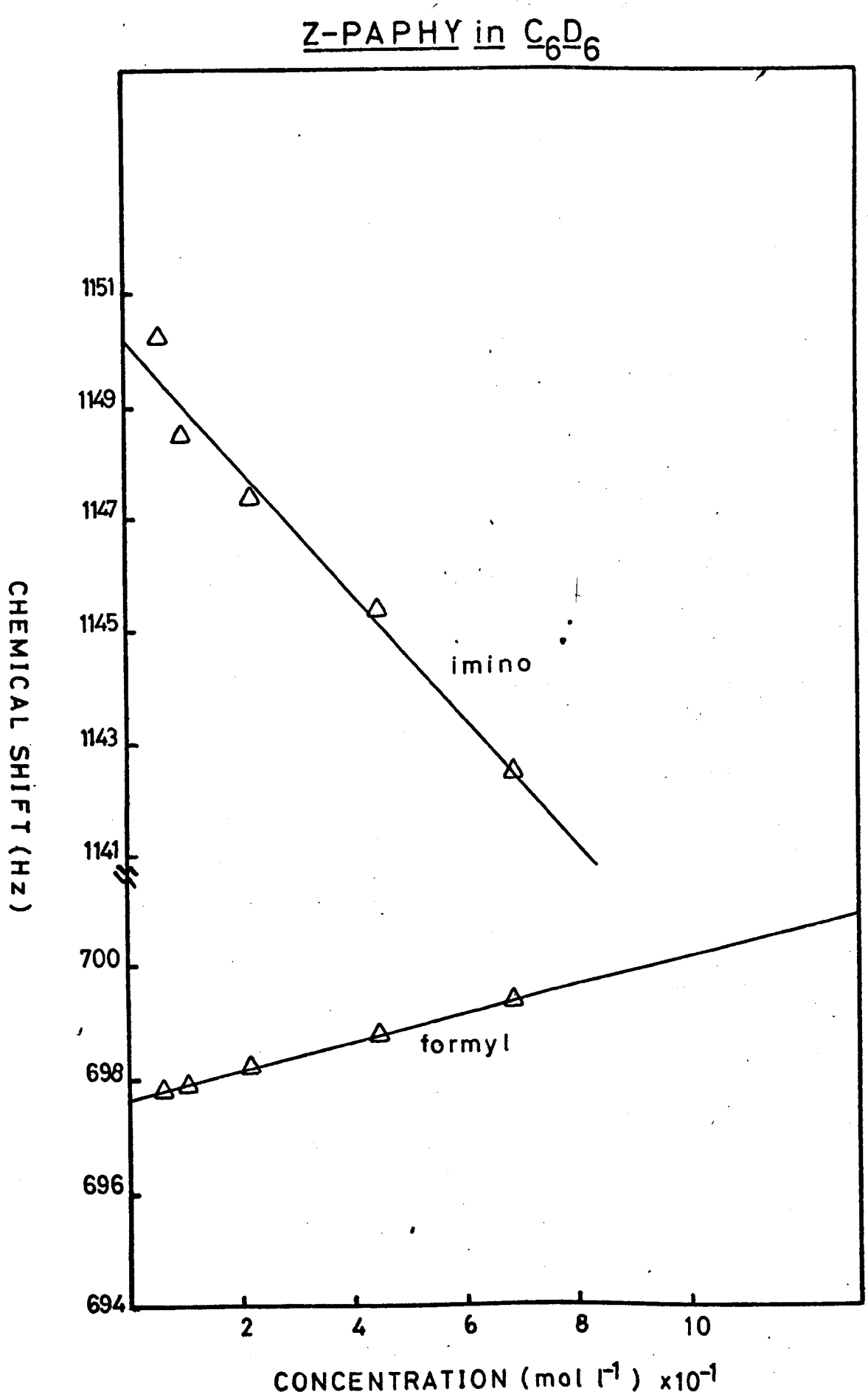

Z-PAPHY in C_6D_6
1151
1149
1147
1145
1143
1141
700
698
696
694
imino
formyl
CHEMICAL SHIFT (Hz)
2
4
6
8
10
CONCENTRATION (mol l^{-1}) $\times 10^{-1}$

Fig. 2.41 (c)

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Chapter 3

Long Range Coupling

Introduction

Long range coupling between protons is generally regarded as that[1-3] occurring via three or more bonds. A number of comprehensive reviews have been written on the topic[2-4] and from these it is clear that long range coupling is found in many types of organic compounds. Discussion here is restricted to aromatic systems in which coupling occurs across four or more bonds.

Coupling of side chain protons to aromatic ring protons is generally of two types.

1) Protons Attached to sp^3-Hybridised Benzylic Carbon atoms.

If the carbon atom to which the side chain proton is bonded is sp^3 hybridised, for example as in methyl substituted rings, the coupling is most likely to be observed across four or six bonds. Five bond (i.e. meta) coupling is considerably smaller[7,8]. Coupling constants (J^{CH_3-H}) are usually less than 1 Hz. Bell et al[9] in studies of 2-amino, 2-chloro and 2-nitropicolines observed coupling of the methyl groups to ortho and para ring protons.

Ortho (i.e. four bond) coupling has been found in 5,5'-dimethyl-2,2'-dipyridyl[10] and methyl substituted phenanthrolines[11]. Hoffman and Gronowitz[12,13] in their study of disubstituted thiophenes observed methyl proton-ring proton coupling. In a recent series of papers on methyl derivatives of fluoropyridines Schaefer and co-workers[14-16] reported couplings between methyl groups and ring protons and investigated the sigma and pi electron contributions to the coupling.

Kotowycz and Schaefer[17] determined $J_{ortho}^{CH_3-H}$ (0.63Hz) and $J_{para}^{CH_3-H}$ (0.58Hz) in 2-bromo-5-chlorotoluene and also determined the relative signs. Similar values of J^{CH_3-H} were obtained from the 100 MHz spectrum of toluene by Williamson et al[18].

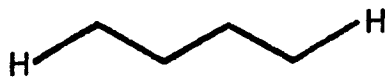
Bramwell and Randall[21] investigated the PMR spectra of α,β and γ-picolines. The spectrum of α-picoline showed the ortho and para couplings with the methyl substituent to be equal (0.3Hz), with the meta coupling even smaller. Methyl coupling with all ring protons was observed in the spectrum of β-picoline and that of γ-picoline showed both ortho and meta coupling.

Work by Rottendorf and Sternhell[8] and Nair and Gopakumar[7] has shown that the magnitude of side chain coupling involving methyl groups may be a measure of bond order, at least for ortho coupling.

11) Protons Attached to sp^2 Hybridised Benzylic Carbon Atoms

In contrast to the situation discussed in the section above protons attached to sp^2 hybridised benzylic carbon atoms usually couple with ring protons in the meta position[19-21] (i.e. through five bonds) although in some cases[22] such protons couple with ortho ring protons.

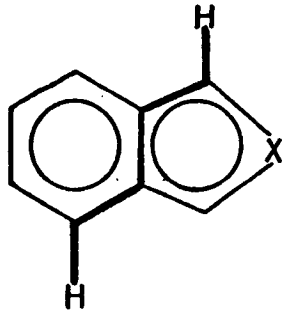
One of the most frequently observed cases of coupling across five bonds is that between aldehydic and meta ring protons[19,20,23-35]. It has been suggested that such coupling is stereospecific[18,20,39] in that for maximum coupling the bonds must be coplanar, that is, arranged in a 'straight' zig-zag (I). This pathway has been shown to be present



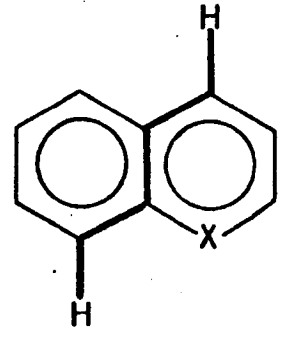
(I)

in a large number of compounds, some of them belonging to rigid cyclic systems, thus emphasising the planar nature of the arrangement.

Martin-Smith et al[36] observed long range coupling in some benzothiophenes and indole derivatives in which the coupling was along the 'straight' zig-zag pathways indicated in (II) and (III) below



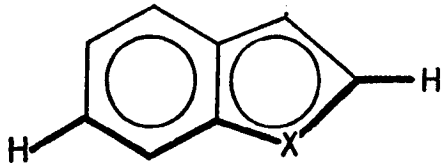
(II)



(III)

Similar observations have been made by Takahashi et al[37,38]. Some other rigid ring systems which exhibit this long range inter-ring coupling are indene,[28,40] acridine,[41] and benzofuran[28]. A fuller list is given in reference 36.

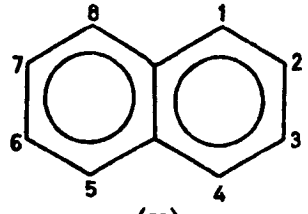
Although the five-bond coupling is the most commonly observed some systems exhibit coupling through six bonds[36-38] as shown below in (IV)



(IV)

The presence of the heteroatom is considered to play an important part in the transmission of the coupling[37].

Recently Crecely and Goldstein[42] have observed extensive (4,5,6 and 7 bond) coupling in the PMR spectrum of naphthalene (V). The values



(V)

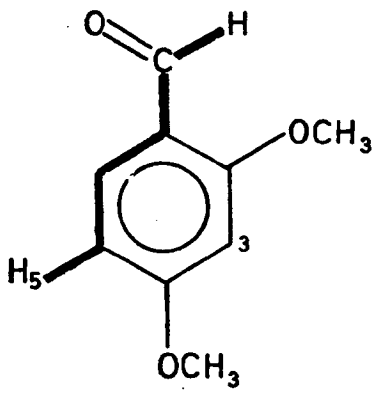
of the coupling constants (in Hz) are given below (neglecting sign)

$J_{1,8}$	(4 bond)	=	0.45
$J_{1,5}$	(5-bond)	=	0.85
$J_{1,7}$		=	0.2
$J_{1,6}$	(6-bond)	=	0.1
$J_{2,7}$		=	0.1
$J_{2,6}$	(7-bond)	=	0.25

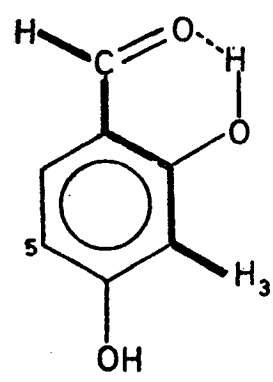
That $J_{1,5}$ is the largest value although it is over a larger number of

bonds than $J_{1,8}$ seems further to indicate the importance of the 'straight' zig-zag pathway.

Kowalewski & Kowalewski[34] investigated long range coupling in 2,4-dimethoxybenzaldehyde(VI) and 2,4-dihydroxybenzaldehyde(VII).



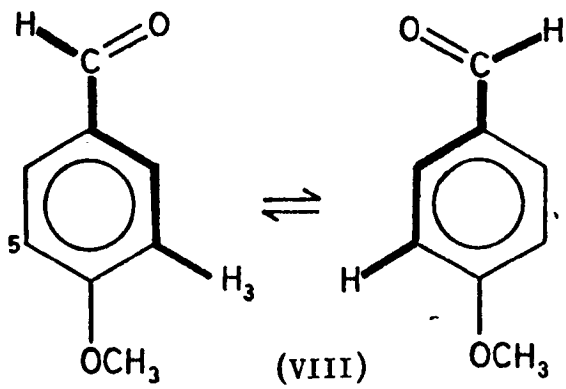
(VI)



(VII)

In (VI) they observed a value of 0.8Hz for J^{CHO-H_5} and attributed this strong coupling to the effect of the bulky methoxy group which forces the aldehyde group to take up the orientation shown in which there is a 'straight' zig-zag coupling path between the protons. No coupling was observed between the aldehyde proton and H_3. In 2,4-dihydroxybenzene such coupling is observed ($J^{CHO-CH3}$ = 0.7Hz) because hydrogen bonding between the aldehyde group oxygen and the hydroxyl group hydrogen restricts the rotation of the aldehyde group and reverses the direction of the zig-zag pathway.

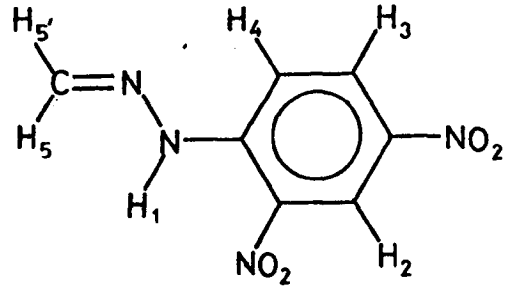
In p-methoxybenzaldehyde(VIII) Martin[43] observed coupling (0.4Hz)



(VIII)

between both H_3 and H_5 and the aldehyde proton. Unrestricted rotation of the aldehyde group allows the existence of the two forms (VIII) and the value of J^{CHO-H_5} and J^{CHO-H_3} are a time average of J=0 and J=0.8Hz.

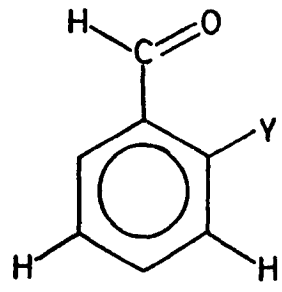
Work by Karabatsos et al[44] on aldehydedinitro phenylhydrazones of the type (IX) showed coupling between H_1 and H_3 (~ 0.7-0.8Hz) but



(IX)

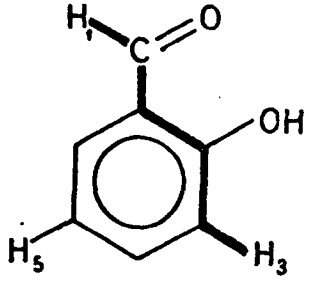
not between H_1 and H_2. Hydrogen bonding between the ortho nitro group and H_1 restricts the molecule to the configuration (IX) thus placing H_1 and H_3 in a trans co-planar conformation which was later shown[43] to be an important requirement for coupling to occur. However, the fact that coupling was observed between H_1 and H_5 but not $H_{5'}$ and also that H_4 showed coupling with $H_{5'}$ (0.1-0.2Hz) and to a lesser extent with H_5 indicate that the stereochemical requirements for long range coupling are complex.

