SOME STUDIES OF HYDROGEN BONDING AND
OF SOME UNSTABLE POSITIVE IONS BY NUCLEAR
MAGNETIC RESONANCE

by

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(i) **Hydrogen Bonding Studies**

The nature of hydrogen bonding in solutions of alcohols, ROH, in various solvents has been studied using nuclear resonance techniques. Data obtained from dilution-shift curves for the OH protons in alcohols have been combined with information derived from infra-red investigations of the OH stretching regions in these compounds. The information obtained has been interpreted in terms of three effects,

(i) The electronic effects of the group R.

(ii) The steric effects of the group R.

(iii) Effects due to other forms of molecular association.

On this basis, deductions have been made concerning the degree and type of association in these compounds. The relative hydrogen bonding strengths have been predicted in some instances. The importance of steric inhibition of hydrogen bonding by bulky substituent groups has also been demonstrated. Some dilution-shift studies of acrylic acid in various solvents have been carried out.

Studies of the effect of temperature on the OH proton resonances of alcohols have led, amongst other things, to a value for the average hydrogen bond energy in a methanol/carbon tetrachloride solution. The temperature-shift curves for a variety of ortho-substituted phenols have also been obtained and discussed in the light of existing infra-red spectral evidence concerning the nature of hydrogen bonding in these substances.

The relation between the association shifts and the integrated absorption intensities of alcohols has been discussed. A correlation
between these two quantities was found for alcohols of a similar type.

(ii) Studies of Unstable Positive Ions.

(a) Triphenyl Carbonium Ions.

The NMR spectra of a variety of substituted triphenyl carbonium ions in a trifluoroacetic acid trifluoroacetic anhydride solvent have been obtained at 40 Mc and 60 Mc. No unequivocal evidence as to the structures of these compounds has been obtained, i.e. no distinction between 'symmetrical propeller' and asymmetric forms was possible, due to the presence of exchange effects. The data have given information about the changes in electron density in the aromatic rings due to the various substituent groups. Partial assignments of the aromatic proton spectra have been given. The importance of hyperconjugative electron release by aliphatic substituents is indicated. Some preliminary investigations of the protonated form of 1,1-Di-p-anisylethylene have also been carried out.

(b) The $I^+$ I on.

The NMR spectra of solutions of iodine in oleum have been investigated to try and shed light on the possibility of the existence of the $I^+$ ion in such systems. The measured broadenings and shifts of the oleum proton resonances at various iodine concentrations have been interpreted in terms of the presence of this species, which should be paramagnetic. A value for the magnetic moment of this ion has been obtained.

Other evidence for the existence of the $I^+$ ion has been fully discussed.
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SOME STUDIES OF HYDROGEN BONDING, AND OF SOME UNSTABLE POSITIVE IONS, BY NUCLEAR MAGNETIC RESONANCE

ABSTRACT

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The NMR spectra of solutions of iodine in oleum have been investigated to try and shed light on the possibility of the existence of the I⁺ ion in such systems. The measured broadenings and shifts of the oleum proton resonances at various iodine concentrations have been interpreted in terms of the presence of this species, which should be paramagnetic. A value for the magnetic moment of this ion has been obtained.

Other evidence for the existence of the I⁺ ion has been fully discussed.
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CHAPTER 1

THEORY OF NUCLEAR MAGNETIC RESONANCE

BASIC THEORY

(a) Introduction

It was postulated by Pauli in 1924 (1) that the nuclei of atoms may possess spin angular momenta and magnetic moments, a conclusion supported by a variety of subsequent experimental evidence (2) (3).

The nuclear spin is characterized by a spin quantum number, \( \hat{I} \), which may assume the values, 0, \( \frac{1}{2} \), 1, 3/2, ... \( \frac{n}{2} \) ... and is related to \( \vec{p} \), the angular momentum vector by (4),

\[
\vec{p} = \left[ \hat{I}(\hat{I} + 1) \right]^{\frac{1}{2}} \cdot \hbar
\]

Classically, the magnetic moment \( \vec{\mu} \) is related to \( \vec{p} \) by,

\[
\vec{\mu} = \frac{q}{2Mc} \vec{p}
\]

for a spherical shell of mass \( M \) and charge \( q \). This classical equation is in conflict with experiment and is replaced by,

\[
\vec{\mu} = g \frac{q}{2Mc} \vec{p}
\]

where \( g \) is the nuclear g factor, which is generally of the order of unity and may have a negative sign. From Eqns. 1 and 3

\[
\vec{\mu} = g \frac{q\hbar}{2Mc} \left[ \hat{I}(\hat{I} + 1) \right]^{\frac{1}{2}}
\]

If \( q = e \), the electronic charge and \( M = M_p \), the proton mass, then

\[
\vec{\mu}_0 = \frac{e\hbar}{2M_pc}
\]
is the nuclear magneton, a unit in terms of which nuclear moments may be expressed. The maximum measurable component of $\bar{\mu}$ is given by,

$$\bar{\mu} = \left[ \frac{I}{(I + 1)} \right]^{\frac{1}{2}} \cdot \bar{\mu}$$

In an external field, $\bar{\mu}$ takes up $2I + 1$ orientations known as Zeeman levels, such that its components in the external field direction have the value $m\mu/l$, where $m$, the magnetic quantum number, has the values $I, I - 1, I - 2, \ldots, -I$.

(b) The theory of nuclear resonance.

The Zeeman levels have different energies, and nuclear resonance phenomena depend on the possibility of causing transitions between these levels with a corresponding emission or absorption of energy. Thus for nuclei with $I = 0$ (e.g. $^{16}O$, $^{32}S$, $^{40}Ca$ etc.) transitions are not possible, resonance being observed only if $I > 0$. If $I > \frac{1}{2}$, the nuclei have quadrupole moments and complications arise due to interactions between the nuclear quadrupole moment and the electric field gradients in the molecule or crystal. The discussion will be largely confined to nuclei having $I = \frac{1}{2}$ ($^{1}H$, $^{19}F$ etc.) giving two Zeeman levels and having no quadrupole moment.

Consider a nucleus of spin $I$ in a strong field $\bar{H}_o$. The components of $\bar{\mu}$ parallel to $\bar{H}_o$ are $m\mu/l$ and the energy levels are given by $-m\mu H_0/l$, the difference between successive levels being $\mu H_0/l$ or $\mu \zeta H_0$. Transitions are only allowed for which

$$\Delta m = \pm 1$$

A transition is thus caused by a quantum $h\nu_o$ such that,

$$h\nu_o = \frac{\mu H_0}{\zeta} = g \frac{\mu \zeta}{l} H_0$$

which is the fundamental equation of NMR (nuclear magnetic resonance).

A nuclear moment in a field $\bar{H}_o$ precesses about the direction of
$H_0$ (z-axis) with a frequency given by

$$\tilde{\omega}_0 = \gamma \tilde{H}_0$$

where $\omega_0$ is the Larmor frequency and $\gamma$ is the magnetogyric ratio.

$$\gamma = \frac{\mu}{I_n}$$

Suppose a circularly polarized R.F. (radio-frequency) field, $\tilde{H}_1$, is applied along the x-axis (Fig. 1a), resulting in a torque which alters the angle $\theta$. If $\tilde{H}_1$ rotates at a frequency $\nu_0$ in synchronism with the Larmor frequency $\omega_0$, the vector $\vec{\mu}$ will be tipped from one Zeeman level to the next with absorption of energy. However, no absorption occurs if $2\pi \nu_0 \neq \omega_0$. Thus resonance occurs if,

$$2\pi \nu_0 = \omega_0 = \gamma H_0 = \frac{\mu H_0}{I_n}$$

In practice, the circularly polarised field $H_1$ is replaced by a linearly polarised field $2H_1$, which is equivalent to two circularly polarised fields rotating in opposite directions with the same frequency $\omega$. Only the component rotating in the same sense as the Larmor precession is effective in producing transitions.

Since the orientations of nuclear moments are changed when resonance absorption occurs, there is a change of nuclear magnetic susceptibility when the system absorbs energy from the R.F. field, $\tilde{H}_1$. This magnetic susceptibility is a complex quantity having a real component $\chi'$ rotating in phase with $\tilde{H}_1$, and an imaginary component $\chi''$, $90^\circ$ out of phase with it, so that the susceptibility $\chi$ is given by,

$$\chi = \chi' - i \chi''$$

$\chi'$ is responsible for the 'u mode' or dispersion signal while $\chi''$ gives the 'v mode' or absorption signal.
PRECESSION OF $\vec{\mu}$ IN A FIELD $\vec{H}_0$
The first successful demonstrations of NMR were made in 1946 by Purcell, Torrey and Pound (5) and Bloch, Hansen and Packard (6) (7) using slightly different methods of detecting changes in $\chi$. Purcell's group used the R.F. bridge system shown in Fig. 2a. Power is supplied from an R.F. oscillator to the sample coil, via an R.F. bridge circuit, which is balanced to prevent direct detection of the R.F. signal by the receiver. (A small signal is in fact let through to act as a carrier for the NMR signal.) When the resonance condition is reached, however, the change in sample susceptibility produces a change in the apparent 'Q' of the sample coil, and leads to unbalance of the R.F. bridge, the signal produced being proportional to the absorption or dispersion signal or any mixture of the two depending on the adjustment of the R.F. bridge. The principal disadvantage of this arrangement is the instability of the R.F. bridge although devices for automatically correcting this drift have been described (8).

Bloch's apparatus depended on the nuclear induction principle, which requires a separate transmitter and receiver coil (Fig. 2a). The axes of the main field, the transmitter coil and the receiver coil are mutually perpendicular. R.F. power is fed to the sample via the transmitter coil and the change in magnetisation of the sample at resonance induces a signal in the receiver coil. To prevent direct pick-up between the two coils, their axes are adjusted to be mutually perpendicular. Since such direct geometric adjustment is difficult to obtain, the lines of flux in the region of the coils are steered by means of flux paddles which consist of metal plates or rings whose position relative to the coils may be adjusted. Thus, the balance achieved in Purcell's apparatus by means of an R.F. bridge is here obtained by geometric means, and allows a similar display of either the absorption or dispersion mode depending on the flux paddle adjustment.
FIG. 2a
SIMPLIFIED NMR SPECTROMETER CCTS.

R.F. OSC.

R.F. BRIDGE

RECEIVER

R.F. BRIDGE CCT.

N

S

NUCLEAR INDUCTION CCT.

RECEIVER

X

Y

Z

N

S

R.F. OSC.
This type of 'crossed coil' arrangement is more stable than R.F. bridge circuits. It is usual to adjust the system to allow an appreciable amount of 'v mode' leakage which acts as a carrier for the NMR signal and reduces the effect of any unwanted 'u mode' component.

NUCLEAR MAGNETIC RELAXATION AND LINE WIDTH

(a) Introduction

Consider a sample containing protons \( I = \frac{1}{2} \) in a constant field \( H_0 \), the energy difference between the Zeeman levels being \( 2 \mu H_0 \). The populations in these levels at equilibrium will obey a Boltzmann distribution law, the excess of nuclei in the lower state being given by

\[
\exp \left( \frac{2 \mu H_0}{kT_s} \right) \sim 1 + \frac{2 \mu H_0}{kT_s} = 4 \times 10^{-6} + 1
\]

\( (H_0 = 5000 \text{ gauss}, T_s = \text{spin temperature} = 255^\circ\text{K}) \) The excess in the lower level is small and it is upon this excess that NMR depends. An R.F. field \( H_1 \) causes a trend towards equalization of level populations and if no other effects were operating, a state of 'saturation' would soon result, with no energy absorption. The temperature of the spin system, \( T_s \), will be distinct from the lattice temperature, \( T_L \), in such a case, saturation corresponding to \( T_s = \infty \). There are two principal processes which allow \( T_s \) and \( T_L \) to come to equilibrium,

1) Spin-lattice interaction
2) Spin-Spin interaction

Both these processes shorten the lifetime of a nucleus in a given spin state and are responsible for the line widths of observed signals, a result following from the Uncertainty Principle,

\[
\Delta E \cdot \Delta t \sim \hbar
\]
A reduction in $\Delta t$, the lifetime, leads to an increase in $\Delta E$ and since

$$\Delta E = h \Delta v_o$$

. . . . . . . 15

a line broadening, $\Delta v_o$, results.

(b) Spin-Lattice interaction and $T_1$

Let the number of nuclei in the ground state be $N_+ \text{ / cm}^3$ and in the excited state $N_- \text{ / cm}^3$. For equilibrium at $T^0 \text{ K}$,

$$W_+ N_+ = W_- N_-$$

. . . . . . . . . 16

where $W_+$ and $W_-$ are the respective transition probabilities. But,

$$\frac{W_-}{W_+} = \frac{N_+}{N_-} = e \frac{2|\mu H_0|}{kT} \sim 1 + \frac{2|\mu H_0|}{kT}$$

. . . . . . . . . 17

and so,

$$W_- = W (1 + \frac{\mu H_0}{kT})$$

. . . . . . . . 18

$$W_+ = W (1 - \frac{\mu H_0}{kT})$$

($W = W_- + W_+$). Suppose now that $T_S \neq T_L$ and that $n = N_+ - N_-$, the excess of nuclei in the lower level, a quantity changing by two for each transition.

Then

$$\frac{dn}{dt} = 2 N_- W_+ - 2 N_+ W_-$$

. . . . . . . . 19

From 18

$$\frac{dn}{dt} = 2 W (n_o - n)$$

. . . . . . . . 20

($n_o = \frac{N \mu H_0}{kT}$ and $N = N_+ + N_-$. Integrating,

$$n_o - n = (n_a - n) e^{-2Wt}$$

. . . . . . . . 21

($n_a = \text{ initial value of } n$). Eqn. 21 shows that equilibrium is approached exponentially with a characteristic time

$$T_1 = \frac{1}{2W}$$

. . . . . . . . 22
known as the spin-lattice relaxation time. This is the time for all but \( e^{-1} \) of the excess number of nuclei in the excited state to reach the ground state.

Two principal origins of spin-lattice relaxation have been considered. Waller (9) considered interaction between the nucleus and modes of the lattice frequency lying at the nuclear resonance frequency \( \nu_0 \) and any two modes of the lattice frequency differing by \( \nu_0 \). Values of \( T_1 \) several powers of ten too large were obtained. An alternative mechanism (10) (11) was proposed involving interaction of the nuclear spins with the spins of paramagnetic ions present in small concentrations, as little as 1 in \( 10^6 \) being effective. Thus suggestion seems to be qualitatively in accord with experiment.*

(c) Spin-Spin Interaction and \( T_2 \)

Nuclei interact with each other as well as with the lattice, each seeing a small field \( \vec{H}_{loc} \), the resultant field due to the other nuclei in the sample. \( \vec{H}_{loc} \) consists of a static component lying along the z-axis and a rotating component in the xy plane. The field due to a dipole at a distance \( r \) is \( \sim \mu r^{-3} \) and so only near neighbours are important. If \( r = 1 \text{Å} \) and \( \mu = \mu_0 \),

\[
\vec{H}_{loc} \sim \mu_0 r^{-3} \sim 5 \text{ gauss}
\]

and a broadening of the resonance by this amount may occur, due to the static component of \( \vec{H}_{loc} \). The Larmor frequencies of the nuclei fall in a range \( \delta \omega_0 \) due to these field variations. From Eqns. 9 and 22,

\[
\delta \omega_0 \sim \gamma H_{loc} = \frac{\mu^2}{9 \pi \varepsilon_0 \hbar^3} \sim 10^4 \text{ sec}^{-1}
\]

Hence two spins, initially in phase and having precession frequencies differing by \( \delta \omega_0 \) are out of phase in a time \( \sim 1/\delta \omega_0 \) or \( 10^{-4} \) secs.