Enlarging upon previous work[44] Karabatsos and Vane[20] investigated the spectra of benzaldehyde and a number of substituted benzaldehydes. They used the system (X). By varying the substituent Y, the carbonyl

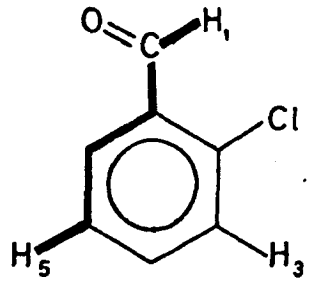


(X)

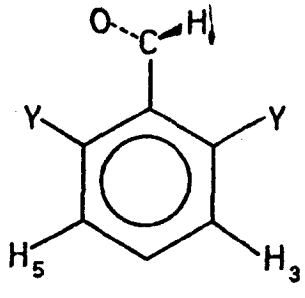
group is forced to assume one of three configurations (XI), (XII), or (XIII).



(XI)



(XII)



(XIII)

They found

(I) H_1 only couples with protons meta to the aldehyde group.

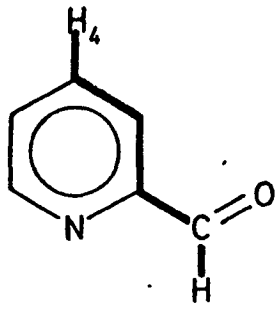
(II) The coupling constant is independent of the electronic effects of the substituent.

(III) When the interacting protons are trans-trans co-planar (dihedral angle 180°) the coupling constant is about 0.7Hz. When they are cis-trans co-planar (dihedral angle 0°) no coupling is observed.

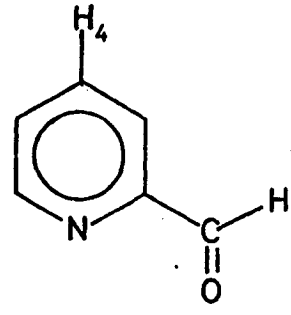
(IV) When there are substituents in both ortho positions H_1 couples with both the protons meta to the aldehyde group. (0.35Hz).

They also concluded that if a compound could exist in two conformations, i.e. one in which long range coupling is present and one in which it is

not, then the size of the observed coupling would be proportional to the amount present of the conformation which shows coupling. For example in the spectrum of pyridine-2-aldehyde which can exist in the conformations (XIV) and (XV) they found the value of J^{CHO-H_4} to be



(XIV)



(XV)

0.6 and 0.5Hz in dimethyl sulphoxide and carbon tetrachloride solutions respectively. Such coupling in a compound of fixed conformation (XIV) is of the order of 0.7Hz and thus they came to the conclusion that pyridine-2-aldehyde exists as 85 or 70. (XIV) and 15 or 30% (XV) in dimethyl sulphoxide and carbon tetrachloride respectively.

Mechanism of Long Range Coupling

The precise mechanism of long range coupling is not well understood and probably differs with the type of compound. However, as the coupling transmitted solely by sigma bonds decreases in magnitude by a factor of $\frac{1}{10} - \frac{1}{20}$ per bond[45] it is not unreasonable to assume a pi-electron contribution to the coupling. Thus the coupling constant between two protons A and B may be expressed as a sum of sigma and pi contributions

$$J_{AB} = J_{AB}^{\pi} + J_{AB}^{\sigma}$$

Although J_{AB}^{π} is much smaller than J_{AB}^{σ}[46] the effect is not attenuated

nearly so rapidly when the number of intervening bonds is increased.

Some estimates have been made of the sigma contribution to $J^{CH_3-H}_{o,m,p}$ in methyl benzenes[47]. For $J^{CH_3-H}_{p}$ the sigma contribution is considered negligible (which is not surprising as it is across six bonds). $J^{CH_3-H}_{m}$ is about $\frac{1}{3}$ and the largest contribution is for $J^{CH_3-H}_{o}$ which is thought to be between $\frac{1}{3}$ and $\frac{1}{2}$.

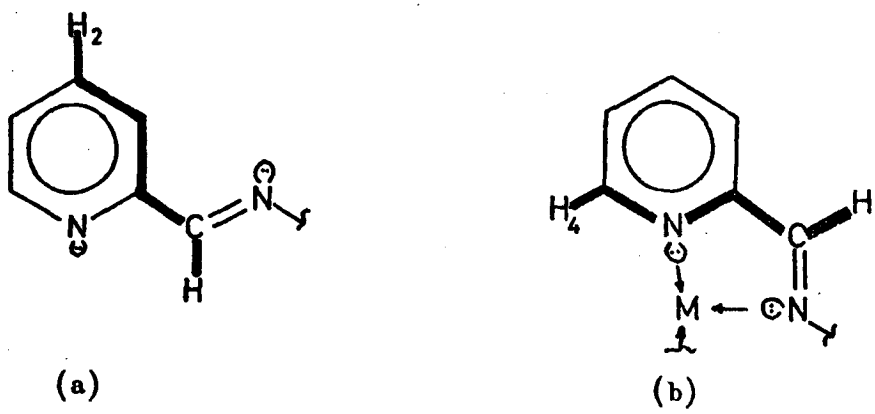
Various suggestions relating to the mechanism of long range coupling have been put forward by Hoffman[49-50], Schaefer[14-16] and McConnell[46,51].

Discussion

3.1. Coupling between Ring Protons and Formyl and Imino Protons

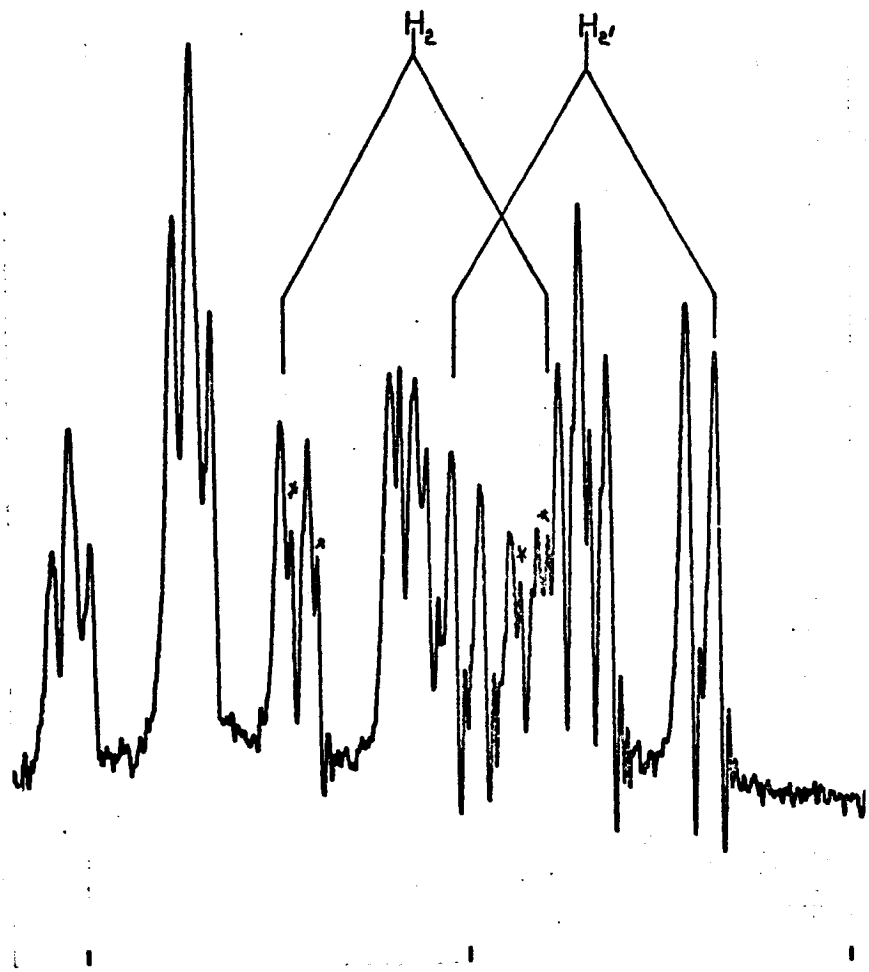
In Chapter 1 long range coupling between the ring protons and formyl protons was mentioned briefly. Inspection of a particularly well resolved spectrum of E-PAPHY (S.3.1) in dimethyl sulphoxide shows fine structure in the octet of H_2 (marked by an asterisk). This is a result of coupling with the formyl proton. Such coupling has also been observed by Cooper et al[54] in the spectrum of E-PAPHY in deuteriochloroform and by Bramwell and Randall[21] in pyridine-2-aldehyde. Table 3.1 gives the magnitude of this and other long range couplings observed in the isomers of PAPHY.

Evidence was given in the Introduction to this chapter for the stereospecificity of such coupling. Karabatsos et al[20,44] showed that maximum coupling (0.6-0.7Hz) between the formyl and appropriate ring proton occurred if they were separated by a 'straight' zig-zag path (I) and the dihedral angle between them was 180°. In PAPHY the conditions for maximum coupling appear to be satisfied and for this to be so PAPHY must have the partial configuration shown in Fig.3.1a. On co-ordination to a



(a) (b)

Fig.3.1.



SPECTRUM S.3.1.

E-PAPHY in d_6DMSO.

H_2-formyl coupling is indicated by asterisks.

Table 3.1

Compound	Coupling Protons	J(Hz)
*E-PAPHY	H_2-formyl	0.6-0.7 (0.5)[a]
Z-PAPHY	H_4-formyl	0.5
	H_2-imino	0.6-0.7
py-2-CHO[b]	H_4-CHO	0.8
py-3-CHO[b]	H_5-CHO	0.5

* Splitting of imino or formyl resonances observed

Ref. 54.

Ref. 55.

metal atom the configuration must change to that in Fig.3.1b in order that the lone pair of the $\geq C = N-$ nitrogen is suitably orientated for donation to the metal. The dihedral angle between the formyl proton and H_2 will become zero but that between H_4 and the formyl proton will become 180^{o}. One should therefore observe the disappearance of formyl-H_2 coupling and the appearance of formyl-H_4 coupling on complexing. Generally the resolution of the metal complex spectra was insufficient for the detection of such fine structure but the quite well resolved spectra of some lead and silver complexes (S.3.3 and S.3.4) show a distortion of the octet of H_4 which may result from long range coupling.

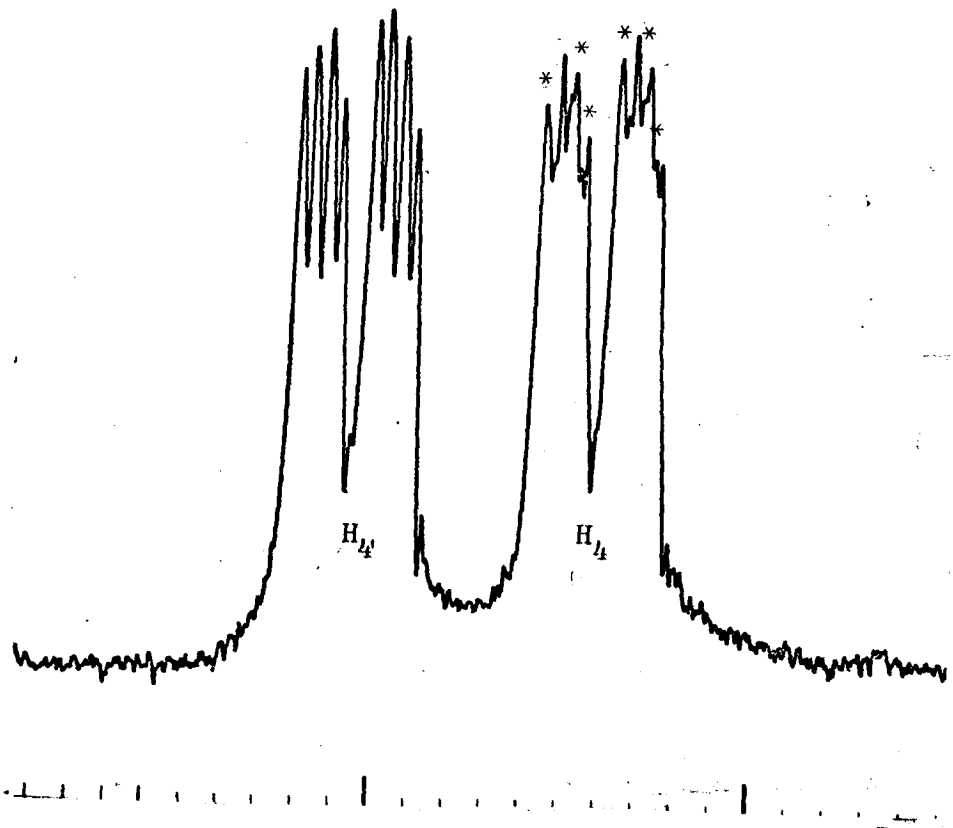
The sharp resonances of the H_2' octet in the spectrum of E-PAPHY (S.3.1.) indicate the absence of any coupling with the imino proton. This may be a result of, or a combination of, two factors.

(I) Intermolecular proton exchange involving the imino proton would prevent coupling with ring protons.

(II) The presumed sp^3 hybridisation of the nitrogen atom means that the imino proton is not coplanar with the hydrazine ring without considerable distortion of the molecule.

On isomerisation to the Z-form the H_2-formyl coupling disappears but is replaced by H_4-formyl coupling (S.3.2) of the order of 0.5Hz. There also appears H_2'-imino coupling of about 0.6 - 0.7 (marked by an asterisk in S.3.2).