The rotating components of \( \vec{H}_{loc} \) may produce spin exchange between nuclei.

* This discussion applies to solids. For liquids dipole-dipole interactions largely determine \( T_1 \).
a process which does not result in relaxation, but leads to line broadening since it limits lifetimes of spin states. Spin-spin exchange occurs at time intervals \( \sim 1/\delta \omega \) giving the limitations of the lifetimes of spin states. From Eqn. 14,

\[
\hbar \delta \omega \sim \hbar \gamma H_{1oc} = g \mu_0 H_{1oc}
\]

Hence, a further broadening \( H_{1oc} \) occurs, but only between identical nuclei, since unlike nuclei have different Larmor frequencies. The lifetime of a spin state may thus be loosely defined in terms of a spin-spin relaxation time \( T_2 \),

\[
T_2 \sim 1/\delta \omega \sim 10^{-4} \text{ secs}
\]

The broadening of a line is thus proportional to \( 1/T_1 + 1/T_2 \). For solids, spin-lattice interaction is small and \( T_1 \) is large. \( H_{1oc} \) is large, however, and \( T_2 \) is small so that broadening is proportional to \( 1/T_2 \). For liquids \( T_1 \) is reduced by greater spin-lattice interaction and \( T_2 \) is increased due to an averaging out of local fields as a result of molecular tumbling. Thus, broadening is proportional to \( 1/T_1 \) and \( T_1 \sim T_2 \).

(d) **Bloch's phenomenological approach**

So far the magnetic properties of the nucleus have been used to arrive at macroscopic predictions, following the arguments of Bloembergen, Purcell and Pound (12). On the other hand, Bloch, in developing his theory of nuclear induction (13) argued mainly in macroscopic terms, an approach well suited to the study of transient effects, e.g. 'spin-echo' phenomena (14) and broadly consistent with the quantum treatment (15).

Consider a nucleus of magnetic moment \( \vec{\mu} \) in a field \( \vec{H} \), which experiences a torque \( \vec{\mu} \times \vec{H} \) which is equal to the rate of change of angular momentum. The angular momentum is \( \vec{\mu}/\gamma \) and so
This equation of motion represents the precession of the vector $\vec{\mu}$ about $\vec{H}$, with angular frequency $\gamma H$. For an assembly of weakly interacting spins, $\vec{M}$, the magnetisation vector is the sum of the $\vec{u}$'s in unit volume, so Eqn. 27 becomes,

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H}$$  \hspace{1cm} 28

This equation is valid, since although derived classically, the quantum mechanical expectation value of any quantity follows in its time dependence the classical equations of motion. Suppose the components of $\vec{H}_0$ are not constant but are,

$$H_x = H_1 \cos \omega t$$

$$H_y = H_1 \sin \omega t$$  \hspace{1cm} 29

$$H_z = H_0$$

representing the situation in an NMR experiment. Eqn. 28 is not complete in a nuclear spin system, since the r.h.s. does not represent all mechanisms by which $\vec{M}$ may change. $M_z$ represents the resultant magnetic moment per unit volume parallel to $\vec{H}_0$. In the absence of $\vec{H}_1$, and with $T_S = T_1$,

$$M_z = M_0 = \chi_0 H_0$$  \hspace{1cm} 30

If $T_S \neq T_1$, then in the absence of $\vec{H}_1$, $M_z$ approaches $M_0$ exponentially with a characteristic time $T_1$ (Eqn. 21). Thus, the z component is,

$$\frac{d\tilde{M}_z}{dt} = \frac{M_0 - M_z}{T_1}$$  \hspace{1cm} 31

This is a rewriting of Eqns. 20 and 21, remembering that $M_z$ is proportional to $N_+ - N_-$. Bloch termed $T_1$ the 'longitudinal' relaxation time, since it determines the approach to equilibrium of the component of $\vec{M}$ parallel to $\vec{H}_0$.

$M_x$ and $M_y$ represent the rotating components of the precessing vector.
In the absence of $H_1$, any phase coherence of the nuclei would be destroyed in a time of the order of $T_2$, bringing $M_x$ to zero. Bloch assumed for simplicity that the approach to zero is exponential, with characteristic time $T_2$, so that,

$$\frac{dM_x}{dt} = - \frac{M_x}{T_2} \text{ and } \frac{dM_y}{dt} = - \frac{M_y}{T_2} \quad \ldots \ldots \ldots \ldots \ldots 32$$

Bloch used the term 'transversal' relaxation time for $T_2$ since it governs the changes in the transverse components $M_x$ and $M_y$ of $M$. Thus, to complete the general case of the equations of motion, the $z$, $x$ and $y$ components of Eqns. 31 and 32 must be added to the components of Eqn. 28, giving the Bloch equations,

$$\frac{dM_x}{dt} = \left( M_y H_o + M_z H_1 \sin \omega t \right) - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \left( M_z H_1 \cos \omega t - M_x H_o \right) - \frac{M_y}{T_2} \quad \ldots \ldots \ldots \ldots \ldots 33$$

$$\frac{dM_z}{dt} = \left( -M_x H_1 \sin \omega t - M_y H_1 \cos \omega t \right) + \frac{M_o - M_z}{T_1}$$

The steady state solution of these equations (13) for the case where $H_1$ is small enough to avoid saturation, which can be shown to be when (13),

$$\gamma^2 H_1^2 T_1 T_2 \ll 1 \quad \ldots \ldots \ldots \ldots \ldots 34$$

gives the components $\chi'$ and $\chi''$ of the susceptibility.

$$\chi' = \frac{1}{2} \chi_o \omega_0 T_2 \left( \frac{(\omega - \omega_0) T_2}{1 + (\omega_0 - \omega)^2 T_2^2} \right)$$

$$\chi'' = \frac{1}{2} \chi_o \omega_0 T_2 \left( \frac{1}{1 + (\omega_0 - \omega)^2 T_2^2} \right) \quad \ldots \ldots \ldots \ldots \ldots 35$$

These susceptibilities are plotted in Fig. 3a as a function of the dimensionless product $(\omega_0 - \omega) T_2$. These curves show typical shapes of absorption and dispersion signals.

Unlike the quantum approach, Bloch's theory thus leads to a definite line shape, which is a Lorentz or damped oscillator curve. Experimental
FIG 3a

BLOCH SUSCEPTIBILITIES
(IN UNITS OF $\frac{1}{2} \chi_0 \omega_0 T_2$)

ABSORPTION

\[ \chi'' \]

\[ (\omega - \omega_0) T_2 \]

DISPERSION

\[ \chi' \]

\[ (\omega - \omega_0) T_2 \]
line shapes obtained with liquid samples approach this but in the case of solids the Bloch description is often less adequate.

CHEMICAL SHIFTS AND SPIN-SPIN SPLITTINGS

(a) Chemical Shifts

It was shown by Dickinson (16) and Proctor and Yu (17) (18) that the resonance frequency of \( \text{N}^{14} \) and \( \text{F}^{19} \) nuclei in liquid samples was dependent on the chemical form in which the element was present, the discrepancy being of the order of one part in \( 10^3 \) of \( 10^4 \). In the case of \( \text{Co}^{59} \), Proctor and Yu (18) found a 1.3% difference between aqueous solutions of \( \text{K}_3\text{Co(CN)}_6 \) and \( \text{K}_3\text{Co(C}_2\text{O}_4)_3 \). It was later found that proton containing samples behave similarly (19), although the frequency differences were smaller, a more sensitive spectrometer being required.

It has since been realised that these frequency differences are a general phenomenon associated with resonances from samples in the liquid state, the name 'chemical shift' being applied to them. This discovery arose as a result of the increasing resolution of spectrometers, and NMR spectroscopy can now be divided into two broad classes, low resolution spectroscopy which is concerned with the resonance of solids, which give signals whose width varies from 1 to 50 gauss, and high resolution spectroscopy of liquids where line widths are of the order of a small fraction of a gauss. This thesis is concerned entirely with liquid resonances, whose study necessitates the use of a high resolution spectrometer with a field and R.F. source stable to one part in \( 10^8 \).

Chemical shifts are normally expressed in cycles per second (c/s) or in terms of the dimensionless parameter, \( \delta \), (20)

\[
\delta = \frac{H - H_{\text{ref}}}{H_{\text{ref}}} \times 10^6
\]
FIG 4a

LOW RESOLUTION EF=OH SPECTRUM

FIG 5a

HIGH RESOLUTION EF=OH SPECTRUM
which gives the chemical shift in parts per million of the applied field \( H_0 \), a quantity which is independent of the field strength. \( H \) is the field value at which resonance of the sample occurs and \( H_{\text{ref}} \) is the position of a reference substance. In this thesis, shifts have been quoted in c/s, since the large majority of measurements have been made at 40 Mc. An example of the effect of chemical shifts is given in Fig. 4a which shows the spectrum of ethanol under low resolution, three peaks being produced, whose areas are in the ratio 1:2:3, which are assigned to the \( \text{OH}^- \), \( \text{-CH}_2^- \) and \( \text{-CH}_3 \) groups respectively. The separations of the peaks are shown in c/s.

(b) **The theory of chemical shifts**

Chemical shifts arise from differences in magnetic shielding of nuclei due to variations in configuration and density of the surrounding electrons clouds. This is primarily a diamagnetic shielding effect, although second order paramagnetic terms also contribute, and since diamagnetic shielding is proportional to the applied field, chemical shifts are proportional to \( H_0 \). The field seen by a nucleus is the sum of four terms,

\[
H_n = H_0 + H_a + H_b + H_c = H_0 (1 + \alpha + \beta + \sigma)
\]

where \( H_a, H_b \) and \( H_c \) are small compared with \( H_0 \), and may be considered as varying linearly with \( H_0 \) in the usual situation. \( H_a \) represents a classical correction due to bulk magnetism in the liquid medium and will be considered fully in the next chapter. \( H_b \) represents the specific medium effect which may arise from solvent anisotropy, either induced or permanent, e.g. in the case of aromatics whose magnetic susceptibilities are anisotropic (21). Solute induced solvent anisotropy has been put forward as an explanation
of deviations of $H_a$ from the classically predicted value (21). The third term, $H_c$, is the contribution due to shielding of the nucleus by its surrounding electron cloud. In the case of systems where rapid exchange is occurring, e.g. hydrogen bonded substances, the term $H_c$ may represent a time average of the shielding seen by the protons in different environments. Changes in the positions of hydrogen-bonding equilibria, e.g. through alterations of temperature and concentration, produce changes in $H_c$. Such shifts are the main concern of this thesis. From Eqn. 37 with the convention $H_n = H_0$ for an external reference signal, we may write,

\[ \sigma = 10^6 (\alpha + \beta + \sigma) \]

Attempts to calculate $\sigma$ theoretically have been made for particular and general cases. The latter has been treated by Ramsey (22) who showed that,

\[ \sigma = \frac{e}{2mc^2} \int \frac{d\gamma}{r} - 2 A u \sum_{n\lambda} \langle \lambda | \Sigma \Sigma m^0_{2k} | \lambda \rangle \langle \lambda | \Sigma \Sigma m^0_{3k} | \lambda \rangle \frac{E_n - E_0}{E_n - E_0} \]

where,

- $\rho$ = Probability density of electrons.
- $\lambda$ = Parameter giving orientation of molecule in the field $H_0$.
- $n$ = No. of excited states of molecule.
- $E_n - E_0$ = Energies of excited states.
- $m^0_{2k}$ = $e/2mc$ times the operator for $z$ component of angular momentum of $k^{th}$ electron.

The first term is of the same form as Lamb's diamagnetic shielding correction for spherically symmetric atoms (23). The second term, or second order paramagnetic term contains matrix elements of $m^0_{2k}$ and $m^0_{2k} | r^{-3}_{k}$ between ground and excited states of the molecule. This expression
unfortunately requires a very complete knowledge of ground and excited state wave functions and has only been applied in an unaltered form to the hydrogen molecule by Ramsey (22) using Nordsieck wave functions (24). It also has the disadvantage of expressing the shift as a small difference between two large quantities. An approximate form of the theory has been used by Richards et al. to explain the spectra of cobalt complexes (25), a good correlation being found between the NMR and electronic spectra and between Ramsey's expression and crystal field theory.

Of the more specialized approaches, Pople has developed a theory (26) to explain the shift to low field of aromatic proton resonances as compared with ethylenic protons. This involves a simple classical calculation of the field due to circulating π electrons, the field due to the circulating current being replaced by an equivalent magnetic moment perpendicular to the plane of the aromatic rings. The ratio of the ring current field to \( H_0 \) in parts per million is given by

\[
\lambda = 10^6 \frac{H_1}{H_0} = 10^6 \frac{e^2a^2}{2mc^2} \sum_1^\infty R_i^{-3}
\]

where,

\( a = \) Radius of aromatic ring.

\( R_1 = \) Distance to centre of \( i^{th} \) hexagon.

This theory has been used to explain successfully the shifts in poly-nuclear alternant hydrocarbons (27) but has not given a good account of shifts for non-alternant hydrocarbons, e.g. azulene (28).

Other theoretical treatments of chemical shifts have been given for particular cases (29) (30) (31) (32) (33) (34).

(c) Spin-Spin Coupling

A further type of fine structure was discovered by Proctor and Yu (35).
(18) for the Sb resonances of aqueous solutions of sodium hexafluoro-
antimonate NaSbF$_6$, a symmetrical set of seven equally spaced lines being observed. It was distinguished from the chemical shift by being independent of $\bar{H}_0$ (36). It was postulated (37) (38) that an interaction of the type,

$$\Delta E = J (\mathbf{i}_1 \cdot \mathbf{i}_2)$$

proportional to the dot product of the magnetic moment vectors was occurring, where $J$ is the 'spin-spin coupling' constant. A mechanism involving the interaction of the nuclear moments via the exchange-coupled spin magnetic moments of the molecular electrons was proposed by Ramsey and Purcell (39) and shown to agree quantitatively with experiments performed on HD (40) (41). The proton resonance was split into three, corresponding to the three possible orientations of the spin magnetic moment of the denteron ($I = 1$). The latter's resonance was likewise a doublet due to the two possible spin orientations of the proton ($I = \frac{1}{2}$), the coupling constant being 43 c/s. An example of spin-spin coupling is shown in Fig. 5a, which represents a high resolution spectrum of pure ethanol. The resonance of the CH$_3$-group is a triplet due to the three possible spin orientations of the -CH$_2$- group ($m = -1, 0, +1$), the intensity ratio, 1:2:1, corresponding to the statistical weights of each quantum state ($m = 0$ can occur in two ways). The -CH$_2$- resonance is complicated, being split into a quartet by the CH$_3$- group ($m = -3/2, -1/2, +1/2, +3/2$) and further split by the -OH group proton ($m = +1/2, -1/2$), the coupling constants being different in each case. The OH- resonance is split into a triplet by the -CH$_2$- group. In general, $n$ equivalent nuclei produce $n + 1$ lines, whose intensities are in the ratio of the binomial coefficients of $(a + b)^n$.

In aliphatic systems, detectable splittings are only transmitted
through two carbon atoms, so that no direct coupling between the CH$_3$- and
-OH groups of ethanol is observable. Meta-coupling constants of the order
of 2 c/s. have been observed in aromatic systems, i.e. through three
carbon atoms and appreciable coupling constants through four carbon atoms
in acetylenic systems (42). A theory of the long range couplings in aromatic
systems has been developed by McConnell (43).