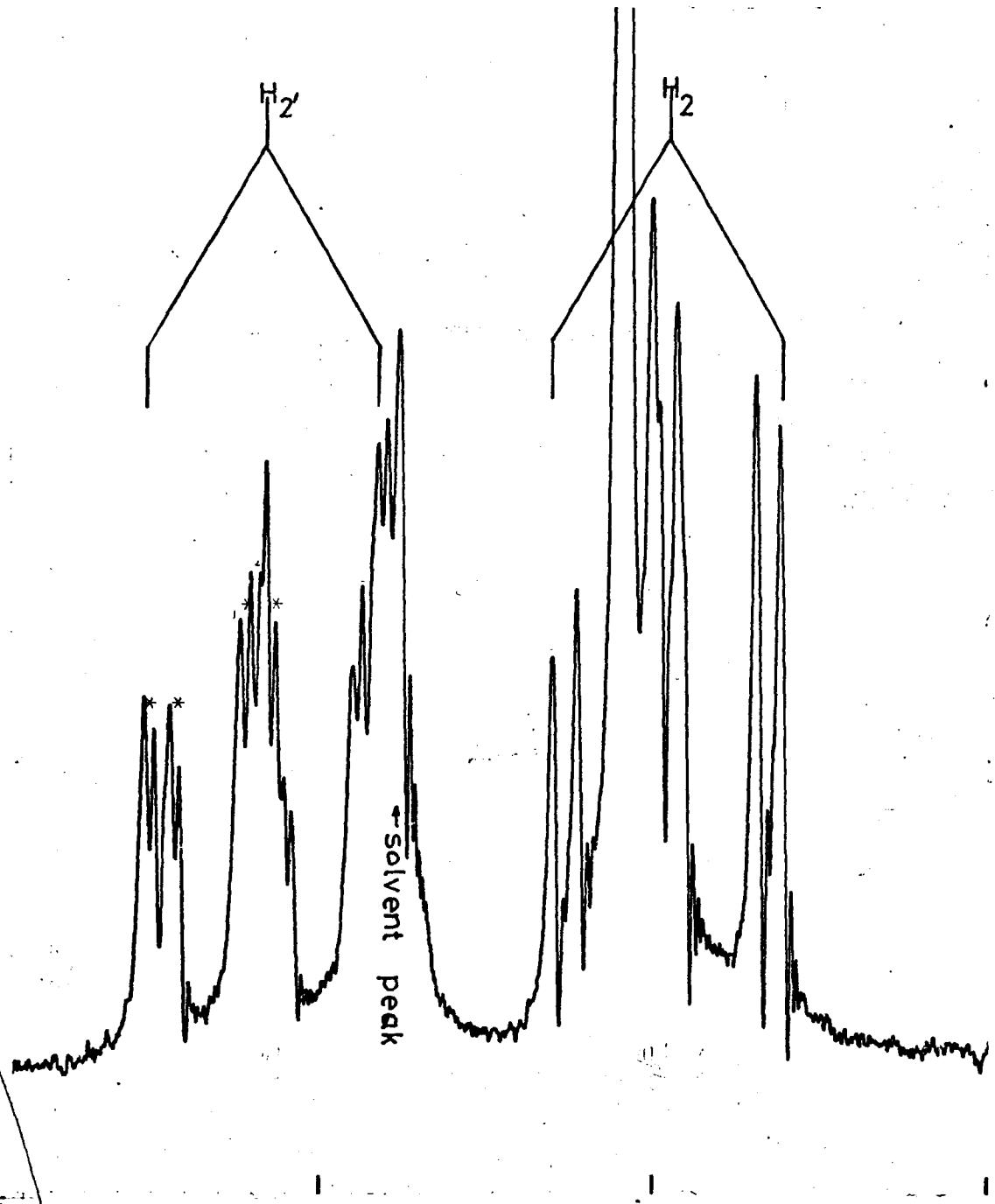
From the structure of Z-PAPHY (Fig.3.2) it is clear why these couplings arise. Their magnitudes indicate that the pairs of protons



SPECTRUM S.3.2.

Z-PAPHY in C_6D_6.

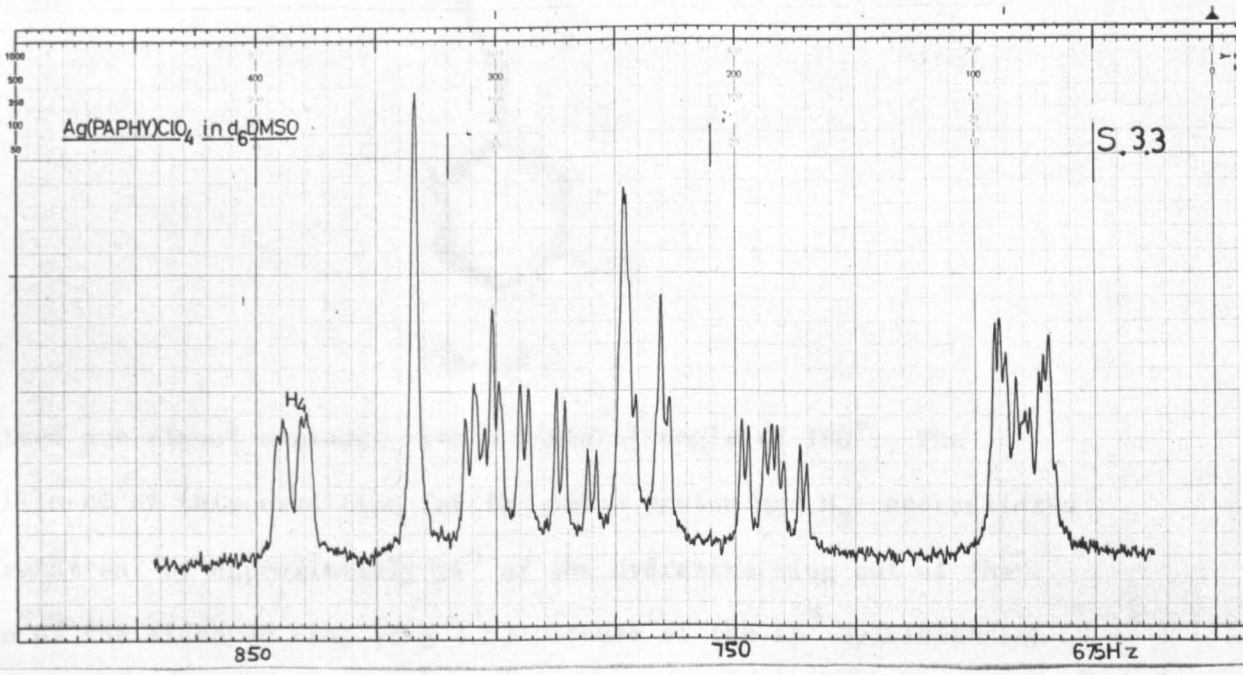
H_4-formyl coupling is indicated by asterisks.

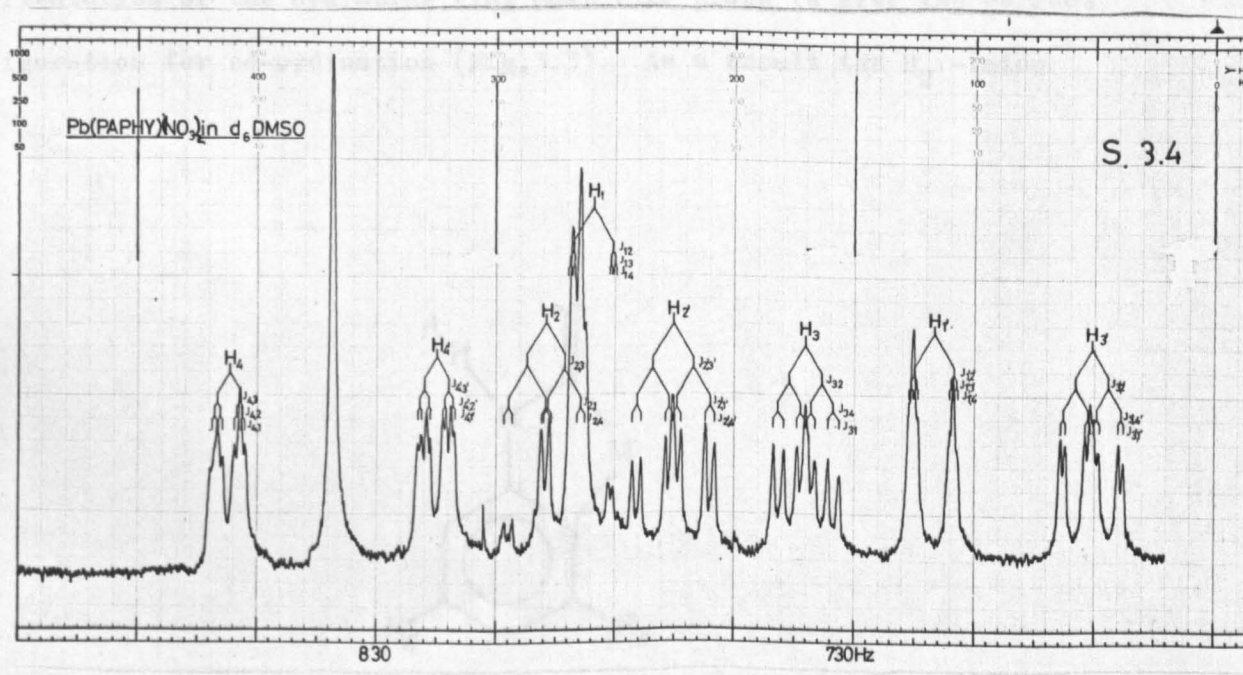


SPECTRUM S.3.2.

Z-PAPHY in C_6D_6.

$H_{2'}$-imino coupling is indicated by asterisks.


Ag(PAPHY)ClO4 in d6DMSO
S. 3.3
H4
850
750
675Hz


Pb(PAPHY)NO3)2 in d6DMSO
S. 3.4
H1
H2
H2'
H3
H4
H4'
H3'
H4
H4'
830
730Hz

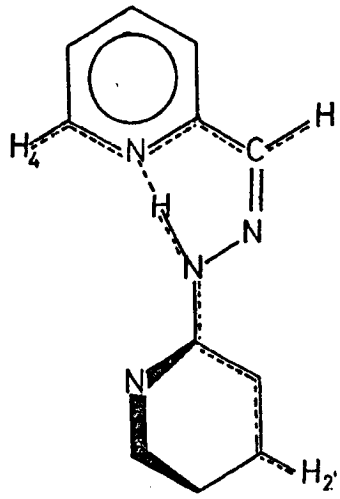


Fig.3.2

involved are almost coplanar with a dihedral angle of 180^{o}. The fulfillment of this condition for the imino proton and $H_{2'}$ necessitates the rotation by approximately 54^{o} of the hydrazine ring out of the plane of the aldehyde ring (Fig.3.2) because of the sp^{3} hydridisation of the nitrogen atom.

Before Z-PAPHY can act as a bidentate donor to a metal atom re-orientation of the hydrazine ring must take place to give the correct configuration for co-ordination (Fig.3.3). As a result the $H_{2'}$-imino

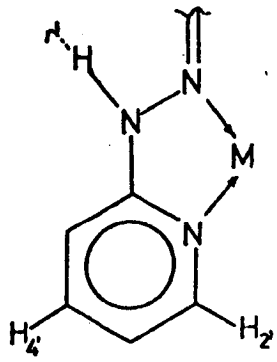


Fig.3.3

coupling will be considerably reduced and may disappear altogether. Some H_4 -formyl coupling may be expected as the dihedral angle between these protons is greater than 90^{o} but no sufficiently well resolved spectra of Z-PAPHY metal complexes have yet been obtained to confirm this.

3.2. Coupling between Ring Protons and Methyl Protons

The couplings observed between ring protons and the protons of the substituent methyl group for various methyl substituted PAPHYS are listed in Table.3.2.

Compound	Coupling Protons	Magnitude (Hz)	Type of Coupling
4'-Me-PAPHY	$CH_3 - H_{3'}$	0.6	ortho
3'-Me-PAPHY	$CH_3 - H_{2'}$	0.7	ortho
2'-Me-PAPHY	$CH_3 - H_{3'}$	0.7-0.8	ortho
4 -Me-PAPHY	$CH_3 - H_3$	0.4-0.5	ortho

Table.3.2.

All the coupling constants were obtained from splitting of the ring proton resonances, in no case was splitting of the methyl resonance observed.

It may be seen from Table.3.2 that only ortho coupling was observed and when a methyl group was flanked by two ortho protons coupling was not observed with both. Nair and Gopakumar[7] and Rottendorf and Sternhell[8] have investigated methyl proton-ring proton coupling and also found this selective ortho coupling. Both sets of workers concluded that the magnitude of the side-chain coupling constant is a funtion of the bond order of the aromatic -C=C- bond involved. As there appears to be no information available at present on the bond

orders of the compounds under consideration it is not possible to relate the findings of the above workers[7,8] to the present work. However, differences in bond order may well be the explanation for the selective ortho coupling.

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Chapter 4

PMR Spectra of Metal Complexes

Introduction

Whether it is feasible or not to measure the PMR spectrum of a metal complex of an organic ligand depends on a number of factors. By far the most significant of these is the electronic configuration of the metal ion. Complexes containing a metal ion with all electron spins paired (i.e. diamagnetic complexes) can give quite well resolved spectra with chemical shifts exhibiting a range similar to that found for organic molecules. However, if the metal complex is paramagnetic by virtue of the presence of unpaired electron(s) some of the unpaired spin density may be transferred to the ligand causing very large upfield or downfield shifts (contact shifts)[1]. La Mar and Van Hecke[2,3] have investigated a number of paramagnetic 1,10-phenanthroline and 2,2'-bipyridyl metal complexes of Cr(II), Fe(III), Co(II) and Ni(II), and obtained well resolved spectra with chemical shifts as large as 50 ppm.

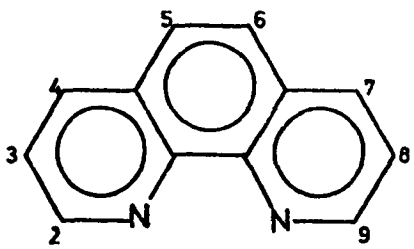
Frequently the spectrum of a paramagnetic complex is not observable because the magnetic moment of the unpaired electron is considerably larger than the nuclear moment and is therefore more effective in causing nuclear relaxation which results in extreme broadening of the resonance lines.

Another factor influencing the type of spectrum arises if the metal atom has a nuclear spin greater than $\frac{1}{2}$. Then it is possible that protons close to the ligand atom bonded to the metal may show resonance peaks broadened as a result of this nuclear spin.

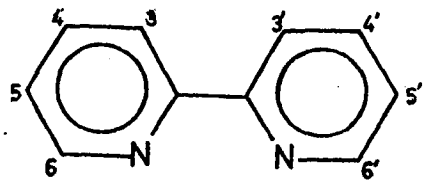
A problem of a more practical nature is that of solubility. Frequently relatively inert solvents such as cyclohexane, n-hexane and carbon tetrachloride do not dissolve a complex in sufficient

concentration for NMR work and it becomes necessary to resort to more polar solvents which have the disadvantage of interacting much more strongly with the complex. It may then be very difficult to determine the exact magnitude of this solvent effect and therefore also an estimate of the absolute chemical shift.

A number of papers have been published on diamagnetic metal complexes containing 1,10-phenanthroline (I) or 2,2'-bipyridyl (II)*



(I)



(II)

On co-ordination to the metal ion the shift is generally downfield. This observation is consistent with withdrawal of electronic charge from the ring.

Castellano et al[4] analysed the spectrum of $Fe^{(II)}(bipy)_3\,Cl_2$ in methanol. The changes in chemical shift on co-ordination are shown in Fig.4.1 where a positive sign before the value of $\nu_{complex} - \nu_{free\ ligand}$ indicates a shift to lower field.

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* Conventionally the nitrogen atoms are numbered 2 and 2'. However, in order to avoid confusion the numbering of (II) follows that of other workers[4,6,7,10-12] investigating the PMR spectra of metal-bipyridyl complexes.

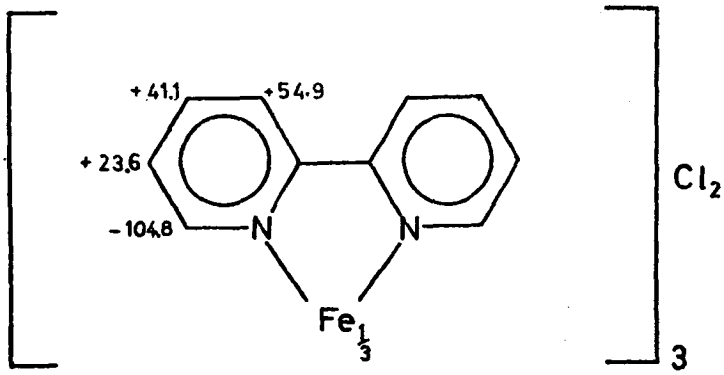


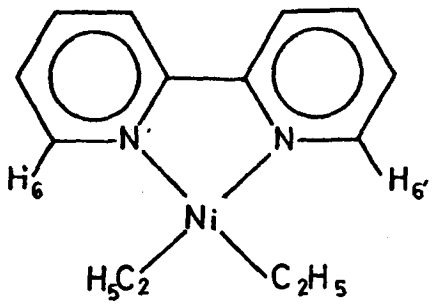
Fig. 4.1.

Apart from $H_{6(6')}$ the shifts are to lower field. The shielding of $H_{6(6')}$ is believed to be a result of its lying close to and above the plane of a pyridine ring of another co-ordinated ligand molecule and hence influenced by the ring current effect in this same ring.

Kanakar et al[5] also analysed the spectrum of $Fe(bipy)_3^{++}$ as well as that of $Co(bipy)_3^{+++}$. The results for the former compound were in general agreement with those of Castellano[4] although there were some small differences in the coupling constants. A similar trend of chemical shifts on complexing was exhibited in the case of the cobalt complex with $H_{6(6')}$ experiencing increased shielding.

De Simone and Drago[6] prepared cis-dichlorobis(bipyridyl)iridium(111) hexafluorophosphate. The PMR spectrum was more complicated than that obtained for tris complexes as the two bipyridyl rings lose their equivalence in the bis complex. Another notable difference was that the 6-protons moved downfield on co-ordination of the ligand as do the rest of the protons. This is because 6-protons in the bis complex do not lie close to the pyridine ring of another ligand molecule. This suggests that the original explanation of Castellano[4] for the 6-proton

upfield shift was correct. Further support for the validity of Castellano's explanation comes from work on diethyldipyridylnickel, (III)[10-12] in which it



(III)

was observed that the resonances due to the 6(6')-proton moved downfield on co-ordination.

Bryant and Fergusson[7] studied the complexes of the ions Fe^{++}, Ru^{++} and Os^{++} and some methyl-substituted bipyridyls. In tris complexes, the increase in upfield shift of H_6 protons observed for increase in atomic number for the series Fe → Ru → Os was correlated with a proposed increase of metal to ligand π-bonding. For the series of complexes $Ru(dmbp)_3^{++}$, $Ru(dmbp)_2(NH_3)_2^{++}$ and $Ru(dmbp)_2(acac)^+$ they suggested from their PMR data, that π-bonding between the ruthenium and nitrogen atoms was greatest in the last complex and least in the first as the acetylacetonate anion is a poor π-acceptor and there are only two dmbp molecules to accept the metal π-electrons.

They prepared the complex ion $Fe(dmbp)(CN)_4^{=}$ and noted that the 6(6')- proton resonance was at much lower field compared with the tris complex $Fe(dmbp)_3^{++}$. This was attributed, in part, to the absence of shielding by the ring current of a pyridine ring in a second dmbp ligand molecule. In the spectra of the bis-dmbp ruthenium complexes they observed two separate ABX systems which led them to believe that the complex had the cis structure shown in Fig.4.2. Also they found that the 6'-proton resonance for each ligand molecule was at higher field than that for the 6-proton. From Fig.4.2. it can be seen that

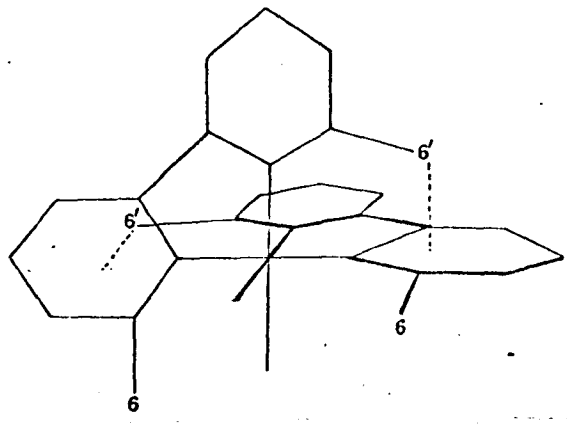
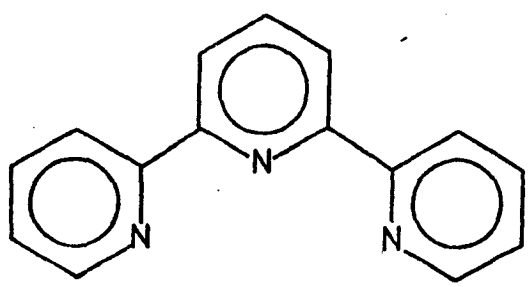


Fig.4.2

the 6'-proton will lie in the shielding cone of an adjacent pyridine ring whereas the 6-proton will not.

The PMR spectra of terpyridine (IV), and bis cobalt(III) and iron (II)



(IV)

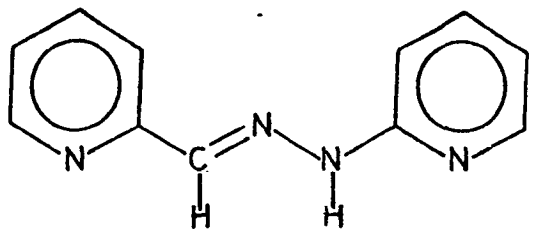
complexes of (IV) have been reported by Elsbernd and Beattie[21]. On co-ordination they observed a downfield shift for all protons resonances except those for the protons α to the nitrogen atoms in the terminal rings which move upfield. The reason for this is most likely to be a result of these protons lying closely above the central pyridine ring of the second ligand molecule.

A number of transition metal 1,10-phenanthroline complexes were studied by Miller & Prince[8,9]. The upfield shift for the 2 and 9 protons, analogous to that for the 6(6') protons in bipyridyl was attributed to a metal-non-bonded hydrogen interaction. This is a different reason from that given by Castellano et al[4] to explain upfield shifts of 6(6') proton in $Fe(bipy)_3Cl_2$. In view of later work by De Simone and Drago[6], Bryant and Fergusson[7], Castellano[10] and Saito[11,12], which support Castellano's original idea the explanation of Miller and Prince should be treated with caution.

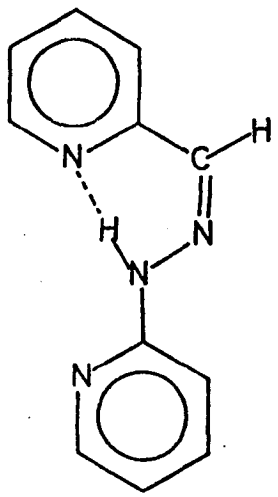
Miller et al extended their PMR studies and applied them to determining the stereochemistries of some mono and bis complexes of 1,10-phenanthroline with cobalt(III) and rhodium(III)[13,14] showing that it was possible to distinguish between cis and trans bis-phenanthroline complexes.

Work by Rosenberger and Pettig[15] attempted to isolate the factors contributing to the chemical shifts of the protons in 1,10-phenathroline and some of its metal complexes. In the case of complexes with magnesium and calcium they deduced from the PMR data that dissociation in solution was extensive, a phenomenon not observed for the zinc and iron complexes.

Dunn and Edwards[16,17] have prepared complexes of the two isomers of pyridine-2-aldehyde-2'-pyridylhydrazone (PAPHY) (V) and (VI),



(V)

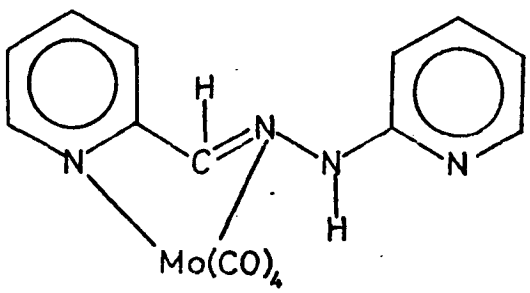


(VI)

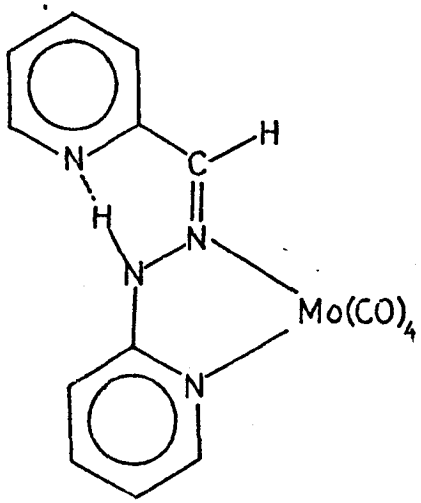
with group VI metal carbonyls and used PMR to help characterise them[16,17]. They were able to conclude which pyridine ring nitrogen atom was involved in the bidentate function of PAPHY as a ligand by observing whether or not the proton α to a particular ring nitrogen moved down field on co-ordination. Only the resonance values for the 4 (4') and imino protons were reported.

Similar work has been carried out by Casey and Horsley[18] who prepared complexes of the type $Mo(CO)_4$(PAPHY) also containing bidentate PAPHY. Some ligands were used with methyl substituents in either the 4 or 4' position. Again only methyl and imino proton resonances were reported.

Bruce et al[19] prepared the linkage isomers (VII) and (VIII) of $Mo(CO)_4$(PAPHY) and also used the shift of the 4 or 4' proton on



(VII)

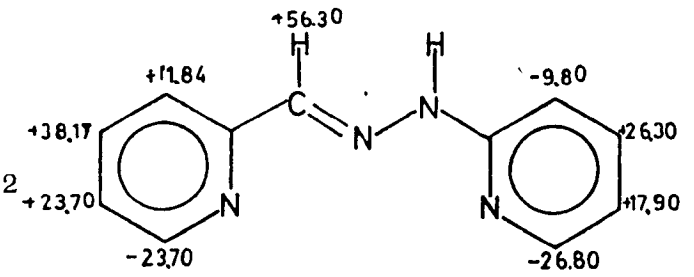


(VIII)

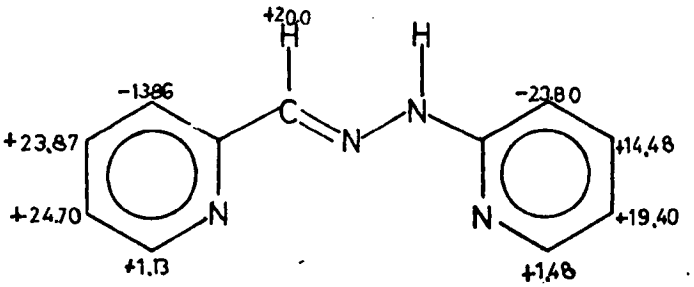
complexing to determine which ring nitrogen atom was bonding to the metal.