Due to the types and intensities of splitting, the phenomenon of
spin-spin coupling is extremely important in providing useful criteria
for the assignment of NMR spectral lines, and also in giving information
about electron densities in molecules and exchange processes.

A second order splitting of the lines of the multiplets in ethanol
was observed under ultra high resolution by Arnold (44) and a theory was
given in terms of the perturbation parameter, $J_{12}/\delta_1 - \delta_2$, the second order
splitting approaching zero as,

$$\frac{J_{12}}{\delta_1 - \delta_2} \rightarrow 0 \quad \cdots \cdots \quad 42$$

($\delta_1$ and $\delta_2$ are the chemical shifts of two groups between which the coupling
constant is $J_{12}$).

(d) The interpretation of high resolution NMR spectra

For molecules where the chemical shifts, $\delta$, are large compared with
the spin-spin coupling constants, $J$, e.g. ethanol or hydrogen denteride,
interpretation of the NMR spectrum is simple as a rule. However, if

$$\frac{J_{12}}{\delta_1 - \delta_2} = \frac{J_{12}}{\Delta \delta} \sim 1 \quad \cdots \cdots \quad 43$$

i.e. the shifts and couplings are of a comparable order of magnitude, a
complicated spectrum results. The theory of such spectra has been worked
out for various groups of nuclei (45) (46) (47) (48) (49). Pople, Bernstein
and Schneider have developed a useful notation for such instances (50) (51)
A group of nuclei (of the same species) for which Eqn. 43 holds are given the symbols A, B, C, .... Another group of nuclei (possibly, though not necessarily of a different species) for which Eqn. 43 also holds but having an average resonance frequency differing considerably from that of the first group are given the symbols X, Y, Z .... Thus, methanol and methyl fluoride are $A_3X$ cases (i.e. Eqn. 42 holds, since $J/\Delta \ll 1$). Further examples are given below.

**TABLE 1a**

**EXAMPLES OF NUCLEAR GROUPINGS EMPLOYING THE A, B, C, ....; X, Y, Z, .... NOTATION**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Grouping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>$A_3X$</td>
</tr>
<tr>
<td>1-Fluoro-2-chloroethylene</td>
<td>AB</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>ABC</td>
</tr>
<tr>
<td>1-2-Dichlorobenzene</td>
<td>$A_2B_2$</td>
</tr>
<tr>
<td>Naphthalene; Biphenylène</td>
<td>$2 \times A_2B_2$</td>
</tr>
<tr>
<td>p-Fluoronitrobenzene</td>
<td>$A_2B_2X$</td>
</tr>
<tr>
<td>Methyl Mercaptan</td>
<td>$A_3B$</td>
</tr>
</tbody>
</table>

A modification of perturbation theory is used to calculate appropriate nuclear spin states which are mixtures of stationary state wave functions when Eqn. 43 holds. If Eqn. 42 holds, however, there is no mixing of spin states and a simple first order spectrum results such as in the case for ethanol or acetaldehyde. Mixing of states leads to the possibility of 'combination lines' which are otherwise forbidden. These are lines due to the simultaneous 'flip' of three nuclei and are usually of low intensity.
Relation of Shifts to Chemical Properties

Numerous correlations between chemical shift values and other chemical properties, e.g. electronegativity and Hammett sigma values have been sought. Thus, the difference in chemical shift between $\text{CH}_3-$ and $-\text{CH}_2-$ in $\text{CH}_3\text{CH}_2\text{X}$ has been compared with the electronegativity of X, a linear graph resulting in the case where X represents a halogen atom (53). Gutowsky et al. attempted to relate shift values for F in a variety of meta- and para-substituted fluorobenzenes to the appropriate sigma values and found a different correlation for the two types of substituent (54). They interpreted their results by ascribing a greater importance to resonance effects than to the other factors determining the overall electrical picture. The situation for protons is not so simple, no obvious difference existing for meta- and para-substituents (55).

NMR has important applications to chemical exchange processes, particularly those occurring in hydrogen-bonded systems. If a small quantity of hydrogen ion is added to a sample of pure ethanol, the rate of exchange of the $-\text{OH}$ proton is considerably increased and when this rate of exchange becomes greater than the spin-spin coupling constant (measured in c/s) with the adjacent $-\text{CH}_2-$ group, a collapse of multiplet structure is observed, the $-\text{OH}$ peak becoming a single line and the $-\text{CH}_2-$ group a quartet, due to coupling with the $\text{CH}_3-$ group only. If a mixture of acetic acid and water is examined, the rate of exchange of the water and $-\text{COOH}$ protons is greater than the shift in c/s between these resonances in the pure compounds. This results in a single line for the $-\text{OH}$ and water protons, the position of the line varying linearly with the mole fraction of acetic acid (50). The signal seen is thus that from protons in a time-averaged
environment, and a similar phenomenon is found in other systems where there is fast proton exchange. The ethanol-water system is remarkable in showing two lines over one concentration range (below 25 Wt.°/° H₂O) and a single coalesced line over the remaining range (57).

The relationship between line shape and exchange rates has been investigated theoretically by Gutowsky and Holm (58) for the simple case where nuclei are exchanging between two sites A and B and spend an equal time in each. When the mean lifetime before exchange (τₐ or τₐ) is long compared with the transition time between magnetic energy states, two sharp resonance separated by δₐb (in c/s) are seen. If τ₀ is small compared with the transition times a single resonance is seen at ½(τₐ + τₐ) c/s. A broad line is seen when the two times are of similar magnitude. It was shown that when the separate lines just coalesce,

\[ \tau_a = \sqrt{\frac{1}{2} \left( \tau T \delta_{ab} \right)^{-1}} \]

The rate constant for \( A \rightleftharpoons B \) is thus \( 1/\tau_a \).

Numerous studies of rate processes have been made, e.g. on keto-enol systems (59), on rates of rotation about \( \textit{CO-N} \) bonds in amides (60) (61), on restricted rotation in ethanes (62), on nitrogen inversion frequencies in cyclic imines (63), etc.
BIBLIOGRAPHY FOR CHAPTER I

CHAPTER II

APPARATUS AND EXPERIMENTAL PROCEDURES

DESCRIPTION AND OPERATION OF SPECTROMETER

(a) The Spectrometer

The large majority of measurements reported in this thesis were made with a Varian 4300 spectrometer operating at 40 Mc. and fitted with a Voltage Regulator and Super Stabilizer. A block diagram of the apparatus is shown in Fig. 1b. A brief description follows.

The 40 Mc., variable output, crystal controlled oscillator supplies the R.F. signal, $H_1$, to the transmitter coils in the probe of the spectrometer which is situated between the poles of a powerful electromagnet. The spectrometer probe is of the Bloch crossed-coil type, i.e. balancing is achieved by rotation of the glass insert on which the receiver coil is mounted, and by use of flux paddles, the adjustment always being such as to produce the 'V' mode or absorption signal. Three sizes of insert tube are available with internal diameters of 5, 8 and 13 mm., allowing samples of varying size to be examined. When using the 5 mm. insert, in order to increase the effective homogeneity of the field seen by the sample, the sample tube may be spun about its vertical axis by means of a compressed air turbine, housed on top of the probe body. This effectively averages out some of the field inhomogeneity in the horizontal plane of the receiver coil, and results in the sample 'seeing' a more homogeneous field than is
BLOCK DIAGRAM OF SPECTROMETER
in fact present in the probe. Spinning produces sidebands, i.e. satellite peaks on either side of the main signal. The separation of these satellites from the parent band is equal to the rate of rotation of the sample in c/s, and the intensity is proportional to the field homogeneity and falls off exponentially as the distance from the main peak increases. Hence, spinning sidebands can be reduced below noise level by improving the field homogeneity and increasing the spinning rate. The intensity of such sidebands is thus a useful qualitative indication of field homogeneity. These effects have been studied quantitatively by Williams and Gutowsky (1) and by Halbach (2).

The signal from the receiver coil is fed to a low noise preamplifier attached to the probe and thence to a 40 Mc. narrow band receiver which amplifies and detects the NMR signal. The signal may then be displayed on a persistent screen Dumont oscilloscope or on a Sanborn or Varian G10 recorder. In order to sweep through the resonance, two sweep units are available. The linear sweep unit produces a variable frequency sawtooth output which is fed to modulation coils on either side of the probe body and also to the time base of the oscilloscope. This sweep unit is used when display of the signal on the oscilloscope is desired. A slow sweep unit is also provided which produces a linear non-recurrent change in field by applying a voltage to the Super Stabilizer coils via the Super Stabilizer. This is used when it is desired to record the signal. In order to improve the stability of the power supply of the spectrometer it was fed through a Sola 2000 V.A. constant voltage transformer.

(b) Recorders

The Varian G10 recorder was used in most cases since it has a greater
sensitivity than the Sanborn recorder and uses wider chart paper, allowing a more adequate signal display. The Sanborn recorder has advantages for certain measurements, however. Thus, if spectra are being recorded merely for the determination of chemical shifts by interpolation, the narrower paper is sufficient and interpolation is facilitated by the 1 mm. grid ruled on this paper. Also, it is of advantage to record signals at a high chart speed in some cases, e.g. if a slow sweep rate causes saturation or in applying the 'wiggles beat' method (3) of measuring chemical shifts, which will be described later. The Sanborn recorder is convenient in this case since it has chart speeds ranging from 1 mm./sec to 20 mm./sec.

(c) The Magnet System

The magnet is a water cooled electromagnet with 12" pole caps and a gap of 1.75" capable of giving fields up to 11,000 gauss, although normally operated at a field of 9400 gauss when proton resonances are being examined. Initially, the magnet power was supplied by a V2100 Regulated Magnet Power Supply in conjunction with a V2101 B Voltage regulator, final stabilization being achieved with a V-K3506 Super Stabilizer. However, later the Voltage regulator was removed, the Super Stabilizer and Power Supply being suitably modified to enable satisfactory operation without use of the Voltage Regulator. At the same time a V-K3513 Field Trimmer was attached to the magnet which, by producing small movements of the pole faces relative to one another, enables small adjustments to be made to the magnetic field at the probe. In order to ensure long term stability of the magnetic field it was found necessary to thermostat the coils of the magnet. This was done by having a closed circuit water cooling system from a large tank. In the tank were immersed a copper cooling coil fed from the mains and a 1 kilowatt heater controlled by a Fenwal 17500-0 'Thermoswitch' and a
Sim-Vic 602 relay. By suitably adjusting the flow of cooling water it was found possible to keep the temperature constant to within 0.1°C. The temperature stability was further improved by covering the pole pieces and inside edges of the magnet coils with a double thickness of polythene sheeting and packing the dead space underneath with glass wool. This also served to protect the pole faces against corrosive chemicals. A polythene cover was also made for the magnet coils to keep dust away from the pole faces and probe and to improve temperature stability.

(d) Setting up the spectrometer and sample requirements

Before all measurements of proton resonances, the performance of the spectrometer was checked by means of a standard sample of acetaldehyde, prepared by distilling a reagent grade sample into a carefully flamed out sample tube cooled in dry ice/acetone mixture and sealed off in vacuo. Care was taken to ensure that the seal was axially symmetric since any asymmetry produces wobbling of the tube when spun and increases the intensity of spinning sidebands. An ethanol sample was also used for the same purpose but is less satisfactory since it appears to deteriorate in the course of time. In all cases where a high resolution spectrum was required the sample was sealed off in vacuo, or de-oxygenated by bubbling dry nitrogen through it. The paramagnetism of dissolved oxygen is sufficient to broaden the signals appreciably and spoil resolution. This procedure was unnecessary in a lot of cases however, where only a dilution shift was being measured.

The principal difficulty in adjusting the spectrometer arises in producing a suitably homogeneous field in the magnet gap. The homogeneity was checked by observing the quartet due to the -CHO group in acetaldehyde.
The signal was first set up on the oscilloscope screen with a sufficiently fast scanning rate to produce 'wiggles'. (See section on calibration of spectra.) The position of the probe and the field trimmer were then adjusted to maximize the 'wiggles', this being a good criterion of homogeneity since, as discussed later, 'wiggles' occur if the line is swept through in a time short compared with \((\gamma \delta H_0)^{-1}\), where \(\delta H_0\) is the inhomogeneity of the field.

To produce a homogeneous field, the magnet must be taken through a suitable 'cycling' procedure. When the magnet is first switched on a graph of field versus distance from the geometrical field centre of the magnet has the shape shown in Fig. 2b. To reduce the field gradient at the probe it was necessary to produce a field whose graph had the flat-topped shape shown by the dotted line. This was done by taking the field up to a position considerably above the resonance value, when it had a form with two maxima as shown, and then moving it back to the resonance position. A suitable cycling procedure was found by trial and error, and changed slowly with time. The signal shape observed on the recorder was used as an indication of field shape as shown in Fig. 2b. If the signal tailed to low field the magnet was overcycled (i.e. a double maximum existed) and if it tailed to high field it was undercycled (and dome shaped).

(e) **Calibration of Spectra**

This may be done in three ways, using,

1. The sideband superposition technique.
2. Interpolation methods.
3. The 'wiggles beat' method.

The sideband technique involves the modulation of the signal with an audie-
CRITERIA OF FIELD HOMOGENEITY

FIG 2b

OVERCYCLED

IDEAL CASE

UNDERCYCLED

H₀

DISTANCE

FIG 3b

'WIGGLES'

'WIGGLES BEATS'

\[ \frac{1}{f} \text{ SEC} \]
frequency sine wave signal (produced by a Hewlett-Packard 200 C-D wide range oscillator) fed to the modulation coils on the probe. This results in the production of audio-frequency sidebands on all the signals. To measure the distance between two peaks in c/s, the sideband from one peak is superimposed on the other peak by varying the frequency of the output from the audio oscillator, this process being observed directly on the oscilloscope screen. When the signal and the sideband are coincident, the distance between the two signals is equal to the frequency of the output of the oscillator. In most cases measurements to within \( \pm 0.5 \) c/s can be made this way.

In some cases superposition of sidebands is difficult due to signal complexity or proximity. If the signals are closer together than about 25 c/s, the audio-frequency modulation renders the signals incoherent and prevents accurate measurements. Interpolation techniques may be used in such cases, a signal being recorded with the audio-frequency modulation switched on at a suitably small intensity, the result being a series of sidebands at a known distance apart, which provide a convenient scale for the spectrum. This method relies on the linearity of the slow sweep unit and recorder motor and it was found to lead to some inaccuracy at low sweep rates. There is a formal similarity between the theories of audio-frequency and spinning sideband formation.

The 'wiggles beat' method (4) may be used to measure spin-spin coupling constants. Under 'rapid passage' conditions a single nuclear resonance signal is followed by a series of transient exponential decay signals known as 'wiggles' (5), shown in Fig. 3b. These 'wiggles' occur after sweeping through a resonance line in a time short compared with \( T_1 \), \( T_2 \) and \( (\gamma S H_0)^{-1} \),...
where $\delta H_0$ is the inhomogeneity of the steady field $H_0$ over the specimen. When the field $H_0$ corresponds to that at the resonance condition,

$$\bar{\omega}_0 = \frac{1}{\gamma} H_0$$

the nuclei are brought into phase and produce an induction signal in the receiver coil. As the field $H_0$ moves away from the value corresponding to the resonance condition, the resultant magnetic moment still precesses with an angular frequency $\gamma H_0$ giving a nuclear induction signal of this frequency, which is not equal to $\omega$. The nuclear induction signal thus beats with the applied R.F. signal, giving alternate maxima and minima. In the case of a multiplet whose peaks have a constant separation the 'wiggles' from each component interfere with one another and produce 'wiggles beats' (Fig. 3b), and it has been shown that if the separation between components is $J$ c/s, then the time between successive beat maxima is $1/J$ sec. (3) (6). The measurement is independent of sweep speed and linearity and multiplet separations can be measured to within $\pm 0.1$ c/s.