Some zinc chloride complexes with 3-picoline have been prepared by Abramovitch et al[20] who found that on complexing all ring protons shifted down field. The α-proton was affected to a lesser extent than the β and γ-protons which was attributed to a possible change in the paramagnetic contribution of the nitrogen atom and π-bonding with the metal atom.

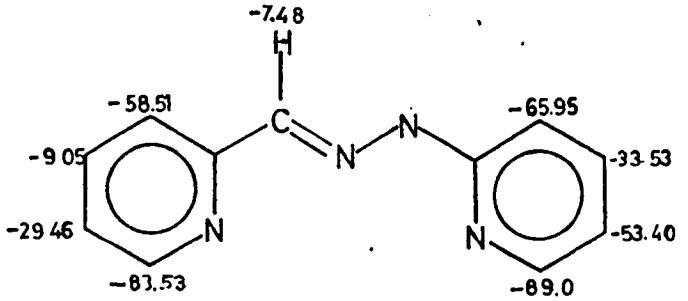
$Zn(PAPHY)_2(ClO_4)_2$



$Zn(PAPHY)Cl_2$



$Zn(PAPY)_2$



$Zn(PAPY)_2$

$\Delta_{complex}^{dep.complex}$

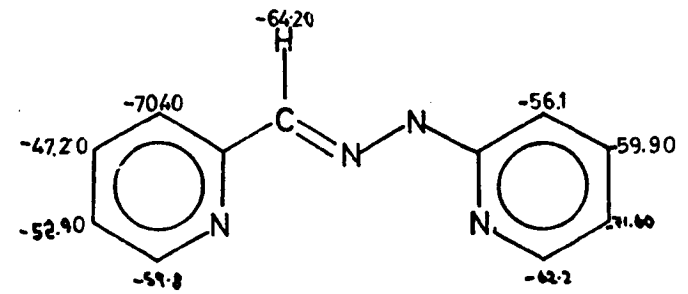


Fig.4.3

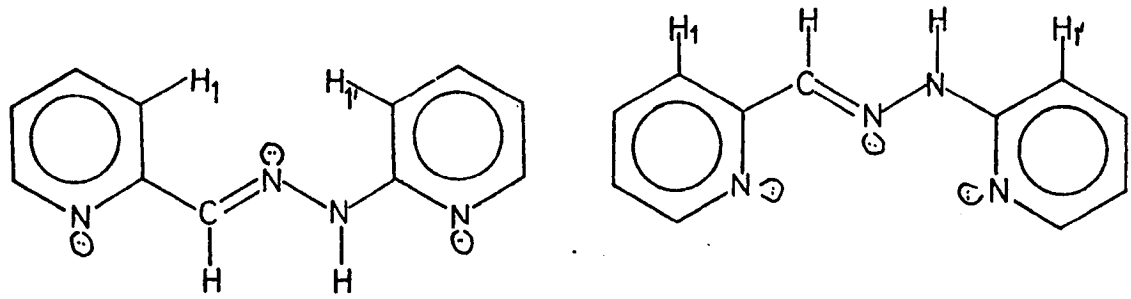
Results and Discussion.

4.1. Bis(PAPHY)-Zinc Complexes.

- shown in Table 4.1. are the spectral parameters for the complexes $Zn(PAPHY)_2(ClO_4)_2$ and $Zn(PAPY)_2$. Values of $\Delta^{complex}_{PAPHY}$ $(= \nu_{PAPHY} - \nu_{complex})$ are given Fig.4.1; a negative sign in front of the value indicating an upfield shift.

Consider first the $\Delta^{complex}_{PAPHY}$ values for the complex, $Zn(PAPHY)_2(ClO_4)_2$. Those for the 2(2') and 3(3') protons are fairly large and positive which is what one would expect as a result of withdrawal of charge from the pyridine rings on co-ordination of the nitrogen atoms to the central zinc atom. The small positive value observed for H_1 and the negative value observed for $H_{1'}$ are considered to be a result of a change in configuration of the ligand on co-ordination.

In Fig.4.4. are shown the proposed configurations for the free*



(a) (b)

Fig. 4.4

*Evidence for the configuration of the aldehyde ring with respect to the carbon-nitrogen double bond has been presented in Sections 1.2. and 3.1. There is no experimental evidence concerning the configuration of the hydrazine ring with respect to the rest of the molecule in the E-isomer. However it is likely, because of steric hindrance between $H_{1'}$ and the sp^2 nitrogen atom, that this ring is twisted out of the plane of the rest of the molecule as in the Z-isomer (Section 3.1.).

Table 4.1. Spectral Parameters (Hz) for E-PAPHY-Zinc Complexes (measured at 100MHz)

	$Zn(PAPHY)_2(ClO_4)_2$	$Zn(PAPHY)Cl_2$	$Zn(PAPY)_2$
H_1	808.3	782.50	737.95
H_2	817.90	803.60	770.68
H_3	752.7	753.70	699.54
H_4	829.60	854.43	769.77
$H_{1'}$	720.55	706.60	664.45
$H_{2'}$	793.1	781.28	733.24
$H_{3'}$	698.9	700.4	627.30
$H_{4'}$	787.1	815.38	724.90
-CHO	865.30	828.50	801.10
$J_{1,2}$	7.50	7.62	7.30
$J_{1,3}$	2.30	1.60	1.08
$J_{1,4}$	0.9	0.80	0.85
$J_{1,5}$	6.55	7.14	6.87
$J_{2,4}$	1.45	1.68	1.80
$J_{3,4}$	5.0	5.08	5.20
$J_{1',2'}$	8.2	8.45	8.20
$J_{1',3'}$	0.45	1.10	1.10
$J_{1',4'}$	0.80	0.95	0.95
$J_{2',3'}$	7.45	7.05	6.54
$J_{2',4'}$	1.40	1.60	1.60
$J_{3',4'}$	5.20	5.20	5.25

and co-ordinated ligands. Inspection of a Courtauld's model of E-PAPHY (see I, General Introduction) shows that both H_1 and $H_{1'}$ are extremely close to, and approximately in the plane of, the central sp^2 hybridised nitrogen atom and thus may experience deshielding resulting from the nitrogen atom anisotropy[22]. The proton H_1 will also experience deshielding resulting from the anisotropy of the carbon-nitrogen double bond (see Section 1.2). On complex formation the configuration of PAPHY must change in order that the three nitrogen atoms are suitably placed for co-ordination to the metal atom (Fig.4.4b). This change will place H_1 and $H_{1'}$ far away from the deshielding effect of the nitrogen atom anisotropy tending to offset the deshielding effect of co-ordination. In addition H_1 will experience shielding from the carbon-nitrogen double bond anisotropy (see Section 1.2). On isomerisation to the Z-isomer in carbon tetrachloride (which also involves re-orientation of the aldehyde ring with respect to the carbon-nitrogen double bond) H_1 is shielded and experiences a downfield shift of approximately 30Hz*. Thus as a rough estimate the deshielding of H_1 on co-ordination (neglecting nitrogen anisotropy effects etc.) would give a downfield shift of about 42Hz.

A considerable upfield shift for both H_4 and $H_{4'}$ is observed on co-ordination. Similar shifts were observed by Miller and Prince[8,9] in tris-1,10 phenanthroline complexes and by Castellano et al[4] in $[Fe(bipy)_3]Cl_2$. This was shown to be due to shielding by the aromatic ring current of the pyridine ring of another ligand molecule[4,6,7,10,] However the present case is somewhat different. The ion $[Zn(PAPHY)_2]^{++}$

*The downfield shift is probably slightly greater than this but is partially offset by the deshielding effect of the intra-molecular hydrogen bond (Section 1.2.).

presumably has a slightly distorted octahedral structure and it will not be possible for the 4(4')-proton to lie over a pyridine ring of the second ligand molecule. Shielding by the anisotropy of the >C=N- bond was considered a possibility but H_4 and $H_{4'}$ do not come into the shielding region of the bond and in fact may even be deshielded by the anisotropy. From the inspection of a Courtauld's model of the complex it appears that H_4 and $H_{4'}$ are situated above and below the central sp^2 hybridised nitrogen atom of the second ligand molecule and it may be that the anisotropy of the nitrogen atom has a shielding effect on protons in this position. These protons may also be correctly placed to experience some long range deshielding from the aromatic ring current of the pyridine rings of the second ligand molecule.

From the discussion in Section 1.2. one would expect an upfield or small downfield shift of the formyl proton on co-ordination but as can be seen from Fig.4.2. there is a downfield shift of +56.3Hz. Such a large shift is probably because charge is withdrawn not only from the nitrogen atom adjacent to the formyl carbon atom but also from the aldehyde ring nitrogen. It was not possible to obtain a $\Delta^{complex}_{PAPHY}$ value for the imino proton because co-ordination to a metal ion increases the acidity of this proton and proton exchange occurs between this and the hydroxyl proton of the water present either in the solvent or as water of crystallisation.

Another result of the enhanced acidity of the imino proton in the metal complex is that it may be readily removed by the addition of base giving rise to the neutral complex $Zn(PAPY)_2$. This deprotonation leads to a flood of negative charge into both

pyridine rings in the molecule which is reflected by an upfield shift of all proton resonances. Values of both $\Delta^{dep.complex}_{PAPHY}$ and $\Delta^{dep.complex}_{complex}$ are given in Fig.4.3. The latter values give a better picture of shift variation on deprotonation. The total upfield shift for the hydrazine ring protons is greater (249.8 Hz) than that for the aldehyde ring (230.3 Hz) which is probably because the imino proton is closer to this ring.

The spectrum of the deprotonated complex (S.4.2.) shows that the 4 and 4' protons are more shielded relative to the other protons on complexing. An explanation for this has been given previously.

4.2. Mono (PAPHY)-Metal Complexes

The mono zinc complex $Zn(PAPHY)Cl_2$ gives a PMR spectrum* (S.4.3.) which is totally different from that of $Zn(PAPHY)_2(ClO_4)_2$ (S.4.1.). The most obvious difference, as can be seen from the $\Delta^{complex}_{PAPHY}$ values in Fig.4.2. is that the H_4 and $H_{4'}$ resonances do not exhibit the large upfield shift observed in the bis complex case which is to be expected in the light of the explanation given for the upfield shifts and is supplementary evidence in support of it. The extremely small $\Delta^{complex}_{PAPHY}$ values of these protons are a result of the cancellation of the deshielding effect of the nitrogen atom anisotropy which offsets the deshielding experienced by the protons from withdrawal of charge by the metal atom.. If one compares the changes inchemical shifts on co-ordination of the protons in the 4 and 4' protons and those of the methyl groups in the corresponding methyl substituted compounds some measure of the shielding due to the nitrogen atom anisotropy may be gained. Values of $\Delta^{complex}_{PAPHY}$ are given in Table 4.1and it is clear that on co-ordination the methyl protons (which are further away from the nitrogen atom than the protons in the unsubstituted compounds and thus less likely to be affected by changes in the nitrogen atom magnetic anisotropy) experience a downfield shift of about 40Hz on co-ordination. The downfield shift of the protons in these positions (in the absence ofshielding from the nitrogen atom) would in fact be a little larger than this because the number of intervening bonds between the metal atom and the proton(s) concerned is greater by one in the methyl substituted compound. The value would probably be between