**HEATING AND COOLING SYSTEMS**

(a) **Introduction**

In studying many chemical systems by NMR it is convenient to be able to alter the temperature of the sample. In the case of the Varian spectrometer this presents a problem since the crossed-coil arrangement of the probe leaves little room for suitable heating or cooling devices. It is necessary to vary the sample temperature without heating the probe appreciably. A similar problem does not exist in spectrometers employing a bridge circuit since the sample, coil and protecting can may be made small enough to be completely immersed in a dewar of refrigerant, the only limitation being the size of the pole gap. Two devices to achieve tempera-
ture variation were constructed and similar apparatus has been used by other workers (7) (8).

(b) **Design I**

A diagram of the apparatus, which used the same stream of air for temperature alteration and spinning, is shown in Fig. 4b. Air (or nitrogen) at the desired temperature was passed down the central inlet tube of the inlet tube assembly and emerged through a series of holes drilled tangentially on the inner glass surface as shown. It then impinged on a teflon cap which formed a turbine attached to the top of the sample tube causing it to rotate and passed down inside a guide tube to the region of the bottom of the sample tube and heated or cooled the sample. The air then passed up the outside of the guide tube and into an outlet tube running concentrically outside the inlet tube, thus producing a heat-exchange effect. The inlet and outlet tubes were further surrounded by a silvered dewar jacket to prevent heat exchange with the surroundings. The inlet tube was provided with a sidearm which allowed a thermocouple to be pushed down to the region of the upper bearing of the sample tube. The lower bearing of the sample was supported by the bottom of a specially constructed tapered dewar which was attached to the inlet tube assembly with a B34 joint and held in place with rubber bands. This dewar was not silvered since this would have shielded the sample from the R.F. field, $H_1$. The end of the dewar was inserted in the Varian 13 mm. insert and the whole assembly supported by a specially constructed double-ended clamp attached to the inlet tube assembly and the preamplifier casing of the probe. The upper bearing for the sample tube was made by inserting a piece of tungsten rod in the previously mentioned teflon cap and allowing this to run freely in a hole bored in a circular piece of teflon sheet, attached to the inlet
FIG 4b

DESIGN I
HEATER & SPINNER

GAS INLET ASSEMBLY

TAPERED DEWAR

TUNGSTEN ROD

TEFLON CAP

SAMPLE TUBE

TEFLON BEARINGS
tube assembly. The lower bearing was formed by rounding the bottom end of the sample tube off smoothly and allowing it to rotate on a flat teflon surface. The tube was kept vertical by means of a tapered teflon ring situated \(\frac{1}{4}\) in. above the flat teflon surface.

The air stream was heated by passing it through a glass tube containing a spiral nichrome heater mounted on a former made of asbestos paper and asbestos cement, the whole assembly being lagged with asbestos string and mounted in a vertical position on a dexion trolley. This was constructed of aluminum to prevent interference with the magnet field. The heating coil was supplied from a Variac and the air supply (from the compressed air line) controlled with a brass needle valve and monitored with a tapered bore flowmeter. Tank nitrogen was used when it was desired to cool the sample, since the cooling system was blocked by frozen water vapour when compressed air was used. To cool the nitrogen, it was passed through a large copper coil immersed in a dewar containing a suitable refrigerant. The temperature was measured with a copper-constantan thermocouple and a Rubicon 2723 potentiometer.

(c) Design II

A second design employed two streams of air, one for heating and one for cooling and consisted of two main parts, a dewar jacketed probe insert and a gas heating and inlet system, shown in Fig. 5b and Fig. 6b respectively.

The insert was constructed from a piece of 9 mm. outside diameter pyrex tubing attached to a modified base from an old Varian 13 mm. insert, the receiver coil being wound from 6 turns of No. 28 (B. & S.) Formel magnet wire. Araldite and radio cement were used as adhesives. Two holes were drilled in the glass tube between the coil and the base to allow passage of the heating gas stream. A small teflon cup provided the bottom bearing for
FIG 5b

DESIGN II. HEATER & SPINNER

SAMPLE TUBE
DEWAR
TEFLON GASKETS
TURBINE
KNURLED SCREW
GAS INLET ASSEMBLY
ALUMINIUM SUPPORTS
ALUMINIUM HOUSING
SILICONE GASKETS
INSERT TUBE & COIL
TEFLON CUP
INSERT BASE
PROBE BODY
the sample tube. The insert was surrounded by a dewar jacket (unsilvered) of 12 mm. internal diameter, mounted on the same base and separated from the insert at the top by a teflon bush. A hole was made through the wall of the dewar at its top end to allow access of the heating gas supply. So that the insert could be rotated to balance the probe without disturbing the air lead-in, a hollow aluminum housing was made to surround the dewar jacket at the same level as the hole mentioned above. Two silicone rubber gaskets separated this housing from the dewar and due to their large deformability and high heat resistance, allowed the housing to be rotated with respect to the dewar whilst providing an air-tight joint. The housing was provided with an aluminum socket to which a glass ball-joint on the end of the gas inlet system could be attached. A teflon bush was used to seat the insert and jacket firmly in the probe.

The gas inlet system consisted of a long tapered dewar jacket which was protected and lagged by wrapping it with asbestos tape, a layer of cardboard and finally asbestos string. The heater was contained in the end of the jacket and consisted of a quartz finger containing a soldering iron element. An inlet was provided for a 250° C. 'Quickfit' thermometer so that the temperature of the gas supply could be monitored and a second inlet allowed a thermocouple to be pushed down as far as the inside of the aluminum housing. In practice it was found easier to measure the temperature directly by removing the sample and placing the thermocouple in the region of the receiver coil.

Spinning the sample was achieved by mounting a Varian turbine housing on an aluminum plate mounted on two aluminum posts attached to the top of the probe, and spinning in the normal way. The only requirement was slightly
longer sample tubes than usual. The ball and socket joint between the inlet system and housing was kept in place by a rubber and aluminum wedge placed between one of the posts on the probe and two glass ears on the inlet system. The gap between the top of the probe and the aluminum plate was filled with two aluminum plates to which specially shaped pieces of styrofoam were attached to provide further lagging for the top of the insert. Cooling was achieved by a similar means to that already mentioned, the cooled nitrogen supply being fed in through a dewar lead attached by a ball and socket joint to the inlet system. Temperature control through use of the heater in conjunction with the cooling system was possible. The whole assembly including the probe was supported on an aluminum bar to which was attached a circular brass bracket which supported the inlet system.

(d) **Comparison of the two designs**

The first design was found to be inconvenient since very carefully prepared sample tubes were required to fit the apparatus and the position of the various components had to be carefully adjusted to allow the sample tube to spin freely. A jig has, however, been constructed in this Department (9) which allows the sealing off of sample tubes with the tungsten rod sealed directly into the glass, allowing one to dispense with the teflon cap. Also, changing the sample required complete dismantling of the apparatus and the necessity of searching for the best spot in the field after every change. The filling factor for the coil was poor since a 13 mm. insert was used. The heat exchanger results in a slight advantage, consumption of refrigerant being lower.

In the second design the sample can be removed from the gap without
disturbing any adjustments. The insert was found to give as good resolution at all temperatures as the Varian 5 mm. insert, although the filling factor was slightly less. This apparatus was used for most of the temperature dependence measurements discussed in this thesis.

REFERENCING PROCEDURES

Since one cannot measure the absolute positions at which proton resonances occur with sufficient accuracy, it is normal to use a reference substance which gives a suitable signal from which the distances of the other resonance signals can be measured. This is a convenient system since one is normally only interested in relative values of nuclear shieldings. A reference compound must give a sharp signal, i.e. contain protons in chemically equivalent positions, which is unaffected by dilution and be miscible with the system being investigated if used as an internal marker. Thus, a resonance signal due to a hydrogen bonded hydrogen atom cannot be used as a reference signal since in most cases these signals are markedly concentration and temperature dependent. A compound is thus required which has no specific interactions with the medium in which it is placed, unless it is used in a separate capillary reference tube.

Reference materials may be used in two ways either as external references, when the reference substance is sealed off in a small capillary tube and included with the sample, or as internal references, when a small amount (~5 mole %) of the substance is added directly to the sample. Using an external reference has the advantage that specific solvent interactions are avoided, but suffers from the disadvantage that it is necessary to correct the measured shifts for bulk susceptibility effects, arising from the difference in volume susceptibility of the reference substance and sample. It can be shown (10) (11) that the field experienced by a nucleus,
\( H_n \), is given by,

\[
H_n = H_0 \left[ 1 + \frac{4}{3} \alpha - K \right]
\]

\[ \text{2} \]

where \( H_0 \) is the external field, \( \alpha \) a 'shape factor' depending on the shape of the sample and \( K \) is the volume susceptibility of the sample. In the case of a cylindrical sample, \( \alpha = 2 \pi \) and so,

\[
H_n = H_0 \left[ 1 - \frac{2}{3} K \right]
\]

\[ \text{3} \]

The chemical shift is defined as the difference in screening constants,

\[
\delta_n = \sigma - \sigma_{\text{ref}} = \frac{H - H_{\text{ref}}}{H_{\text{ref}}}
\]

\[ \text{4} \]

Substitution leads to the following equation,

\[
\delta_n = \delta_0 + \frac{2}{3} (K_{\text{ref}} - K)
\]

\[ \text{5} \]

Expressed in units of c/s, this may be rewritten as (12),

\[
\delta_n = \delta_0 + 83.8 (K_{\text{ref}} - K) \times 10^6
\]

\[ \text{6} \]

Bothner-By and Glick (13) tested the applicability of this equation for a variety of mixtures of aliphatic compounds and came to the conclusion that the quantitative agreement of Eqn. 6 with experiment was poor. They proposed an empirically corrected equation,

\[
\delta_n = \delta_0 + 104 (K_{\text{ref}} - K) \times 10^6
\]

\[ \text{7} \]

which has been used in this thesis and by other workers (14) for calculating susceptibility corrections, and suggested that the discrepancy was caused by solute-induced solvent anisotropy as mentioned in the previous chapter. It was also shown by these workers that an external reference capillary is an absolute standard, the position of its signal not depending on the volume susceptibility of the surrounding medium. No change in signal position was observed when the capillary was surrounded by a diamagnetic solid (BiI3 or a paramagnetic sample (\( \psi_2 \))), In the case of an internal
reference compound, both sample and reference are in the same medium and so the susceptibility difference in Eqn. 7 is zero, and no correction has to be applied.

The validity of Eqn. 7 for reducing shifts measured with respect to an external marker to shifts measured from an internal marker and vice-versa was examined in the following way. The shift between an internal and external cyclohexane marker was measured in a variety of solvents and compared with the shifts obtained from Eqn's. 7 and 6.* The internal marker was 3% by volume in each solvent. The results are collected in Table 1b which lists the measured corrections, \( C_M \), and the empirically corrected theoretical correction, \( C_T' \), and the classical correction \( C_T \), as well as \( C_T' - C_M \) and \( C_T - C_M \). The convention is employed here and elsewhere in this thesis that shifts to higher values of the applied field have a positive sign.

It can be seen that using Eqn. 7 a positive correction of the order of +3 c/s is obtained, a more divergent series of corrections being obtained using Eqn. 6. It thus seems that the use of Eqn. 7 does not give an accurate correction when a capillary marker is used, possibly due to the necessity of applying a shape factor correction. Eqn. 7 is strictly applicable (15) to the case where the reference compound is contained in an accurately coaxial cylindrical annulus around the sample tube, and it has been recommended that proton resonance spectra should be referred to an external marker in this way (16). The divergence in the values of the quantity \( C_T' - C_M \) may in part be due to uncertain susceptibility values

* A list of susceptibilities used in this thesis is given in the next section which describes susceptibility measurements.
TABLE 1b

LIST OF EXPERIMENTAL AND THEORETICAL SOLVENT SUSCEPTIBILITY CORRECTIONS (c/s)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CM</th>
<th>CT</th>
<th>CT' - CM</th>
<th>CT</th>
<th>CT' - CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>-13.0</td>
<td>-10.9</td>
<td>+2.1</td>
<td>-8.8</td>
<td>+4.2</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>-11.5</td>
<td>-6.5</td>
<td>+5.0</td>
<td>-5.2</td>
<td>+6.3</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>+4.2</td>
<td>+5.6</td>
<td>+1.4</td>
<td>+4.5</td>
<td>+0.3</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>+20.9</td>
<td>+25.0</td>
<td>+4.1</td>
<td>+20.2</td>
<td>-0.7</td>
</tr>
<tr>
<td>1,2 Dichloroethane</td>
<td>-14.2</td>
<td>-13.2</td>
<td>+1.0</td>
<td>-10.6</td>
<td>+3.6</td>
</tr>
<tr>
<td>Dioxane</td>
<td>0</td>
<td>+4.3</td>
<td>+4.3</td>
<td>+3.5</td>
<td>+3.5</td>
</tr>
<tr>
<td>Methanol</td>
<td>+6.6</td>
<td>+11.7</td>
<td>+5.1</td>
<td>+9.4</td>
<td>+2.8</td>
</tr>
</tbody>
</table>

which often differ appreciably from author to author.

Both internal and external references have been used in the work of this thesis. In some cases it has been necessary to convert measurements made with an external reference on a substance in varying dilutions in the same solvent to an internal reference. This has been done by correcting the shifts for a medium of the same susceptibility as the solvent, in most cases carbon tetrachloride, using Eqn. 7 (14) and then using the experimentally determined corrections in Table 1b to shift the origin of the curve by an appropriate amount. The susceptibilities of the solutions were determined by assuming the susceptibilities to be additive in the volume fractions, i.e. using an expression,

\[
K_{\text{solution}} = \frac{\sum K_i v_i}{\sum v_i} \quad \ldots \quad 8
\]

where the v's are the volume fractions for the components, i, of the system.

The sign of the correction may be determined as follows. If |\(K_{\text{solvent}}\)|
then the corrections are negative, i.e. the corrected signal lies at a lower field than the observed signal. On the other hand, if \(|K_{\text{solute}}| < |K_{\text{solvent}}|\), the corrections are positive and the observed signal is moved to higher field. These rules follow from Eqn. 3

\[ H_n = H_0 \left[ 1 - \frac{2 \pi K}{3} \right] \]

since, for instance, if \(|K_{\text{solvent}}| > |K_{\text{solute}}|\), the signals are being referred to a medium of greater diamagnetic susceptibility and the positive quantity \(-\frac{2 \pi}{3} KH_0\) (diamagnetic susceptibilities being negative) becomes larger. To keep \(H_n\) constant, \(H_0\) must therefore decrease, and the signal moves to lower field on correction. A similar argument holds if \(|K_{\text{solvent}}| < |K_{\text{solute}}|\).

The most commonly used external reference compounds are cyclohexane, benzene, water and tetramethyl silane. The latter signal has the great advantage of appearing at a higher value of the applied field than the majority of other proton resonances, and it therefore seldom overlaps anything that is to be measured. It has the disadvantage of being rather volatile, however (B.P. 26.5°C). Cyclohexane is a useful standard but frequently overlaps other aliphatic proton resonances. A table of useful external reference standards is given below, with their separations from benzene and their relative temperature coefficients with respect to benzene (16).

Another compound, not yet widely tested is hexamethyl disiloxane, which has 18 equivalent protons, has a resonance which occurs at high field values (7 c/s lower than tetramethyl silane) and a higher B.P. than this compound.

Of the compounds mentioned, tetramethyl silane, cyclohexane and
benzene are perhaps the most generally useful internal standards.

TABLE 2b

NMR EXTERNAL REFERENCE SIGNALS AT 40 Mc

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ in c/s at 30° C. (Distance from C₆H₆)</th>
<th>dδ/dT in c/s/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde (-CHO)</td>
<td>-107.0</td>
<td>0.01</td>
</tr>
<tr>
<td>Chloroform</td>
<td>-34.2</td>
<td>-0.079</td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>Toluene (ring H)</td>
<td>+3.1</td>
<td>+0.010</td>
</tr>
<tr>
<td>Water</td>
<td>+68.6</td>
<td>+0.384</td>
</tr>
<tr>
<td>1-4 dioxane</td>
<td>+125.7</td>
<td>+0.039</td>
</tr>
<tr>
<td>Dimethyl Sulphoxide</td>
<td>+161.9</td>
<td>+0.040</td>
</tr>
<tr>
<td>Toluene (-CH₃)</td>
<td>+199.4</td>
<td>0.01</td>
</tr>
<tr>
<td>Acetone</td>
<td>+202.4</td>
<td>+0.042</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>+212.1</td>
<td>+0.029</td>
</tr>
<tr>
<td>Tetramethyl Silane</td>
<td>+278.2</td>
<td>+0.055</td>
</tr>
</tbody>
</table>

SUSCEPTIBILITY MEASUREMENTS

(a) Introduction

Since some of the susceptibilities of the compounds investigated were not available in the literature, they were measured using a conventional Gouy balance.* The magnet was a 4" Varian electromagnet and power supply and the balance an adapted Spoerhase balance weighing to 10⁻⁵ gm.

* This balance was constructed in the Department by Dr. H.C. Clark and Mr. R. J. O'Brien.
The force acting on the sample suspended in the magnet gap is given by,
\[ f = \frac{1}{2} (K - K_0) H^2 A = C (K - K_0) \] .......................... 9
where \( C \) is a constant for a given measurement and,
\[ f = \text{force on the sample (in gms).} \]
\( K = \text{Volume susceptibility of sample.} \)
\( K_0 = \text{" " \" the atmosphere.} \)
\( H = \text{Magnetic field strength.} \)
\( A = \text{Cross sectional area of sample.} \)

The balance must first be calibrated using a substance of known susceptibility, in this case benzene whose mass susceptibility, \( \chi \), at 25\(^\circ\) C. is \(-0.702 \times 10^{-6}\) c.g.s. units (17). Since,
\[ \chi = \frac{K}{\rho} \] .......................... 10
where \( \rho \) is the density of benzene (0.879), \( K = -0.617 \times 10^{-6}\) c.g.s. for benzene. Also, \( K \) for the atmosphere is \( 0.029 \times 10^{-6}\) c.g.s. (17). From Eqn. 9,
\[ f (\text{benzene}) = C (K_{\text{benzene}} - K_0) \] .......................... 11
\[ f (\text{sample}) = C (K_{\text{sample}} - K_0) \]

Thus,
\[ K_{\text{sample}} = \frac{f (\text{sample})}{k (\text{benzene})} (K_{\text{benzene}} - K_0) + K_0 \] .......................... 12
Substituting the above figures and omitting the factor \( 10^{-6} \) throughout gives,
\[ K_{\text{sample}} = -0.646 \frac{f (\text{sample})}{f (\text{benzene})} + 0.029 \] .......................... 13

(b) Results
In the results below, \( A \) refers to the weight of sample (or benzene standard) and tube without the field, and \( B \) to the weight of tube and
sample in the presence of the field. Since all the samples are
diamagnetic, A > B and A - B = f.

Series I

<table>
<thead>
<tr>
<th>Calibration</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A = 9.88856 gm.</td>
<td></td>
</tr>
<tr>
<td>B = 9.87341 gm.</td>
<td></td>
</tr>
<tr>
<td>f = 0.01515 gm.</td>
<td></td>
</tr>
</tbody>
</table>

Measurements

(a) Propyn-1-61  H-C ≡ C-CH₂OH

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A = 10.12933 gm.</td>
<td></td>
</tr>
<tr>
<td>B = 10.11385 gm.</td>
<td></td>
</tr>
<tr>
<td>f = 0.01543 gm.</td>
<td></td>
</tr>
</tbody>
</table>

(b) 2-Butyn-1-61  CH₃-C ≡ C-CH₂OH

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A = 10.55271 gm.</td>
<td></td>
</tr>
<tr>
<td>B = 10.53626 gm.</td>
<td></td>
</tr>
<tr>
<td>f = 0.01645 gm.</td>
<td></td>
</tr>
</tbody>
</table>

(c) Benzhydrol  (C₆H₅)₂ CHOH

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A = 10.71806 gm.</td>
<td></td>
</tr>
<tr>
<td>B = 10.70181 gm.</td>
<td></td>
</tr>
<tr>
<td>f = 0.01625 gm.</td>
<td></td>
</tr>
</tbody>
</table>

(d) 2-Chloroethanol  CH₂Cl CH₂OH

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A = 10.96900 gm.</td>
<td></td>
</tr>
<tr>
<td>B = 10.95264 gm.</td>
<td></td>
</tr>
<tr>
<td>f = 0.01636 gm.</td>
<td></td>
</tr>
</tbody>
</table>
The benzhydrol, M.P. 69° C., was melted into the sample tube.

Series II

Calibration Benzene
A = 8.66063 gm.
B = 8.64513 gm.
f = 0.01481 gm.

Measurement 2-2'-Dichloroethanol CHCl₂ CH₂OH
A = 9.65779 gm.
B = 9.64100 gm.
f = 0.01679 gm.

A separate calibration was made for each compound since insufficient 2-2' dichloroethanol was available to fill the sample tube to the normal level.

Series III

Calibration Benzene
A = 9.85762 gm.
B = 9.84225 gm.
f = 0.01531 gm.

Measurement Acetonitrile CH₃CN
A = 9.54324 gm.
B = 9.52882 gm.
f = 0.01442 gm.

Using these results and the relation derived (Eqn. 13), the values shown in Table 3b were obtained.
TABLE 3b
MEASURED VOLUME SUSCEPTIBILITIES

<table>
<thead>
<tr>
<th>Substance</th>
<th>$K \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propyn-1-öl</td>
<td>-0.631</td>
</tr>
<tr>
<td>2-Butyn-1-öl</td>
<td>-0.671</td>
</tr>
<tr>
<td>Benzhydrol</td>
<td>-0.664</td>
</tr>
<tr>
<td>2-Chloroethanol</td>
<td>-0.669</td>
</tr>
<tr>
<td>2-2'-Dichloroethanol</td>
<td>-0.671</td>
</tr>
<tr>
<td>Acrylic Acid</td>
<td>-0.562</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>-0.576</td>
</tr>
</tbody>
</table>

Since none of the compound was still available, the susceptibility of methyl ethyl t-butyl carbinol was calculated using Pascal's constants (17). The compound has the formula C₈H₁₈O. Hence,

$$\chi_M = -(8 \times 6.3 + 18 \times 2.93 + 4.61) = -105.35$$

Since $M.W = 130$ and $c = 0.842$,

$$\chi = -\frac{105.35}{130} = -0.810$$

and

$$K = \chi c = -0.682$$

A further list of susceptibilities used in this thesis is given in Table 4b, the source of information also being quoted.
TABLE 4b

LIST OF SUSCEPTIBILITIES

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\chi \times 10^6$</th>
<th>$\varphi$</th>
<th>$K \times 10^6$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenyl carbinol</td>
<td>-0.675</td>
<td>1.188</td>
<td>-0.802</td>
<td>Int. Crit. Tables</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>-0.427</td>
<td>1.590</td>
<td>-0.692</td>
<td>Rubber Handbook</td>
</tr>
<tr>
<td>Chloroform</td>
<td>-0.488</td>
<td>1.498</td>
<td>-0.735</td>
<td>&quot;</td>
</tr>
<tr>
<td>Acetone</td>
<td>-0.581</td>
<td>0.785</td>
<td>-0.464</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-0.810</td>
<td>0.779</td>
<td>-0.630</td>
<td>&quot;</td>
</tr>
<tr>
<td>Water</td>
<td>-0.720</td>
<td>1.000</td>
<td>-0.720</td>
<td>Selwood (17)</td>
</tr>
<tr>
<td>Benzene</td>
<td>-0.702</td>
<td>0.879</td>
<td>0.617</td>
<td>&quot;</td>
</tr>
<tr>
<td>1,4 Dioxane</td>
<td>-0.569</td>
<td>1.035</td>
<td>-0.589</td>
<td>J.C.P. 26, 1647</td>
</tr>
<tr>
<td>1,2 Dichloroethane</td>
<td>-0.602</td>
<td>1.257</td>
<td>-0.757</td>
<td>&quot;</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>-0.345</td>
<td>1.130</td>
<td>-0.390</td>
<td>J.C.S. 1950, 308</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY FOR CHAPTER II

CHAPTER III

HYDROGEN BONDING STUDIES BY NMR

INTRODUCTION

(a) Experimental Observations

It was first observed in 1951 independently by Liddell and Ramsey (1) and Arnold and Packard (2) that the chemical shift of the OH proton in ethanol was markedly concentration and temperature dependent, similar phenomena not being observed in the case of most other proton resonances. The OH proton signal was found to move to higher values of the applied field when the dilution was increased or the temperature raised, the simultaneous movement of the resonances of the CH$_3$- and -CH$_2$- protons being negligible by comparison. This movement of the OH proton signal was ascribed to the change in shielding of the proton as hydrogen bonds between ethanol molecules were broken, due to increase in dilution or temperature.

It has since been found that the above behaviour is general for systems containing hydrogen bonds where there is an equilibrium or series of equilibria between a variety of hydrogen bonded species. Thus, alcohols and organic acids, water, inorganic acids, chloroform, etc. exhibit similar behaviour. Gutowsky and Saika investigated aqueous solutions of mineral acids and acetic acid (3), and found a single resonance line in all cases, due to protons exchanging rapidly between water, undissociated acid and hydronium ions, a further concentration independent resonance being observed for the CH$_3$- group in acetic acid. This situation is similar to that observed in the case of ethanol in that a single
resonance line is observed due to rapid exchange of protons between a variety of magnetically non-equivalent positions, but differs inasmuch as the identity of the species between which exchange is occurring is fairly clear for the case of aqueous solutions of acids. The nature of the various polymeric species present in ethanol and in alcohols generally is not known, and the present investigations were undertaken partly with a view to elucidating the nature of the polymeric species present in alcohol solutions. In cases where rapid exchange of protons between a variety of positions is occurring, the observed resonance position is given by,
\[ \delta_{\text{obs}} = \frac{\sum_i n_i \delta_i}{\sum_i n_i} \]  

where \( \delta_i \) is the chemical shift of a proton in an environment \( i \), and \( n_i \) is the mole fraction of protons in this environment.

Huggins, Pimentel and Shoolery (4) investigated the following hydrogen bonding equilibria,

(a) \( \text{CCl}_3\text{H} + \text{OC(CH}_3\text{)}_2 \rightleftharpoons \text{CCl}_3\text{H}.\text{OC(CH}_3\text{)}_2 \)

(b) \( \text{CCl}_3\text{H} + \text{N(C}_2\text{H}_5\text{)}_3 \rightleftharpoons \text{CCl}_3\text{H}.\text{N(C}_2\text{H}_5\text{)}_3 \)

by observing the concentration dependence of the chloroform proton signal. An equilibrium constant was defined in mole fraction units and the assumption made that free and complexed chloroform have characteristic precessional frequencies which were determined by extrapolation of the dilution-shift curves. The observed resonance was taken as a weighted mean of these characteristic frequencies. Values for the equilibrium constants for these reactions were derived by comparing the observed dilution-shift curves with those obtained by assuming arbitrary values of
the equilibrium constant. Observations at two different temperatures led to a rough value for the heats of formation of the complexes, which were -2500 cal. for chloroform-acetone and -4000 cal. for chloroform-triethylamine.

Korinek and Schneider made a similar study of the hydrogen bonding of chloroform to a variety of acceptor molecules (5), i.e. (Et)₃N, (Et)₂O, PrF, (Me)₂CO and EtCN, which are all virtually non-associated in the liquid state. All were expected to form 1:1 complexes with chloroform, whose existence was substantiated by freezing point measurements. The measured association shifts correlated well with expected hydrogen bond strengths. No equilibrium constants were calculated.

Huggins et al. (6) also investigated the behaviour of the proton resonance of the OH group in a variety of substituted phenols on dilution with carbon tetrachloride. The dilution curves were used to calculate equilibrium constants for dimer formation by making linear extrapolations to infinite dilution. The results obtained showed a qualitative correlation with the fraction of molecules in the monomeric state and the mean association energy of hydrogen bonded species present in 1 M solutions, as recorded in a compilation of infra-red data by Mecke (7). The form of the dilution-shift curve for o-chlorophenol was different from that found for the other phenol derivatives, having a slope of zero at infinite dilution. This was ascribed to the occurrence of intramolecular hydrogen bonding in this substance. The assumption of a linear extrapolation of the dilution-shift curve to infinite dilution is not a good one since the present work and other investigations have shown that a decrease in slope occurs at concentrations which are almost at the limit of sensitivity of NMR spectrometers (8) (9) (10).
Similar dilution studies have been carried out by Martin and Herail (11) on a series of substituted phenols and ethanol, using a wide variety of solvents.

Cohen and Reid demonstrated the existence of a point of inflection in the dilution-shift curve for the methanol-chloroform system at a concentration of 0.3 M (8). The limiting shifts on dilution, or 'isolated molecule' shifts, for a variety of hydrogen bonded substances were measured in various solvents. It was shown that no appreciable shifts occurred in the case of acetaldehyde and trichloroacetaldehyde on change of temperature or dilution, indicating the absence of hydrogen bonds of the type

\[
\begin{array}{c}
\text{H} \\
\text{R} \\
\text{C} = \text{O} \\
\text{R} \\
\end{array}
\]

The presence of a cyclic trimer in which current circulation through sigma bonds can occur was postulated in order to explain the observed shape of the dilution-shift curve for methanol-chloroform mixtures. This idea will be considered more fully when discussing results quoted in this thesis.

Further dilution studies of alcohols have been made by Diehl (12), Becker, Liddell and Shoolery (9), and by Saunders and Hyne (10). Diehl studied the systems benzene-ethanol, benzene-methanol and dioxane-water and concluded that the shifts observed were due to changes in electostatic dipole-dipole association on dilution, the phenomenon of hydrogen bonding being attributed entirely to this cause.

Becker et al. studied the OH proton resonance of ethanol in carbon tetrachloride, and calculated a dimer association constant from the limiting slope of the dilution-shift curve. Their estimate depended on the structure
assumed for the dimer, i.e. whether the dimer has an open form (one hydrogen bond) or is cyclic (two hydrogen bonds). They were not able to decide on the basis of NMR data which of these structures was most likely but concluded by analogy with low temperature matrix isolation studies of methanol in the infra-red (13) that the dimer was probably cyclic.