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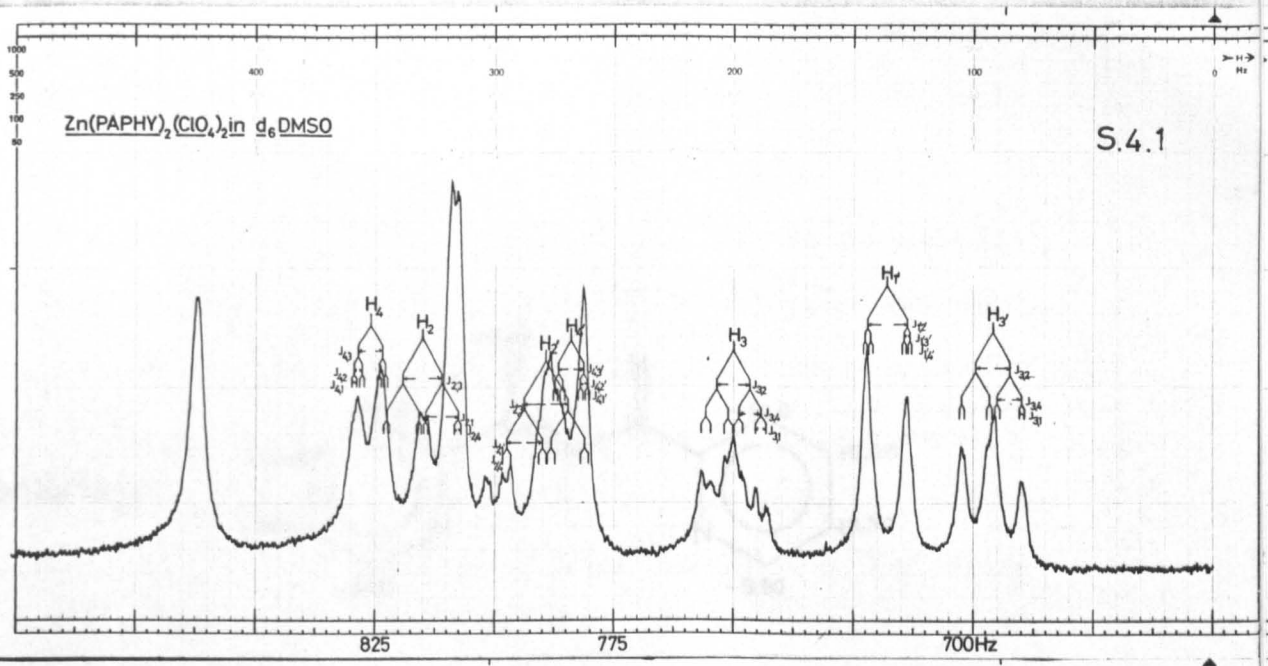
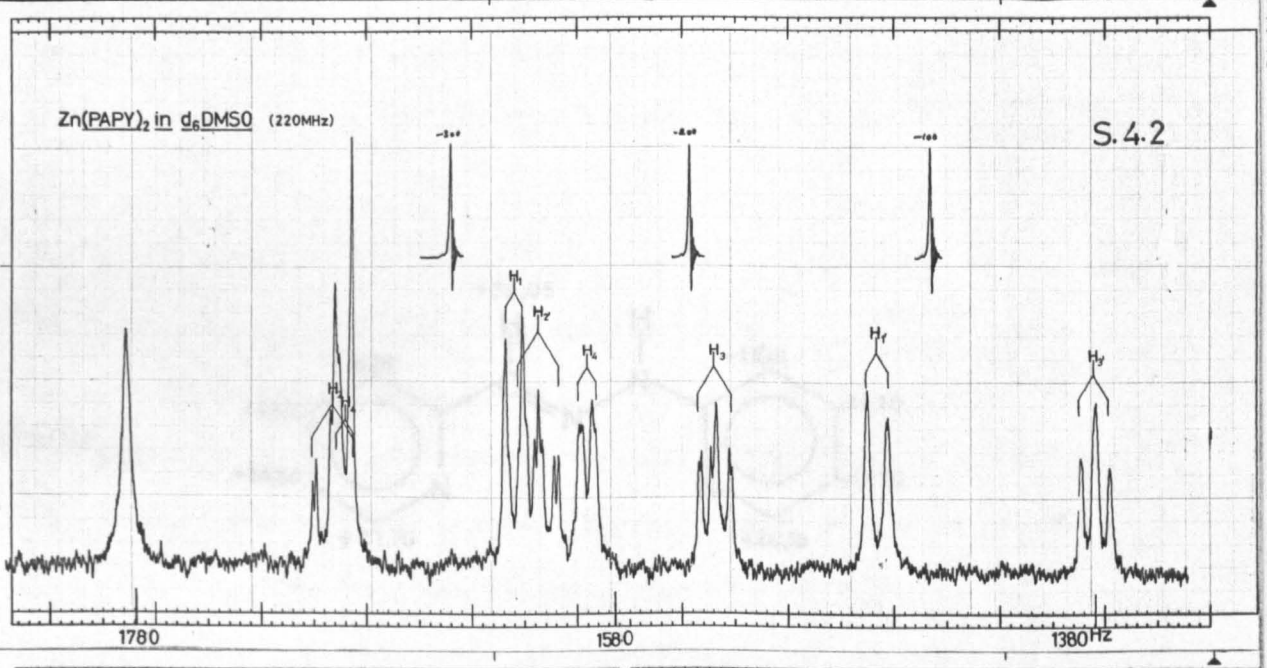
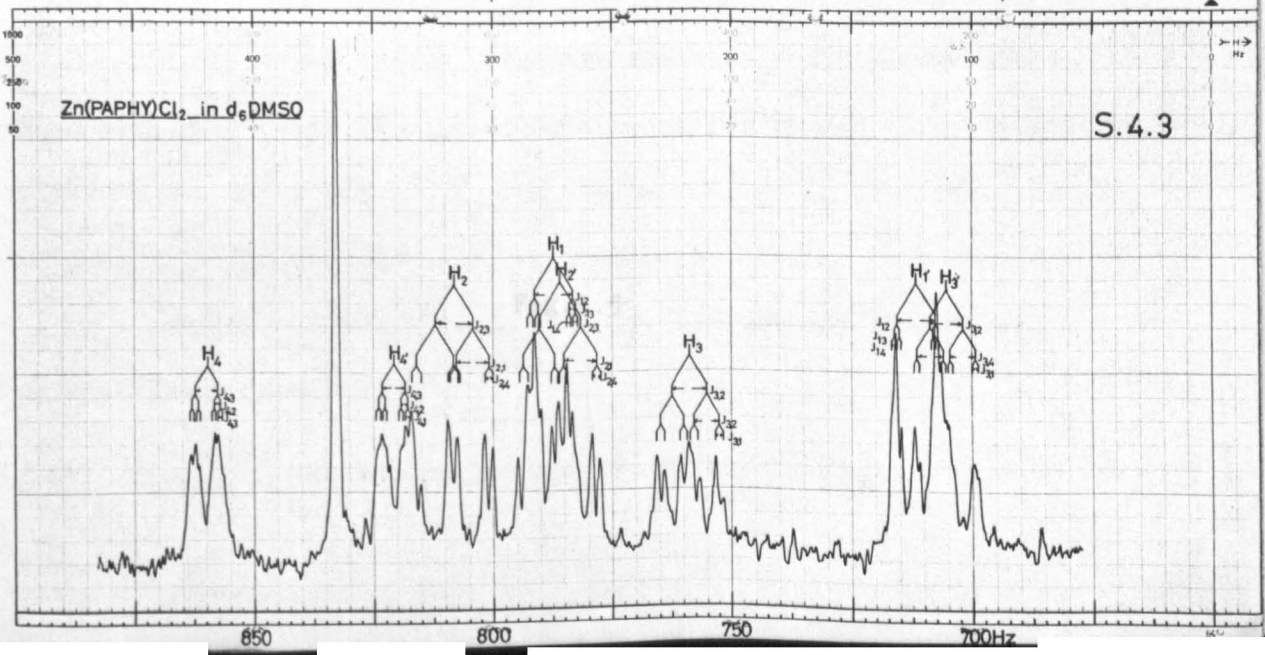
* The mono PAPHY-zinc complex discussed above was prepared as described in the Experimental Section. That prepared by the method of Bryson and Nuttall[25] gave an almost identical spectrum but of much poorer quality (S4.4.). This was probably because of the reduced solubility of this latter compound in DMSO. It may be that this complex can exist in two forms like the complex $Co(PAPHY)Cl_2$[24]

Table 4.2. Change in chemical shift ($\Delta^{\text{complex}}_{\text{free ligand}}$) of α-protons and α-methyl groups on complexing.

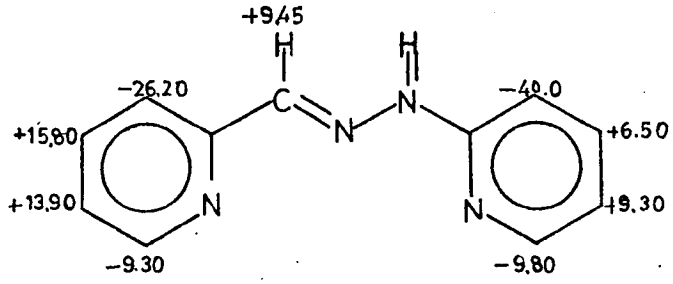
Compound	α-Methyl group	α-Proton
$Zn(PAPHY)Cl_2$	-	+ 1.48($H_{4'}$)
$Zn(4'\text{-Me-PAPHY})Cl_2$	+ 37	-
$Zn(PAPHY)Cl_2$	-	+ 1.13(H_4)
$Zn(4\text{-Me-PAPHY})Cl_2$	+ 38	-


Zn(PAPHY)$_2$(ClO$_4$)$_2$ in d$_6$DMSO
S.4.1
825
775
700Hz


Zn(PAPY)$_2$ in d$_6$DMSO (220MHz)
S.4.2
1780
1580
1380Hz


Zn(PAPHY)Cl$_2$ in d$_6$DMSO
S.4.3
850
800
750
700Hz

$Ag(PAPHY)(ClO_4)$



$Pb(PAPHY)(NO_3)_2$

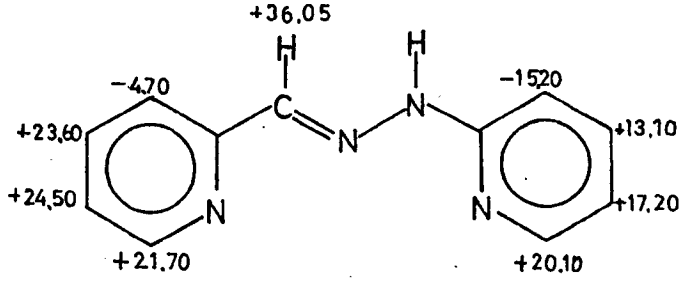


Fig.4.5

40 and 50Hz which agrees well with the deshielding effect (of the nitrogen atom anisotropy) of 43Hz at the α-proton as calculated by Spotswood and Tanzer[23].

Although the $\Delta^{complex}_{PAPHY}$ values for H_3 and $H_{3'}$ are approximately the same as those obtained for the bis-perchlorate complex the values for $H_{2(2')}$, $H_{1(1')}$ and the formyl proton are considerably less positive indicating an increase in negative charge in this region. A possible cause of this is an association between the imino proton and a chloride ion. Conductivity measurements would give an indication of such an association in solution.

Mono complexes of PAPHY with lead and silver have been investigated. The chemical shifts are given in Table 4.3, and Fig. 4.5 gives $\Delta^{complex}_{PAPHY}$ values.

The silver (I) complex $Ag(PAPHY)ClO_4$, which is presumably of distorted tetrahedral structure exhibits much smaller positive $\Delta^{complex}_{PAPHY}$ values and the protons to the nitrogen atoms move upfield by about 9.0Hz. This upfield shift and general increase in negative charge density in the rings relative to the zinc chloride complex (Fig.4.3) could be due to greater donation of d-electrons from the silver (compared with zinc) to the antibonding orbitals of the ligand pyridine rings. If the cause of the proton upfield shift was a more effective removal of the paramagnetic nitrogen atom anisotropy by complexing with silver rather than zinc then one would expect the value of $\nu_\alpha - \nu_\beta$ to be smaller in the former case. The values of $\nu_\alpha - \nu_\beta$ are, however, virtually the same in each case ($\nu_\alpha - \nu_\beta$ = 100.8Hz and 100.73Hz, $\nu_{\alpha'} - \nu_{\beta'}$ = 114.0Hz and 115.0Hz for silver and zinc respectively.)

The $\Delta^{complex}_{PAPHY}$ values for the complex $Pb(PAPHY)(NO_3)_2$ (Fig.4.5)

Table 4.3. Spectral Parameters for mono PAPHY complexes with lead and silver (measured at 100MHz).

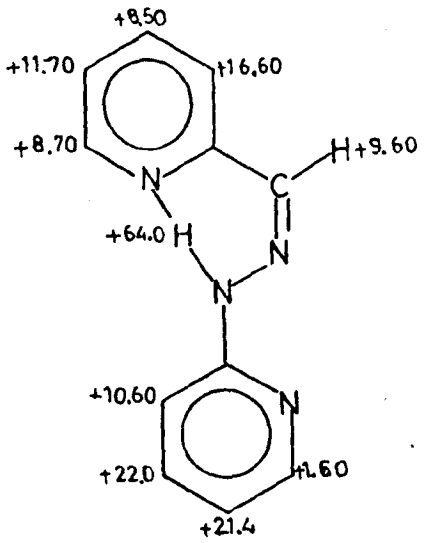
	$Pb(PAPHY)(NO_3)_2$	$Ag(PAPHY)(ClO_4)$
H_1	791.8	770.30
H_2	802.8	795.0
H_3	753.5	742.90
H_4	874.7	843.70
$H_{1'}$	715.2	690.4
$H_{2'}$	779.9	773.30
$H_{3'}$	698.2	690.30
$H_{4'}$	834.1	804.20
-CHO	844.5	818.20

are similar in many respects to those obtained for the complex $Zn(PAPHY)Cl_2$ (Fig.4.3). That values for H_1 and $H_{1'}$ are less negative in the lead complex may be attributed to an absence of the imino proton-chloride ion association proposed for the zinc complex. The most notable differences in the $\Delta^{complex}_{PAPHY}$ values are those for the α-protons which are large and positive in the lead case. This is considered to be a result of one of, or a combination of, two factors:

I. Absence of back donation of d-electrons from the lead atom, thus reducing the negative charge at the α-position relative to the zinc case.

II. Less efficient removal of paramagnetic nitrogen atom anisotropy of the lead atom. This proposal is supported by comparision of values of $\nu_\alpha - \nu_\beta$ and $\nu_{\alpha'} - \nu_{\beta'}$ which are 121.2Hz and 135.9Hz in the lead complex and 100.73Hz and 115.0Hz in the zinc complex.