Saunders and Hyne investigated the dilution shifts of methanol, t-butanol and phenol in carbon tetrachloride going to low concentrations using a 13 mm. outside diameter spinning sample and in all cases observed a point of inflection in the dilution shift curves at low concentrations. They interpreted their results by considering a variety of possible equilibria, i.e.

(a) Monomer ⇌ Dimer
(b) Monomer ⇌ Trimer
(c) Monomer ⇌ Tetramer
(d) A statistical model including all n-mers.

They concluded that (b) gave a satisfactory agreement in the case of phenol and t-butanol whereas the methanol data fitted with model (c). However, such agreement appears to some extent fortuitous since the actual situation is undoubtedly more complex than is implied by these assumptions.

NMR and heat of dilution studies of methanol and water in the hydrogen bonding solvents acetone and dimethyl sulfoxide have been made by Drinkard and Kivelson (14). No close correlation was found between the two sets of data. The results were, however, consistent with formation of the following hydrogen bonds in order of increasing strength,

\[ >\text{CO} \cdots \text{HO}^\prime; >\text{SO} \cdots \text{HO}^\prime; \text{HO} \cdots \text{HO}^\prime \]

A similar nuclear resonance study of water in a variety of solvents,
i.e. dioxane, acetone, tetrahydrofuran and pyridine has been made by Mavel (15).

Some studies of the dimerisation of organic acids have been carried out. Reeves and Schneider investigated dilution shifts of acetic acid in a number of non-interacting solvents of varying dielectric constant (16). Contrary to the behaviour of the systems already discussed, the OH proton resonance was found to move to low field on dilution, reaching a minimum value before moving to high field on further decrease in concentration. These changes were explained in terms of a polymer-dimer equilibrium at high concentrations and a monomer-dimer equilibrium at low concentrations. Investigations of gaseous acetic acid between 200° C. and 300° C. enabled the difference in isolated molecule shifts for monomer and dimer to be determined. Reeves has studied long chain acids (17) and found the dilution-shift curve to be virtually independent of chain length, all the shifts on dilution being to high field in contrast to the behaviour of acetic acid. Similar studies on acids and related systems have been made by Bhar et al (18) (19).

Several studies of hydrides have been made with a view to determining the 'liquid association shifts' due to hydrogen bonding or similar phenomena. Ogg (20) (21) studied ammonia and water in the gaseous and liquid states and found a large difference in shift, the vapour signals occurring to high field. Comparison was made with propane, a non-associated liquid, where no difference in the position of the liquid and vapour resonances was found. Bernstein, Pople, and Schneider (22) have made a more detailed study of such effects and suggested that the association or hydrogen bond shifts in a system Y ... H — X can be interpreted largely in terms of a reduction in the diamagnetic circulation in the H — X bond by the electro-
static field of the Y donor. The large association shift found for acetylene was interpreted in terms of an association by a proton of one molecule with the TT electrons of another.

A study of the complexes formed by chloroform with aromatic molecules and olefines has been made by Reeves and Schneider (23). The concentration dependence of the proton resonance signal of chloroform was examined in benzene, toluene, mesitylene, chlorobenzene, o-dichlorobenzene, bromobenzene, nitrobenzene, and the olefinic solvents 1-hexene and cyclohexadiene. The observed shifts indicated specific complex formation. In benzene, toluene and mesitylene, the chloroform molecule appeared to be oriented with the hydrogen atom on the 6-fold axis above the ring, with the chlorines pointing away from the ring. Association with the O atoms of the -NO₂ group seemed to occur in nitrobenzene, a similar type of n-donor association occurring to a small extent with the halogenated benzenes. Weak TT-donor association appeared to exist between chloroform and olefines. Freezing point measurements seemed to be in agreement with these suggestions.

A number of studies of systems where proton exchange is taking place have been made, where the exchange mechanism involves hydrogen bonding. Reeves and Schneider (24) (25) investigated proton transfers in acetylacetone under a variety of conditions using di- and triethylamine, cyclohexane, acetic acid and pyrrole as solvents. In di- and triethylamine, acetylacetone is present predominantly in the enolic form. A rapid proton exchange was found to occur between the =CH- and OH- groups of the enol tautomer and the =CH- and OH- occurred in triethylamine but at a slower rate since the solvent lacks an -NH- group but does possess a basic nitrogen atom. Cyclohexane and acetic acid did not perturb the keto-enol equilibrium. An interaction between the >C = 0 groups of the keto form and the -NH- group of pyrrole was postulated to explain the small shifts in the pyrrole and
-CH₂- group spectra. Freezing point diagrams indicated a 1:2 complex as shown.

\[ \text{CH₃} \quad \text{CH₂} \quad \text{CH₃} \]

From changes of signal intensity with temperature in pure acetylacetone, an enthalpy of conversion of 2700 ± 100 cal. between keto and enol forms was calculated.

A similar study of the effect of the complexing of pyrrole with acetone, acetylacetone, dioxane and pyridine has been made by Freyman and Freyman (26). The pyrrole α and β proton resonances were found to shift to low field in all cases, indicating a decrease in shielding on hydrogen bond formation. In all cases there is presumably a competition between solute-solute and solute-solvent interactions.

Toyoda et al. (27) measured the dilution shifts of acetic acid, phenol and water in pyridine and found an initial shift to low field for the OH proton resonances in all three cases, a minimum occurring in the curves for 50 mole % mixtures. This indicates in each case that the proton is less shielded in the one to one complexes of the type

\[ \text{N} \quad ... \quad \text{H} - \text{O} \quad \text{R} \]

Assuming that a shift to low field implies a stronger hydrogen bond, these results indicate that solute-solvent interaction is stronger than solute-solute interaction. Similar dilution shift curves were found by Martin and Herail (11) for substituted phenols dissolved in pyridine. This type of
behaviour is analogous to that observed by Reeves and Schneider for acetic acid (16) where the OH proton resonance initially moved to low field on dilution.

Anbar, Loewenstein and Meiboom studied the kinetics of proton exchange between H$_2$O$_2$ and H$_2$O by NMR in the pH range 2.5 to 6.5 (28). In the region pH < 4.5 the reaction was found to involve H$_3$O$^+$ and H$_2$O$_2$ while for pH > 4.5 it was found to involve HO$_2^-$, H$_2$O$_2$ and H$_2$O, rate constants being found in each case. These conclusions were derived from line width measurements in these solutions using Gutowsky et al's. theory of these effects (3) (29). A six membered cyclic intermediate was postulated as a possible reaction step. This group have made similar quantitative studies of protolysis in other systems (30) (31).

Weinberg and Zimmerman studied the OH proton resonances of mixtures of H$_2$O and EtOH (32), and found that rapid exchange does not occur until 20% of H$_2$O has been added, two OH proton resonances being observed at concentrations < 20% H$_2$O, coalescence of lines occurring at higher concentrations. The average lifetime of H in OH at the critical concentration was calculated to be 0.05 sec., and a change in the spin-spin interaction with the -CH$_2$- group was observed at this concentration. Below 20% H$_2$O, coupling occurred with the CH$_3^-$ and OH- groups resulting in an ill defined quintuplet for the -CH$_2$- group. Above 20% H$_2$O, on the other hand, a quadruplet was observed due to spin-spin coupling with the CH$_3^-$ group only.

The effect of acetone on the -OH proton resonance of methanol was examined by Corio, Rutledge and Zimmerman (33). They found that molecular association between solvent and solute prevented rapid exchange of the methanol -OH proton and at certain concentrations resulted in an AB$_3$ type
spectrum for methanol, instead of the usual AX₃ spectrum.

(b) Theoretical Interpretations

The problem of correlating observed hydrogen bonding shifts with the known properties of the hydrogen bond is an extremely difficult one, since the nature of these bonds is still not clearly understood and no satisfactory quantum mechanical treatment has been given.

An approximate estimate of the magnitude of the shifts to be expected on a purely electrostatic basis, by considering the change in magnetic properties of a free hydrogen atom when placed in an electric field \( E \), has been made by Pople et al. (22). The diamagnetic susceptibility of a free hydrogen atom (considering only the orbital contribution, since although an H atom has a free spin, this will be paired on bonding) is given by,

\[
\chi_o = - \frac{e^2}{6mc^2} \langle r^2 \rangle = - \frac{e^2 a^2}{2mc^2} \quad \ldots \ldots \ldots \quad 4
\]

where \( a \) is the Bohr radius. When the atom is placed in a uniform field \( E \), the magnetic susceptibility is reduced and becomes anisotropic, having different values in directions parallel and perpendicular to the axis of the field \( E \). The two values are (34),

\[
-\chi_{\|} = \frac{e^2 a^2}{2mc^2} - \frac{159 a^6}{16 mc^2} E^2 \quad \ldots \ldots \ldots \quad 5
\]

\[
-\chi_{\perp} = \frac{e^2 a^2}{2mc^2} - \frac{797 a^6}{48 mc^2} E^2
\]

The fractional decrease in mean susceptibility is thus,

\[
\frac{\chi_0 - 1/3 (\chi_{\|} - 2\chi_{\perp})}{\chi_o} = 28.76 \frac{a^4 E^2}{e^2} \quad \ldots \ldots \ldots \quad 6
\]

If it is supposed that the fractional change of the screening field at the nucleus is the same as the fractional change of the mean susceptibility (35),
6 is also the ratio of the change in screening constant, $\Delta \sigma$, to the screening constant, $\sigma_0$, for an isolated hydrogen atom, which is obtained from the Lamb formula, 4, as $17 \times 10^{-6}$. A shift of 4 parts per million, i.e. 160 cycles at 40 Mc, characteristic of a strong hydrogen bond would be produced by a field of 0.09 a.u. or $1.5 \times 10^6$ esu. Such a field would arise from a single electronic charge at a distance of $1.7 \AA$, and is of the correct order of magnitude. This treatment is very much an approximation since the electron distribution around the proton in an -OH group will be considerably distorted as compared with that round a free hydrogen atom, because this distribution now forms part of a bond and has axial rather than spherical symmetry. Also, the change in shielding of the proton due to distortion of its charge distribution on formation of a hydrogen bond is not considered. This type of distortion may be considered in terms of the participation of ionic structures such as

$$\bar{X} \quad H \quad .. \quad Y$$

in the hydrogen bond, and will be expected to reduce the proton shielding and cause a shift of its resonance to low field. (see also (22a)).

No other theoretical approaches have been attempted. It seems reasonable to expect that some sort of correlation should exist between the strength of a hydrogen bond and the association shift for the proton in the bond for a given system, e.g. a linear O-H .... O bond. The effect of bending the bond would presumably destroy the correlation since the axial symmetry would be partially removed. This would result in a reduction of the paramagnetic high field shift (22).

(c) **Aims of the present work.**

The dilution-shift curves for the OH proton resonances of a wide variety of alcohols and related systems have been obtained. It was hoped
that these might provide information about,

(1) The types of polymeric species present in solutions of alcohols.

(2) The effects on hydrogen bonding of groups adjacent to the OH groups, which may be broadly classified into,
   i) Inductive effects.
   ii) Steric effects.

(3) Possible means of relating hydrogen bonding shifts in a semi-empirical manner to other molecular properties such as integrated infra-red absorption intensities, dipole moments, etc.

Temperature coefficients of the OH proton chemical shifts have also been obtained for a variety of systems, from which it was hoped that some information regarding hydrogen bond strengths might be derived.

RESULTS

1. Dilution-shift studies

   (a) Choice and purification of solvents (36)

   In most cases carbon tetrachloride was employed as a solvent in dilution studies, since it has apparently no tendency to associate with itself or with any solute and may hence be classed as a non-interacting solvent. Also, most of the alcohols studied were miscible with it in all proportions or if solid, were sufficiently soluble for an adequate concentration range to be studied. In some cases the polar solvent chloroform was used when solubility problems were encountered. As discussed in the previous section, this solvent has a marked tendency to associate with itself and suitable donor molecules (4) (5) (23), although the magnitude
of the association shifts observed are small compared with those of the majority of OH proton shifts on dilution. In some studies of acrylic acid, the interacting solvents dioxane and acetone were also employed.

Reagent grade carbon tetrachloride was dried over phosphorus pentoxide and distilled from it in an atmosphere of dry nitrogen directly into a bulb which was finally sealed off and detached from the distillation apparatus. These bulbs were fitted with a glass side arm and stopcock which allowed access of dry nitrogen under pressure when necessary. This pressure served to expel the solvent from the bulb when required through a drawn out teflon jet fitted with a Mohr clip. The solvent could thus be dispensed without coming into contact with the air. All the solvents used were stored in this manner under a positive pressure of dry nitrogen. Distillation was also always carried out under a positive pressure of nitrogen.

Reagent grade chloroform was purified in the same way, the distillation over phosphorus pentoxide serving to remove water and also the ethanol which is added as a stabilizer to reagent grade chloroform. The bulb in which the solvent was stored was covered with aluminum foil to prevent photo-chemical decomposition.

Reagent grade acetone was dried with calcium sulphate ('Drierite') and distilled. Reagent grade dioxane was also dried with calcium sulphate and distilled after standing over sodium for several hours.

The absence of water as a solvent impurity in these experiments was a critical factor, since at low dilutions of solute, the amount of water present could possibly become comparable with the amount of substance being studied and interference with the hydrogen bonding equilibria at these concentrations would result. From this point of view extreme dryness of
the solutes was of less importance since the high concentration region is relatively insensitive to impurities.

Besides helping to prevent solvent decomposition, storing the solvents under nitrogen also helped to reduce the amount of oxygen dissolved in the samples, thereby improving the resolution of the spectrometer, as discussed in Chapter II.

(b) **Dilution shifts of methanol and related compounds**

The dilution shifts of the OH proton were observed for the series of compounds shown in Table 1c which also lists the reference substance used for making the measurements. This table also indicates whether the reference was used externally (E) in a capillary tube enclosed with the sample or internally (I). The low field side (l.f.s.) of the -CH$_3$ doublet was used as an internal marker in the case of dl-α-methyl benzyl alcohol. These and all subsequent dilution shift measurements were made at 40 Mc using side band superposition or interpolation techniques to measure shifts, as described in Chapter II. Interpolation was found most convenient at low solute concentrations, an average value from several traces being taken.

Methanol was purified by refluxing over magnesium turnings and distilling in an atmosphere of dry nitrogen. It was stored in a bulb as previously described under a positive pressure of nitrogen to prevent oxidation to formaldehyde. The benzyl alcohol and dl-α-methyl benzyl alcohol were Eastman Kodak 'White Label' grade and were dried with calcium sulphate and distilled. The benzhydrol and triphenyl carbinol were also White Label grade and were used, as was the α-α-methyl benzhydrol*, without further purification.

* The α-α-methyl benzhydrol was prepared by Mr. A.L. Gatzke. The product consisted of fine white needles with a M.P. of 81°-82° C. (Lit. value 80°-81° C.) (37).
Carbon tetrachloride was used as a solvent for all the compounds except triphenyl carbinol. This was not sufficiently soluble in this solvent to allow the study of an adequate concentration range and so chloroform was used instead.

### TABLE 1c

REFERENCE PROCEDURES USED WITH METHANOL AND RELATED COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Marker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>CH$_3$OH</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>C$_6$H$_5$CH$_2$OH</td>
<td>-CH$_2$-</td>
</tr>
<tr>
<td>dl-$\alpha$-Methyl benzyl alcohol</td>
<td>C$_6$H$_5$C(CH$_3$)OH</td>
<td>-CH$_3$ (l.f.s.)</td>
</tr>
<tr>
<td>Benzhydrol</td>
<td>(C$_6$H$_5$)$_2$CHOH</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>$\alpha$-Methyl benzhydrol</td>
<td>(C$_6$H$_5$)$_2$C(CH$_3$)OH</td>
<td>-CH$_3$</td>
</tr>
<tr>
<td>Triphenyl carbinol</td>
<td>(C$_6$H$_5$)$_3$COH</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
</tbody>
</table>

The results obtained are listed in Tables 2c to 7c, all shifts being quoted in c/s and concentrations in mole fraction units. Susceptibility corrections made as described in Chapter II are listed for benzhydrol and triphenyl carbinol, and their shifts have been expressed with reference to an internal cyclohexane marker by applying the experimentally determined corrections, C$_M$, listed in Table 1b in Chapter II. These corrections are also given at the top of the appropriate dilution-shift tables.

For those compounds where an internal marker other than cyclohexane was used, the shift between the marker and an added internal cyclohexane marker was measured and is given at the top of the appropriate table. This was used to correct the shifts, and so all shifts both for externally and internally referenced solutes have been referred to a common internal
### TABLE 2c

**DILUTION SHIFTS FOR THE OH PROTON OF METHANOL**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl₄</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>- 138.0</td>
</tr>
<tr>
<td>.707</td>
<td>- 133.0</td>
</tr>
<tr>
<td>.264</td>
<td>- 122.5</td>
</tr>
<tr>
<td>.170</td>
<td>- 113.5</td>
</tr>
<tr>
<td>.100</td>
<td>- 93.5</td>
</tr>
<tr>
<td>.083</td>
<td>- 84.5</td>
</tr>
<tr>
<td>.063</td>
<td>- 77.0</td>
</tr>
<tr>
<td>.045</td>
<td>- 49.5</td>
</tr>
<tr>
<td>.032</td>
<td>- 20.0</td>
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<tr>
<td>.023</td>
<td>0</td>
</tr>
<tr>
<td>.014</td>
<td>+ 27.0</td>
</tr>
<tr>
<td>.0095</td>
<td>+ 36.5</td>
</tr>
<tr>
<td>.0072</td>
<td>+ 37.5</td>
</tr>
<tr>
<td>.0048</td>
<td>+ 40.0</td>
</tr>
<tr>
<td>.0024</td>
<td>+ 37.0</td>
</tr>
</tbody>
</table>
### TABLE 3c
DILUTION SHIFTS FOR THE OH PROTON OF BENZYL ALCOHOL

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>-160.5</td>
</tr>
<tr>
<td>.652</td>
<td>-149.75</td>
</tr>
<tr>
<td>.429</td>
<td>-140.5</td>
</tr>
<tr>
<td>.223</td>
<td>-127.0</td>
</tr>
<tr>
<td>.158</td>
<td>-119.0</td>
</tr>
<tr>
<td>.105</td>
<td>-109.75</td>
</tr>
<tr>
<td>.057</td>
<td>-94.0</td>
</tr>
<tr>
<td>.036</td>
<td>-71.5</td>
</tr>
<tr>
<td>.027</td>
<td>-64.0</td>
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<tr>
<td>.0184</td>
<td>-42.0</td>
</tr>
<tr>
<td>.0093</td>
<td>-26.0</td>
</tr>
<tr>
<td>.0056</td>
<td>-2.0</td>
</tr>
<tr>
<td>.0037</td>
<td>+13.0</td>
</tr>
</tbody>
</table>

**Correction**
$\text{C}_6\text{H}_4$ to $\text{-CH}_2^-$ = -119.0 c/s

**Solvent**
$\text{CCl}_4$
# Table 4c

**Dilution Shifts for the OH Proton in d1-α-Methyl Benzyl Alcohol**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CC1₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Correction</strong></td>
<td>C₆H₁₂(l) to -CH₃(l.f.s.) = 0 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>-150.5</td>
</tr>
<tr>
<td>0.616</td>
<td>-140.5</td>
</tr>
<tr>
<td>0.445</td>
<td>-135.5</td>
</tr>
<tr>
<td>0.287</td>
<td>-125.5</td>
</tr>
<tr>
<td>0.139</td>
<td>-106.5</td>
</tr>
<tr>
<td>0.074</td>
<td>-84.0</td>
</tr>
<tr>
<td>0.046</td>
<td>-65.25</td>
</tr>
<tr>
<td>0.032</td>
<td>-48.5</td>
</tr>
<tr>
<td>0.023</td>
<td>-39.0</td>
</tr>
<tr>
<td>0.016</td>
<td>-24.0</td>
</tr>
<tr>
<td>0.0111</td>
<td>-14.25</td>
</tr>
<tr>
<td>0.0080</td>
<td>-9.0</td>
</tr>
<tr>
<td>0.0048</td>
<td>+4.0</td>
</tr>
<tr>
<td>0.0064</td>
<td>Undetectable due to interference of CH₃ signal. About 0 c/s</td>
</tr>
</tbody>
</table>
### TABLE 5c

DILUTION SHIFTS FOR THE OH PROTON OF BENZHYDROL

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Correction</th>
<th>Concentration (m.f.)</th>
<th>Susceptibility Correction (c/s)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>C₆H₁₂(E) to C₆H₁₂(I) = +11.5 c/s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0513</td>
<td>&lt;-0.3</td>
<td>-53.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0255</td>
<td>-</td>
<td>-30.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0129</td>
<td>-</td>
<td>-16.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0065</td>
<td>-</td>
<td>-7.5</td>
</tr>
</tbody>
</table>

### TABLE 6c

DILUTION SHIFTS FOR THE OH PROTON OF \(\alpha\)-METHYL BENZHYDROL

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Correction</th>
<th>Concentration (m.f.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>C₆H₁₂(I) to -CH₃ = -14.5 c/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0578</td>
<td>-32.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0336</td>
<td>-25.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0169</td>
<td>-14.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0085</td>
<td>-12.5</td>
</tr>
</tbody>
</table>
TABLE 7c
DILUTION SHIFTS OF THE OH PROTON OF TRIPHENYL CARBINOL

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CHCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction</td>
<td>C₆H₁₂(l) to C₆H₁₂(E) = + 13.0 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Susceptibility Correction (c/s)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.047</td>
<td>+ 1.0</td>
<td>- 43.5</td>
</tr>
<tr>
<td>0.0221</td>
<td>+ 0.5</td>
<td>- 42.0</td>
</tr>
<tr>
<td>0.0112</td>
<td>-</td>
<td>- 42.0</td>
</tr>
<tr>
<td>0.0056</td>
<td>-</td>
<td>- 42.0</td>
</tr>
</tbody>
</table>

reference substance, cyclohexane. All measurements are thus directly comparable. A similar procedure has been followed for all the dilution shifts listed for alcohols.

These results are compared graphically in Fig. 1c, which shows the dilution shift curves for methanol, benzyl alcohol and α-methyl benzyl alcohol. Fig. 2c is an expansion of the lower concentration region of these curves and also includes the curves for benzhydrol, α-methyl benzhydrol and triphenyl carbinol. In all captions to dilution-shift curves, the relevant proton has been underlined.

(c) Dilution shifts for acetylenic alcohols

The compounds studied and the reference procedures used are given in Table 8c. Both OH proton shifts and shifts of acetylenic protons were observed. Carbon tetrachloride was used as a solvent except for propargyl alcohol which was not completely miscible in the high concentration range. Chloroform was used instead.
DILUTION-SHIFT CURVES

- **CH$_3$OH**
- **$\phi$CH$_2$OH**
- **$\phi$C(CH$_3$)HOH**
TABLE 8c
REFERENCE PROCEDURES USED WITH ACETYLENIC ALCOHOLS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Marker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propargyl alcohol</td>
<td>H-C $\equiv$ C-CH$_2$OH</td>
<td>C$_6$H$_2$E</td>
</tr>
<tr>
<td>2-Butyn-1-ol</td>
<td>CH$_3$-C $\equiv$ C-CH$_2$OH</td>
<td>C$_6$H$_2$E</td>
</tr>
<tr>
<td>3-Butyn-2-ol</td>
<td>H-C $\equiv$ C-C(CH$_3$)HOH</td>
<td>- CH$_3$(l.f.s.) I</td>
</tr>
<tr>
<td>2-Methyl-3-butyn-2-ol</td>
<td>H-C $\equiv$ C-C(CH$_3$)$_2$OH</td>
<td>- CH$_3$ I</td>
</tr>
</tbody>
</table>

These chemicals were all research grade chemicals obtained from the Farchan Chemical Co. and were dried with calcium sulphate and distilled through a short column. Colourless distillates resulted in all cases and the substances were stored in dark glass bottles over calcium sulphate. No indications of the presence of impurities were obtained from the NMR spectra.

In order to substantiate the assignment of the spectrum (38) and to allow the comparison of the acetylenic proton shifts of propargyl alcohol with those of a non-hydroxylic compound, a derivative, propargyl acetate, was made. The reaction used was,

\[
\text{HC} \equiv \text{C} \text{CH}_2\text{OH} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{HC} \equiv \text{C} \text{CH}_2\text{COCH}_3 + \text{CH}_3\text{COOH}
\]

The acetic acid was removed by adding potassium carbonate solution and extracting with ether, the ester passing into the ethereal layer, which was separated. The ether was removed by distillation giving a product whose boiling point was 123° C., and whose NMR spectrum showed only the expected peaks. The spectrum is recorded in Fig. 3c, and shows clearly that the high field triplet (at - 56 c/s) observed in propargyl alcohol is due to the acetylenic proton, whereas the low field singlet peak (- 140.5 c/s) is
FIG 3c NMR SPECTRA

a) PROPARGYL ALCOHOL

b) PROPARGYL ACETATE

OH CH₂ COOCH₃

H c/s
due to the OH group.

The dilution shifts of the HCΞ and -CH₂- groups were measured for propargyl acetate, using the CH₃ group as an external marker, and then correcting to an internal cyclohexane marker. The shifts are recorded in Table 9c. Measurements were not carried to very low concentrations since the splittings of the acetylenic proton peak rendered this impractical. The concentrations are given in moles/litre.

**TABLE 9c**

DILUTION SHIFTS IN PROPARGYL ACETATE

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction</td>
<td>C₆H₁₂(l) to -O COCH₃ = - 24.0 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (m/1.)</th>
<th>-CH₂- Shift (c/s)</th>
<th>HCΞ Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.25</td>
<td>- 127.0</td>
<td>- 51.0</td>
</tr>
<tr>
<td>6.84</td>
<td>- 126.0</td>
<td>- 47.0</td>
</tr>
<tr>
<td>4.55</td>
<td>- 126.0</td>
<td>- 43.0</td>
</tr>
<tr>
<td>3.04</td>
<td>- 125.5</td>
<td>- 41.0</td>
</tr>
<tr>
<td>2.02</td>
<td>- 125.5</td>
<td>- 40.0</td>
</tr>
</tbody>
</table>

Tables 10c to 13c give the corrected dilution shifts for the OH protons of the four acetylenic alcohols and the dilution shifts for the corresponding acetylenic protons. All shifts are referred to an internal cyclohexane marker. The OH proton dilution shifts for all four alcohols are plotted in Fig. 4c. The CHΞ dilution shifts for these alcohols are shown in Fig. 5c.
(d) Dilution shifts of chloroethanols

The OH proton dilution shifts of the compounds 2-chloroethanol, 2,2-dichloroethanol and 2,2,2-trichloroethanol were studied. The mono- and di-substituted ethanols were examined using an external cyclohexane marker, the -CH₂- group being used as an internal reference for trichloroethanol. Carbon tetrachloride was used as a solvent.

The 2-chloroethanol was White Label grade and the other two alcohols were obtained from the K. & K. Chemical Co. All were dried over calcium sulphate and distilled before use. The 2,2,2-trichloroethanol showed some impurity peaks in the aliphatic proton region when examined by NMR. Further distillation did not appreciably reduce the amounts of these impurities. Since compounds with resonances lying in this region are not likely to effect hydrogen bonding equilibria, the compound was used in this slightly impure state (1-2% impurities from intensity measurements).

The shifts of the OH proton in these compounds at various concentrations are recorded in Tables 14c to 16c. These results are plotted in Fig. 6c which also shows Becker et al's. results for ethanol (9).

(e) Dilution shifts of miscellaneous alcohols

Three other alcohols were also investigated.

1. Propanol. The dilution shift was studied in a carbon tetrachloride solvent using the central peak of the -CH₃ group as an internal reference. The shifts were corrected to an internal cyclohexane reference, and are given in Table 17c and Fig. 7c. The compounds was E. & A. reagent grade and was dried with calcium sulphate and distilled before use.

2. Allyl Alcohol. The solvent used was carbon tetrachloride, with the low field side of -CH₂- doublet as an internal reference signal,
### TABLE 10c

**DILUTION SHIFTS FOR PROPARGYL ALCOHOL**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CHCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Correction</strong></td>
<td>$C₆H₁₂(1)$ to $C₆H₁₂(E)$ = + 13.0 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Susceptibility Correction (c/s)</th>
<th>-OH Shift (c/s)</th>
<th>-CH₂- Shift (c/s)</th>
<th>=CH Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>- 10.8</td>
<td>- 138.3</td>
<td>- 116.3</td>
<td>- 53.8</td>
</tr>
<tr>
<td>.735</td>
<td>- 7.2</td>
<td>- 130.2</td>
<td>- 114.8</td>
<td>- 50.2</td>
</tr>
<tr>
<td>.527</td>
<td>- 4.9</td>
<td>- 121.9</td>
<td>- 114.4</td>
<td>- 47.4</td>
</tr>
<tr>
<td>.369</td>
<td>- 3.1</td>
<td>- 110.1</td>
<td>- 113.6</td>
<td>- 45.1</td>
</tr>
<tr>
<td>.255</td>
<td>- 2.1</td>
<td>- 97.1</td>
<td>- 113.6</td>
<td>- 45.1</td>
</tr>
<tr>
<td>.182</td>
<td>- 1.6</td>
<td>- 86.1</td>
<td>- 112.6</td>
<td>- 44.1</td>
</tr>
<tr>
<td>.124</td>
<td>- 1.0</td>
<td>- 71.0</td>
<td>- 115.0</td>
<td>- 43.5</td>
</tr>
<tr>
<td>.083</td>
<td>- 0.7</td>
<td>- 56.7</td>
<td>- 115.7</td>
<td>- 43.7</td>
</tr>
<tr>
<td>.056</td>
<td>- 0.4</td>
<td>- 40.9</td>
<td>- 110.4</td>
<td>- 42.4</td>
</tr>
<tr>
<td>.040</td>
<td>-</td>
<td>- 32.5</td>
<td>- 111.0</td>
<td>- 41.0</td>
</tr>
<tr>
<td>.027</td>
<td>-</td>
<td>- 24.0</td>
<td>- 115.0</td>
<td>- 43.0</td>
</tr>
<tr>
<td>.0177</td>
<td>-</td>
<td>- 17.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.0118</td>
<td>-</td>
<td>- 13.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.0083</td>
<td>-</td>
<td>- 12.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>.0042</td>
<td>-</td>
<td>- 12.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE 11c
DILUTION SHIFT OF THE OH PROTON IN 2-BUTYN-1-OL