$Zn(Z\text{-}PAPHY)_3(ClO_4)_2$



$Zn(Z\text{-}PAPHY)Cl_2$

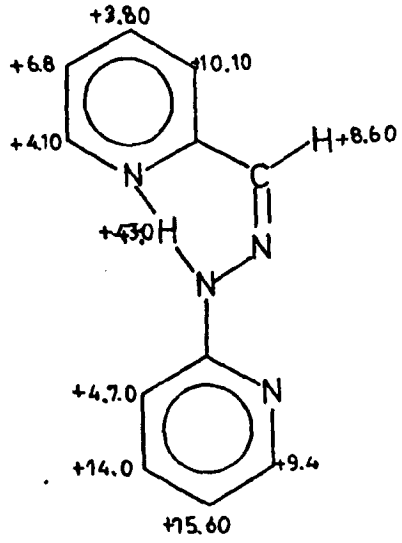


Fig.4.6

4.3. Zinc Complexes with Z-PAPHY

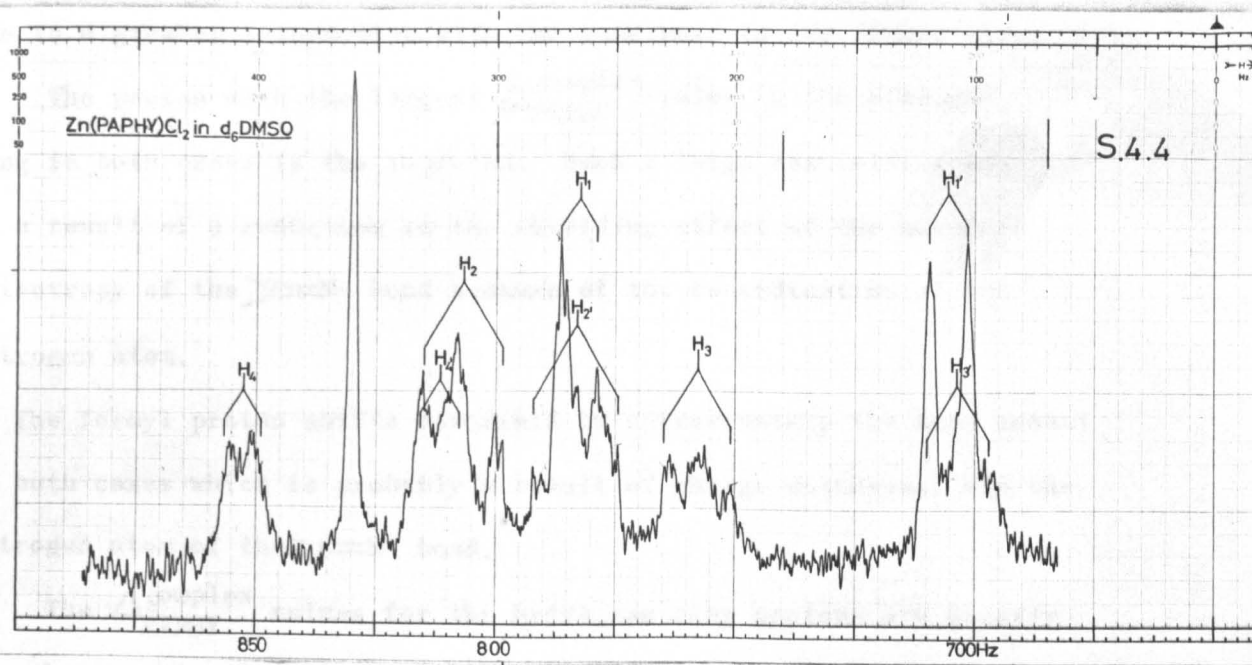
The spectra of the complexes $Zn(Z\text{-}PAPHY)_3(ClO_4)_2$ and $Zn(Z\text{-}PAPHY)Cl_2$ are shown in S.4.5. and S.4.6. respectively. The spectrum for the latter compound shows small peaks due to the presence of a small amount of $Zn(E\text{-}PAPHY)Cl_2$. At moderately elevated temperatures isomerisation of the Z-PAPHY complex to the E-PAPHY complex occurs fairly readily and this may have occurred during the preparation of the PMR sample.

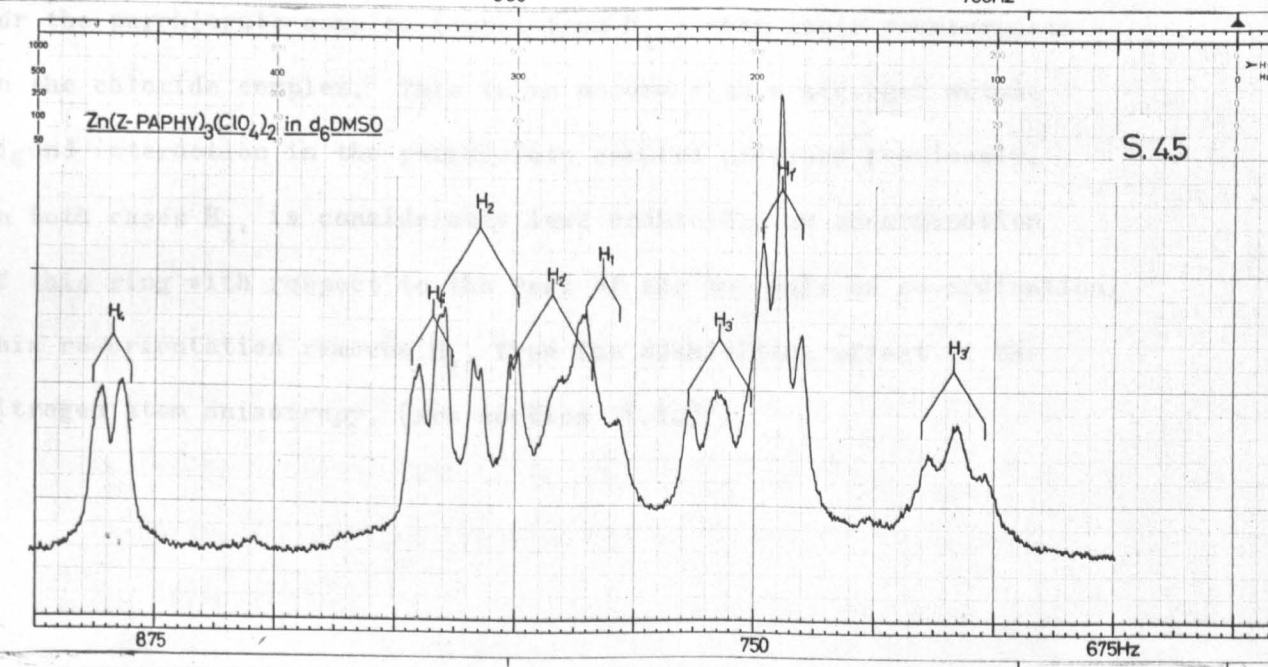
The values of $\Delta^{complex}_{PAPHY}$ are shown in Fig.4.4. They are contrary to what one would expect. PAPHY can now only act as a bidentate donor by means of the hydrazine ring nitrogen atom and the nitrogen atom of the C N bond and thus no appreciable change in shift would be expected for the aldehyde ring protons on complexing as this ring is not involved. However, there is a general downfield shift for all the aldehyde ring protons in both cases. The most likely explanation for this is that co-ordination enhances the acidity of the imino proton which will in turn strengthen the interaction with the nitrogen atom and decrease the charge density in the ring. These effects will be reflected in a downfield shift for all protons. The $\Delta^{complex}_{PAPHY}$ values for the imino protons are particularly large and positive in both cases under consideration which would be expected from increased acidity and hydrogen bonding interaction. The resonance position of the imino proton is much further downfield in the perchlorate complex than it is in the chloride indicating a greater hydrogen bonding interaction with the ring nitrogen atom. This would explain the larger $\Delta^{complex}_{PAPHY}$ values for the aldehyde rings protons in the perchlorate complex.

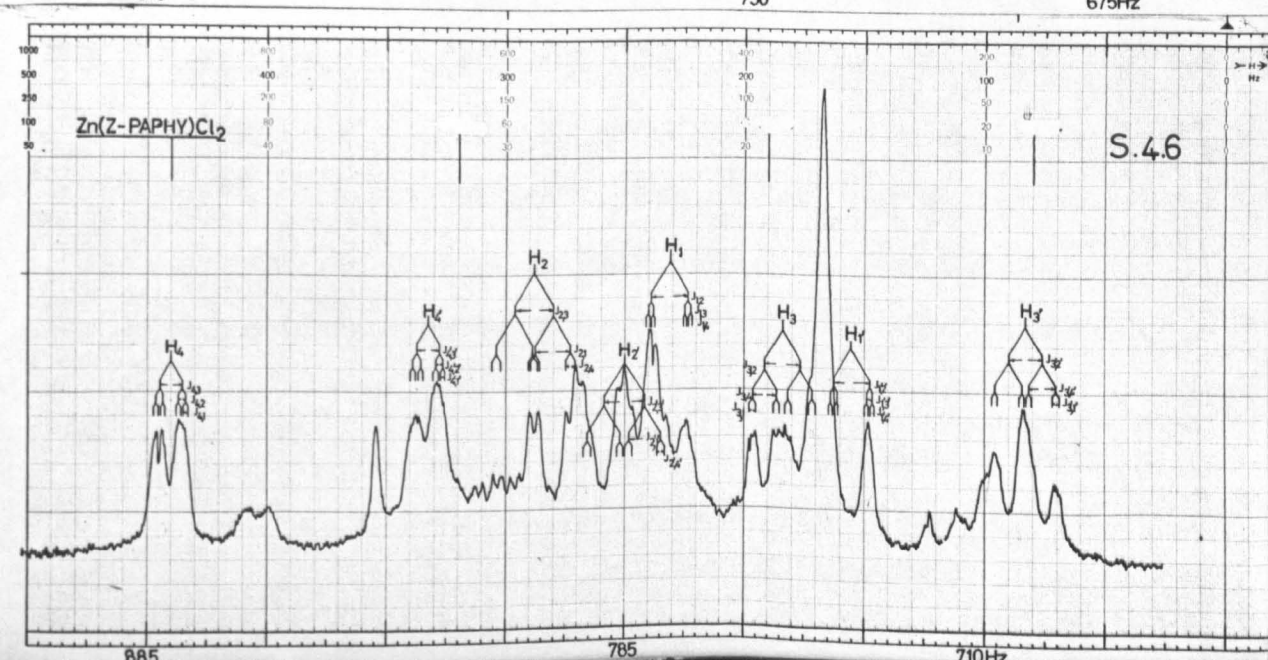
Consideration of the values of $\nu_\alpha - \nu_\beta$ for the protons of the aldehyde ring in each case shows that in the perchlorate complex $\nu_\alpha - \nu_\beta$ (= 110.3Hz) is smaller than in the chloride (= 123.9Hz). This

Table 4.4. Spectral Parameters (Hz) of Z-PAPHY-Zinc Complexes (measured at 100MHz).

	$Zn(Z\text{-}PAPHY)_3(ClO_4)_2$	$Zn(Z\text{-}PAPHY)Cl_2$
H_1	782.90	776.40
H_2	809.0	804.30
H_3	757.70	752.80
H_4	886.30	881.70
H_1'	744.80	738.90
H_2'	793.60	785.60
H_3'	703.40	702.60
H_4'	818.70	826.50
-CHO	745.20	744.20
imino	1456.0	1435.0


Zn(PAPHY)Cl2 in d6DMSO
S.4.4
H1
H1'
H2
H2'
H2''
H3
H3'
H4
850
800
700Hz


Zn(Z-PAPHY)3(ClO4)2 in d6DMSO
S.4.5
H1
H1'
H2
H2'
H3
H3'
H4
875
750
675Hz


Zn(Z-PAPHY)Cl2
S.4.6
H1
H1'
H2
H2'
H3
H3'
H4
785
710Hz

seems to imply a more effective removal of the anisotropy of the nitrogen due to a greater interaction with the lone pair in the former case.

The proton with the largest $\Delta^{complex}_{PAPHY}$ value in the aldehyde ring in both cases is the 1-proton. Such a large deshielding may be a result of a reduction in the shielding effect of the magnetic anisotropy of the $\geq C{=}N-$ bond because of the co-ordination of the nitrogen atom.

The formyl proton shifts downfield by approximately the same amount in both cases which is probably a result of charge withdrawal via the nitrogen atom of the $\geq C{=}N-$ bond.

The $\Delta^{complex}_{PAPHY}$ values for the hydrazine ring protons are greater for the perchlorate complex (apart from $H_{1'}$) than their counterparts in the chloride complex. This is in accord with a stronger metal-ligand interaction in the perchlorate complex proposed previously. In both cases $H_{1'}$ is considerably less deshielded on co-ordination of this ring with respect to the rest of the molecule on co-ordination. This re-orientation removes $H_{1'}$ from the deshielding effect of the nitrogen atom anisotropy. (see section 4.1.) .

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Experimental Section.

Preparations

E-pyridine-2-aldehyde-2'-pyridylhydrazone (E-1, 3-bis(2'-pyridyl)-1, 2-diaza propene, PAPHY)[2], (I).

2-chloro-pyridine (1 mole) was refluxed under nitrogen overnight with hydrazine hydrate (2 moles). The 2-pyridylhydrazine was extracted with ether and distilled under reduced nitrogen pressure to remove either and unchanged 2-chloro-pyridine PMR spectroscopy was used to confirm the identity of the product, 2-pyridylhydrazine.

Freshly distilled pyridine-2-aldehyde (1 mole) was refluxed with 2-pyridylhydrazine (1 mole) in ethanol for ten minutes. Cooling produced a quantitative yield of pale yellow crystals of pyridine-2-aldehyde-2'-pyridylhydrazone. They were recrystallised once from ethanol.

M.P. 178-179°C.

6-methyl-pyridine-2-aldehyde-2'-pyridylhydrazone (VI)

6-methyl-pyridine-2-aldehyde 1(mole) was condensed with 2-pyridylhydrazine (1 mole) as for (I) above.

M.P. 209-211°C

Pyridine-2-aldehyde-3'methyl-2'-pyridylhydrazone (II)

Pyridine-2-aldehyde-4'-methyl-2'-pyridylhydrazone (III)

Pyridine-2-aldehyde-5'-methyl-2'-pyridylhydrazone (IV)

Pyridine-2-aldehyde-6'-methyl-2'-pyridylhydrazone. (V)

The compounds (II) - (V) were prepared by condensing the appropriate methyl-2-pyridylhydrazine with pyridine-2-aldehyde as for (I).

Melting Points.

(II) Oily liquid.

(III) 185-184°C.

(IV) 157-159°C.

(V) 149-150°C.

Analyses.

Compound.	Found (%).			Calc. (%).		
	C.	H.	N.	C.	H.	N.
I	66.61	5.20	28.50	66.67	5.05	28.30
II	67.40	5.50	26.20	67.9	5.66	26.40
III	67.96	5.58	26.10	67.9	5.66	26.40
IV	68.10	5.71	26.30	67.90	5.66	26.40
V	68.0	5.58	26.60	67.90	5.66	26.40
VI	67.83	5.70	26.35	67.90	5.66	26.40

3-methyl-2-pyridyl hydrazine (via pyridone[1] and chloropicoline[3])

A solution of sodium nitrite (4 moles) in water (35 ml.) was slowly added to 2-amino-3-picoline (4 moles) dissolved in concentrated sulphuric acid (30 ml.) keeping a constant low temperature (-5°C). Stirring was continued for an hour at this temperature after which the solution was heated (90°C), made basic by potassium carbonate addition, filtered, and the filtrate evaporated leaving the pyridone as a yellow solid (yield 76%). This was extracted with benzene and recrystallised once.

M.P. 137-139°C.

To convert the pyridone (1 mole) to 3-methyl-2-chloropyridine it was heated at 180°C for four hours with phenylphosphonic dichloride (2 moles). The mixture was cooled, added to water and the solution neutralised with ammonia. The chloropicoline was extracted with cold chloroform. Distillation of the extract under reduced nitrogen pressure gave pure 2-chloro-3-picoline. (Yield 85.4%).

Refluxing of 2-chloro-3-picoline (1 mole) with hyrazine hydrate (2 moles) for eight hours under nitrogen gave the 3-methyl-2-pyridyl-hydrazine. (Yield 72%).

5-methyl-2-pyridylhydrazine.

The method of preparation was the same as that described above for 3-methyl-2-pyridylhydrazine except that the refluxing of the 2-chloro-5-picoline with hydrazine hydrate was continued for a longer period i.e. overnight.

6-methyl-2-pyridylhydrazine and 4-methyl-2-pyridylhydrazine.

Both were preparedby refluxing, under nitrogen, overnight with hydrazine hydrate as described previously.

Pyridine-2-aldehyde-3'-methyl-2'-pyridylhydrazone.

Difficulty was experienced with the preparation of this compound. Condensation of the aldehyde and hydrazine produced a dark red solution from which no crystals could be obtained. Evaporation left a dark red oil which was purified by chromatography on an alumina column (B.D.H. neutral alumina, Brockmann Grade 1)using benzene as the eluting agent. The first brown band eluted contained pyridine-2-aldehyde. Further elution with benzene removed a second (yellow) band. When no more material could be eluted with benzene ethanol was used giving an orange eluate.

Solvent was removed from the yellow benzene solution and the orange ethanol solution under vacuum leaving respectively a yellow and

an orange oil. The PMR spectra of their solutions in dimethyl sulphoxide were measured. That of the orange oil was very poorly defined and the sample was not further investigated. The yellow oil gave a reasonably good spectrum which indicated that it was mainly the required compound and that it also contained some impurities. No further purification could be achieved and no microanalysis was obtained.

Z-pyridine-2-aldehyde-2'-pyridyl hydrazone (VII).

E-PAPHY (5 gms.) was dissolved in benzene (1L) and the solution irradiated for 22 hours using a Hanovia Photochemical Reactor with a medium pressure lamp (emitting radiation mainly at 5461A° 4358A° and 3660A°). The conversion of the E-to the Z-isomer was followed both by PMR and uv spectroscopy. Samples were taken after various intervals of irradiation and the uv spectrum measured. It showed a gradual shift of the intense absorption peak at 335 mμ in E-PAPHY to 364 mμ in Z-PAPHY. In the PMR spectrum the conversion was followed by the intensity of the resonance from the proton α to the aldehyde ring nitrogen in the E-isomer and the appearance further downfield of another resonance from the corresponding proton in the Z-isomer. After 22 hours irradiation the former peak had completely disappeared indicating that conversion is virtually complete after this length of time.

The solution after irradiation was reduced to about 10 ml. on a rotary evaporator and adsorbed onto an alumina column (B.D.H. neutral alumina, Brockmann Grade 1) and eluted with benzene. As it was found that the Z-isomer reverted to the E-form quite readily on the column it was necessary to use as short a column as possible consistent with good separation. The eluate was reduced in volume on the rotary evaporator and evaporated to dryness under vacuum leaving Z-PAPHY as a pale yellow solid. M.P. 78-80°C

Preparation of Metal Complexes.

Bis-(E-1,3-bis(2'pyridyl)-1,2 diaza-z-propene) zinc(II) perchlorate. (III).

To a solution of E-PAPHY (2 mmoles) in 15ml. of ethanol was added zinc sulphate (1 mmole) dissolved in a minimum quantity of water. Addition of a saturated solution of sodium perchlorate caused precipitation of the required complex, which was filtered amd recrystallised once from ethanol.

Analysis.

Calculated for $Zn(E\text{-}PAPHY)_2(ClO_4)_2 2H_2O$: C,37.9; H,3.44; N,16.1.

Found: C,37.2; H,3.02; N,16.52.

Deprotonation of (VIII).

Addition of aqueous sodium hydroxide to an ethanolic solution of (VIII) gave the deprotonated form of the complex (IX), which immediately precipitated out. The deprotonation was accompanied by a change and intensification of the colour of the mixture from the pale yellow of the protonated complex to the intense orange of the deprotonated species. It was not possible to prepare mono deprotonated complexes by this method.

Analysis.

Calculated for $Zn(PAPY)_2.1.5H_2O$; C,54.2; H,4.37; N,22.0.

Found: C,53.8; H,4.0; N,21.70.

Dichloro-(E-1,3 bis(2'-pyridyl)-1,2 diaza-2-propene) zinc(II). (X).

To a solution of E-PAPHY (2 mmoles) in ethanol (15ml) was added aqueous zinc cholride (1 mmole in a minimum of water). There was immediate precipitation of (X) which was filtered, and recrystallised once from ethanol.

Analysis.

Calculated for $Zn(E\text{-}PAPHY)Cl_2$: C,39.4; H,2.93; N,16.73.

Found: C,39.73; H,3.04; N,16.77.

From infra-red studies this was found to be identical with the compound prepared by Bryon and Nuttall[4] under anhydrous condition.

(E-1,3 bis(2'-pyridyl)-1,2 diaza-2-propene) Lead(II) nitrate. (XI).

A solution of lead nitrate (1 mmole) in a minimum quantity of water was added to a solution of E-PAPHY (1 mmole) in ethanol (15ml). The resulting orange-yellow precipitate was filtered and recrystallised from ethanol.

Analysis.

Calculated for $Pb(E\text{-}PAPHY)(NO_3)_2$: C,24.95; H, 1.88; N, 15.12.

Found: C, 25.09; H, 1.84; N, 15.12.

(E-1,3-bis(2'-pyridyl)-1,2 diaza-2-propene) silver(I) perchlorate. (XII).

To E-PAPHY (1 mmole) in ethanol (15ml) was added silver perchlorate (1 mmole) in a minimum quantity of water. A yellow precipitate was formed which was light sensitive and readily decomposed on heating. No micro-analysis has so far been obtained to confirm the proposed formula of $Ag(PAPHY)ClO_4$.

Tris- (Z-1,3 bis(2'-pyridyl)-1,2 diaza-propene) zinc(II) perchlorate. (XIII).

To Z-PAPHY (4 mmoles) in ethanol (15ml) was added dried zinc perchlorate (1 mmole) in ethanol. The resulting yellow precipitate was filtered and washed with ethanol. Heating caused decomposition to the bis complex (VIII).

Analysis

Calculated for $Zn(Z\text{-PAPHY})_3(ClO_4)_2$: C,46.2; H,3.13; N,19.58.

Found: C, 46.3; H,3.88; N,18.31.

Dichloro -(Z-1,3 bis(2'-pyridyl)-1,2 diaza-2-propene) zinc(II).(XIV).

To Z-PAPHY (4 mmoles) in ethanol (15ml) was added anhydrous zinc chloride (1 mmole) suspended in ethanol. After stirring a yellow precipitate formed which was filtered and washed with ethanol. Heating caused decomposition to (X):

Analysis

Calculated for $Zn(Z\text{-PAPHY})Cl_2$: C, 39.50; H, 2.99; N, 16.75; Cl, 21.2.

Found: C, 39.56; H,3.17; N, 16.62; Cl, 20.28.

Methylation of $Zn(PAPHY)_2$ (IX).

To (IX) (1 mmole) in a minimum of hot ethanol was added dropwise dimethyl sulphate until a colour change of orange to yellow occurred. Addition of zinc chloride or zinc perchlorate caused precipitation on cooling of the chloride or perchlorate complex.

Analysis.

Calculated for $Zn(methylated\text{-}PAPHY)Cl_2$: C, 36.5; H, 4.05; N, 14.2.

Found. C, 37.0; H,3.31; N, 14.35.

Calculated for $Zn(methylated\text{-}PAPHY)(ClO_4)_2$: C, 30.2; H, 2.58; N, 11.75.

Found: C, 30.73; H, 3.34; N, 12.03.

PMR Spectra.

Much preliminary work was done on a Varian T.60 spectrometer including following the uv induced isomerisation of the E to Z-isomer of PAPHY. For quantitative work 100MHz spectra were run on a Varian HA-100 spectrometer at P.C.M.U. (Harwell) at ambient temperature ($35^{o}C$) unless stated otherwise. The chart paper was calibrated with frequency markers by means of a frequency counter on the spectrometer.

220MHz spectra were run on a Varian HR-220 spectrometer also at the P.C.M.U.

Chemical shifts and coupling constants are quoted in hertz with respect to T.M.S. as an internal reference unless specified otherwise.

Preparation of Samples

For the dilution studies samples were weighed directly into the PMR tubes and the solvent added using an 'Agla' micrometer syringe. Metal complexes were examined as saturated solutions. Samples were not degassed before measurement of their spectrum.

Far Infra-Red Spectra

Far infra-red spectra were run at the P.C.M.U. on a Beckman-RIIC Model FS 720 interferometer ($400-20cm^{-1}$) using a wax disc and a Perkin-Elmer 225 Spectrophotometer ($500-200cm^{-1}$) using a nujol mull between polythene plates.

Melting Points

A Gallenkamp heated block type melting point apparatus was used. Melting points are uncorrected.

Micro-analyses

These were performed variously by the National Physical Laboratory, and Drs. Weiler and Strauss, Oxford.

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Appendix I

Far Infra-Red Spectra

The far infra-red spectra of a number of mono PAPHY-zinc complexes have been measured. The observed bands are listed in Table A.1.1.

The compounds originally thought by Rose[2] to be of the form [Zn(PAPHY)X]X where X=halogen were found to have identical far infra-red spectra (Table AI.1a.) to those obtained by Bryson and Nuttall[1] for the complexes $Zn(PAPHY)X_2$ indicating that the original formulation is probably incorrect.

Methylation of $Zn(PAPHY)_2$ with dimethyl sulphate and consequent precipitation with the appropriate halogen acid gave a complex which analysed as Zn(methylated-PAPHY)X_2. The far infra-red bands are listed in Table AI.1b and the metal-halogen stretching bands (underlined) occur at almost the same frequencies as those observed by Postmus et al[3] for the terpyridyl complexes $Zn(terpy)X_2$. These terpyridyl complexes have been found X-ray spectroscopy[4] to possess trigonal bipyramidal structure.

The cobalt analogue of the Bryson and Nuttall compound was found by Gerloch[5] to be square pyramidal in structure. It seems likely therefore that whereas simple protonation of $Zn(PAPY)_2$ gives a five co-ordinate square pyramidal mono PAPHY complex methylation gives rise to a five co-ordinate trigonal bipyramidal complex.

Some complexes of Z-PAPHY with zinc have been studied by far infra-red spectroscopy and the bands listed in Table Al.1c. The metal-halogen bands are underlined.

Bryson and Nuttall[1,6] considered that distinction could probably

be made between 4, 5, and 6 co-ordinate stereochemistries by means of variations in the positions of the peaks assignable to the metal-halogen vibrations.

They found Zn-X stretching frequencies for tetrahedral pyridine complexes which were close to those observed for the complexes $Zn(Z\text{-}PAPHY)X_2$ in keeping with the presumed four co-ordinate tetrahedral structure of these complexes.

Table AI.1. Far Infra-red Spectra of some (PAPHY)-Zinc Complexes.

(Bands in cm^{-1})

(a)	$Zn(PAPHY)Cl_2$	$Zn(PAPHY)Br_2$	$Zn(PAPHY)I_2$
	72(m)	72(m)	72(m)
	104(m)	96(b)	142(m)
	145(b)	126(s)	178(s)
	256(w)	167(m)	203(m)
	279(s)	194(s)	230(w)
	310(s)	214(s)	255(m)
	330(m)	230(s)	290(s)
	414(v.s)	255(m)	318(s)
	514(s)	300(m)	415(s)
	519(s)	406(m)	510(m)
		415(m)	
		502(w)	
		510(m)	

(b)	$Zn(L)^*Cl_2$	$Zn(L)^*Br_2$	$Zn(L)^*I_2$
	72(m)	72(m)	72(m)
	124(w)	88(w)	120(m)
	140(w)	160(w)	187(s)
	158(w)	182(m)	264(m)
	234(w)	209(s)	290(m.b)
	256(m)	224(s)	360(w)
	292(s)	266(w)	415(s)
	355(w)	310(m,b)	510(s)
	393(m)	355(w,b)	522(w)

* L. = Methylated PAPHY

$Zn(L)^*Cl_2$	$Zn(L)^*Br_2$	$Zn(L)^*I_2$
413(s)	417(s)	-
435(m)	514(s)	
462(w)		
502(s)		
514(s)		

(c) $Zn(Z\text{-PAPHY})Cl_2$	$Zn(Z\text{-PAPHY})Br_2$	$Zn(Z\text{-PAPHY})I_2$
72(m)	72(m)	72(m)
143(w)	166(v.w)	144(w)
175(m)	176(w)	166(m)
236(v.w)	224(s)	208(s)
258(m)	262(s)	220(s)
290(s)	284(m)	254(s)
295(sh)	296(sh)	283(s)
320(m,b)	403(m)	403(m)
410(s)	413(s)	415(s)
510(m)	435(vw)	435(m)
Spectrum not extended beyond this frequency.	467(m)	467(s)
	512(m)	510(w)
	580(v.s)	532(w)
		580(v.s)

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