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Correction</th>
<th>Correction (c/s)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl4</td>
<td>C6H12(I) to C6H12(E) = + 11.5 c/s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Susceptibility Correction (c/s)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>- 2.2</td>
<td>- 128.7</td>
</tr>
<tr>
<td>.570</td>
<td>- 1.1</td>
<td>- 123.6</td>
</tr>
<tr>
<td>.398</td>
<td>- 0.7</td>
<td>- 117.2</td>
</tr>
<tr>
<td>.249</td>
<td>- 0.4</td>
<td>- 103.9</td>
</tr>
<tr>
<td>.210</td>
<td>- 0.3</td>
<td>- 98.8</td>
</tr>
<tr>
<td>.156</td>
<td>-</td>
<td>- 91.5</td>
</tr>
<tr>
<td>.117</td>
<td>-</td>
<td>- 82.0</td>
</tr>
<tr>
<td>.074</td>
<td>-</td>
<td>- 64.0</td>
</tr>
<tr>
<td>.050</td>
<td>-</td>
<td>- 48.5</td>
</tr>
<tr>
<td>.038</td>
<td>-</td>
<td>- 34.5</td>
</tr>
<tr>
<td>.026</td>
<td>-</td>
<td>- 20.5</td>
</tr>
<tr>
<td>.018</td>
<td>-</td>
<td>- 7.5</td>
</tr>
<tr>
<td>.013</td>
<td>-</td>
<td>+ 4.5</td>
</tr>
<tr>
<td>.0079</td>
<td>-</td>
<td>+ 15.5</td>
</tr>
<tr>
<td>.0053</td>
<td>-</td>
<td>+ 16.5</td>
</tr>
<tr>
<td>.0040</td>
<td>-</td>
<td>+ 20.5</td>
</tr>
</tbody>
</table>
### TABLE 12c

DILUTION SHIFTS FOR 3-BUTYN-2-OL

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction</td>
<td>$C_6H_{12}(l)$ to -CH$_3$ (l.f.s.) = -3.5 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>-OH group</th>
<th>Concentration (m.f.)</th>
<th>Shift (c/s)</th>
<th>Concentration (m.f.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>-137.5</td>
<td>1.000</td>
<td>-48.5</td>
<td></td>
</tr>
<tr>
<td>.732</td>
<td>-128.0</td>
<td>.710</td>
<td>-44.0</td>
<td></td>
</tr>
<tr>
<td>.559</td>
<td>-124.0</td>
<td>.559</td>
<td>-42.5</td>
<td></td>
</tr>
<tr>
<td>.384</td>
<td>-117.5</td>
<td>.384</td>
<td>-40.5</td>
<td></td>
</tr>
<tr>
<td>.263</td>
<td>-109.5</td>
<td>.198</td>
<td>-37.5</td>
<td></td>
</tr>
<tr>
<td>.181</td>
<td>-100.5</td>
<td>.106</td>
<td>-35.5</td>
<td></td>
</tr>
<tr>
<td>.129</td>
<td>-94.5</td>
<td>.059</td>
<td>-35.5</td>
<td></td>
</tr>
<tr>
<td>.087</td>
<td>-80.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.059</td>
<td>-65.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.047</td>
<td>-59.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.032</td>
<td>-41.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.021</td>
<td>-25.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>.014</td>
<td>-11.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 13c
DILUTION SHIFTS FOR 2-METHYL-3-BUTYN-2-OL

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction</td>
<td>C₆H₁₂(1) to -CH₃ = - 3.0 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>-OH Shift (c/s)</th>
<th>=CH Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>- 121.5</td>
<td>- 45.25</td>
</tr>
<tr>
<td>.662</td>
<td>- 112.75</td>
<td>- 40.75</td>
</tr>
<tr>
<td>.462</td>
<td>- 105.5</td>
<td>- 39.0</td>
</tr>
<tr>
<td>.292</td>
<td>- 98.0</td>
<td>- 37.25</td>
</tr>
<tr>
<td>.195</td>
<td>- 88.5</td>
<td>- 36.25</td>
</tr>
<tr>
<td>.120</td>
<td>- 75.75</td>
<td>- 35.25</td>
</tr>
<tr>
<td>.080</td>
<td>- 63.5</td>
<td>- 34.75</td>
</tr>
<tr>
<td>.053</td>
<td>- 50.0</td>
<td>- 34.75</td>
</tr>
<tr>
<td>.035</td>
<td>- 37.75</td>
<td>- 33.75</td>
</tr>
<tr>
<td>.019</td>
<td>- 24.0 ± 3.0</td>
<td>- 33.0 ± 3.0</td>
</tr>
</tbody>
</table>
FIG 4c  DILUTION-SHIFT CURVES

\[ \text{SHIFT} \]

\[ \text{CONC. m.f.} \]

- \[ \text{HC:CCH}_2\text{OH} \]
- \[ \text{HC:CC(CH}_3\text{)HOH} \]
- \[ \text{HC:CC(CH}_3\text{)_2OH} \]
- \[ \text{CH}_3\text{C:CCH}_2\text{OH} \]
**TABLE 14c**

**DILUTION SHIFTS FOR OH PROTON OF 2-CHLOROETHANOL**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction</td>
<td>C₆H₁₂(1) to C₆H₁₂(E) = + 11.5 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Susceptibility Correction (c/s)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>- 2.4</td>
<td>- 141.9</td>
</tr>
<tr>
<td>.747</td>
<td>- 1.6</td>
<td>- 134.1</td>
</tr>
<tr>
<td>.589</td>
<td>- 1.2</td>
<td>- 130.7</td>
</tr>
<tr>
<td>.417</td>
<td>- 0.8</td>
<td>- 124.3</td>
</tr>
<tr>
<td>.323</td>
<td>- 0.6</td>
<td>- 115.6</td>
</tr>
<tr>
<td>.265</td>
<td>- 0.4</td>
<td>- 108.4</td>
</tr>
<tr>
<td>.167</td>
<td>-</td>
<td>- 99.5</td>
</tr>
<tr>
<td>.127</td>
<td>-</td>
<td>- 92.5</td>
</tr>
<tr>
<td>.079</td>
<td>-</td>
<td>- 82.5</td>
</tr>
<tr>
<td>.054</td>
<td>-</td>
<td>- 66.0</td>
</tr>
<tr>
<td>.041</td>
<td>-</td>
<td>- 55.0</td>
</tr>
<tr>
<td>.028</td>
<td>-</td>
<td>- 38.5</td>
</tr>
<tr>
<td>.020</td>
<td>-</td>
<td>- 27.5</td>
</tr>
<tr>
<td>.014</td>
<td>-</td>
<td>- 20.0</td>
</tr>
</tbody>
</table>
### TABLE 15c

**DILUTION SHIFTS FOR THE OH PROTON OF 2,2-DICHLOROETHANOL**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Correction</th>
<th>Concentration (m.f.)</th>
<th>Susceptibility Correction (c/s)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>C₆H₁₂(1) to C₆H₁₂(E) = + 11.5 c/s</td>
<td>1.000</td>
<td>- 2.2</td>
<td>- 149.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.371</td>
<td>- 0.4</td>
<td>- 119.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.191</td>
<td>-</td>
<td>- 105.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.080</td>
<td>-</td>
<td>- 84.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.045</td>
<td>-</td>
<td>- 73.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.036</td>
<td>-</td>
<td>- 59.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.026</td>
<td>-</td>
<td>- 45.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.019</td>
<td>-</td>
<td>- 35.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.015</td>
<td>-</td>
<td>- 28.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.011</td>
<td>-</td>
<td>- 23.0</td>
</tr>
</tbody>
</table>
### TABLE 16c

**DILUTION SHIFTS FOR THE OH PROTON OF 2,2,2-TRICHLOROETHANOL**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Correction</strong></td>
<td>C₆H₁₂(l) to -CH₂⁻ = -109.5 c/s</td>
</tr>
<tr>
<td><strong>Concentration (m.f.)</strong></td>
<td><strong>Shift (c/s)</strong></td>
</tr>
<tr>
<td>1.000</td>
<td>-159.0</td>
</tr>
<tr>
<td>.681</td>
<td>-153.0</td>
</tr>
<tr>
<td>.514</td>
<td>-139.5</td>
</tr>
<tr>
<td>.433</td>
<td>-135.5</td>
</tr>
<tr>
<td>.334</td>
<td>-124.0</td>
</tr>
<tr>
<td>.158</td>
<td>- 94.5</td>
</tr>
<tr>
<td>.121</td>
<td>- 82.5</td>
</tr>
<tr>
<td>.111</td>
<td>- 74.5</td>
</tr>
<tr>
<td>.073</td>
<td>- 63.0</td>
</tr>
<tr>
<td>.045</td>
<td>- 51.5</td>
</tr>
<tr>
<td>.020</td>
<td>- 38.0</td>
</tr>
</tbody>
</table>
FIG 6c  DILUTION-SHIFT CURVES

- $\text{CH}_2\text{CICH}_2\text{OH}$
- $\text{CHCl}_2\text{CH}_2\text{OH}$
- $\text{CCl}_3\text{CH}_2\text{OH}$
- $\text{CH}_3\text{CH}_2\text{OH}$
later corrected to refer to an internal cyclohexane marker. It was purified in the same way as propanol. The shifts are recorded in Table 18c and Fig. 7c.

3. Methyl Ethyl t-Butyl Carbinol*. An external water marker was used as a reference since the large aliphatic peak observed a cyclohexane reference signal and was not sharp enough to use as an internal reference signal. The solvent was carbon tetrachloride. Shifts are given in Table 19c and Fig. 7c. The compound was dried and distilled before use, the fraction boiling around 150° C. being employed.

(f) Dilution Shifts of Acrylic Acid

The dilution shifts (Tables 20c to 22c and Fig. 8c) of the COOH proton were studied in the solvents carbon tetrachloride, acetone and dioxane, using an external water marker in each case. The compound was White Label quality, stabilized with a small quantity of the monomethyl ether of hydroquinone (<0.1%). It was purified as usual by drying and distilling.

II. Temperature-Shift studies

The temperature coefficients of the chemical shifts for the OH protons in a variety of compounds were measured, using the apparatus described in Chapter 11.

(a) Methanol and related compounds

The temperature dependence of the OH proton shift for pure methanol and for a number of solutions of methanol in carbon tetrachloride and chloroform were measured. Cyclohexane was used as an internal reference and the results are given in Tables 23c and 24c and plotted in Figures 9

* Obtained from Dr. R.H. Wright of the British Columbia Research Council.
TABLE 17c

DILUTION SHIFTS FOR THE OH PROTON OF PROPAHOL

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction</td>
<td>C₆H₁₂(l) to -CH₃ (centre) = + 23.0 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>- 150.0</td>
</tr>
<tr>
<td>0.7933</td>
<td>- 144.5</td>
</tr>
<tr>
<td>0.499</td>
<td>- 134.0</td>
</tr>
<tr>
<td>0.375</td>
<td>- 128.0</td>
</tr>
<tr>
<td>0.251</td>
<td>- 119.5</td>
</tr>
<tr>
<td>0.168</td>
<td>- 109.5</td>
</tr>
<tr>
<td>0.123</td>
<td>- 95.0</td>
</tr>
<tr>
<td>0.079</td>
<td>- 87.5</td>
</tr>
<tr>
<td>0.053</td>
<td>- 72.5</td>
</tr>
<tr>
<td>0.033</td>
<td>- 47.5</td>
</tr>
<tr>
<td>0.025</td>
<td>- 28.5</td>
</tr>
<tr>
<td>0.019</td>
<td>- 19.0</td>
</tr>
<tr>
<td>0.014</td>
<td>- 8.0</td>
</tr>
<tr>
<td>0.0077</td>
<td>+ 17.0</td>
</tr>
</tbody>
</table>

### TABLE 19c

DILUTION SHIFTS FOR THE OH PROTON OF ALLYL ALCOHOL

| Solvent | CCl₄ |
| Correction | C₆H₁₂(l) to -CH₂- (l.f.s.) = -106.5 c/s |

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>-151.0</td>
</tr>
<tr>
<td>0.882</td>
<td>-146.0</td>
</tr>
<tr>
<td>0.820</td>
<td>-144.0</td>
</tr>
<tr>
<td>0.704</td>
<td>-141.0</td>
</tr>
<tr>
<td>0.578</td>
<td>-137.0</td>
</tr>
<tr>
<td>0.335</td>
<td>-127.0</td>
</tr>
<tr>
<td>0.187</td>
<td>-115.0</td>
</tr>
<tr>
<td>0.153</td>
<td>-109.0</td>
</tr>
<tr>
<td>0.123</td>
<td>-102.0</td>
</tr>
<tr>
<td>0.058</td>
<td>-75.0</td>
</tr>
<tr>
<td>0.042</td>
<td>-56.0</td>
</tr>
<tr>
<td>0.033</td>
<td>-37.0</td>
</tr>
<tr>
<td>0.021</td>
<td>-20.0</td>
</tr>
<tr>
<td>0.012</td>
<td>-6.0</td>
</tr>
<tr>
<td>0.0075</td>
<td>-1.5</td>
</tr>
</tbody>
</table>
### TABLE 19c

**DILUTION SHIFT OF THE OH PROTON IN METHYL ETHYL t-BUTYL CARBINOL**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction</td>
<td>C₆H₁₂(1) to C₆H₁₂(E) = +11.5 c/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Susceptibility Correction (c/s)</th>
<th>Shifts (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.628</td>
<td>-0.8</td>
<td>-29.8</td>
</tr>
<tr>
<td>0.371</td>
<td>-0.5</td>
<td>-18.5</td>
</tr>
<tr>
<td>0.230</td>
<td>-0.3</td>
<td>-8.3</td>
</tr>
<tr>
<td>0.148</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>0.095</td>
<td>-</td>
<td>+8.0</td>
</tr>
</tbody>
</table>
FIG 7c DILUTION-SHIFT CURVES

- \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)
- \( \text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)
- \( \text{MeEt } t-\text{Bu COH} \)
TABLE 20c
DILUTION SHIFTS OF THE -COOH PROTON IN ACRYLIC ACID

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Susceptibility Correction (c/s)</th>
<th>Shifts (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>- 13.6</td>
<td>- 288.1</td>
</tr>
<tr>
<td>.827</td>
<td>- 10.5</td>
<td>- 290.0</td>
</tr>
<tr>
<td>.741</td>
<td>- 9.0</td>
<td>- 292.0</td>
</tr>
<tr>
<td>.588</td>
<td>- 6.8</td>
<td>- 295.3</td>
</tr>
<tr>
<td>.417</td>
<td>- 4.5</td>
<td>- 299.5</td>
</tr>
<tr>
<td>.299</td>
<td>- 3.1</td>
<td>- 301.1</td>
</tr>
<tr>
<td>.222</td>
<td>- 2.3</td>
<td>- 302.3</td>
</tr>
<tr>
<td>.125</td>
<td>- 1.2</td>
<td>- 303.2</td>
</tr>
<tr>
<td>.067</td>
<td>- 0.7</td>
<td>- 302.7</td>
</tr>
<tr>
<td>.041</td>
<td>- 0.3</td>
<td>- 301.3</td>
</tr>
<tr>
<td>.028</td>
<td>-</td>
<td>- 299.0</td>
</tr>
<tr>
<td>.021</td>
<td>-</td>
<td>- 298.0</td>
</tr>
<tr>
<td>.014</td>
<td>-</td>
<td>- 291.0</td>
</tr>
<tr>
<td>.011</td>
<td>-</td>
<td>- 285.0</td>
</tr>
<tr>
<td>.0071</td>
<td>-</td>
<td>- 279.5</td>
</tr>
<tr>
<td>.0035</td>
<td>-</td>
<td>Not visible</td>
</tr>
</tbody>
</table>
## TABLE 21c

**DILUTION SHIFTS OF THE -COOH PROTON IN ACRYLIC ACID**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Concentration</strong> (m.f.)</td>
<td><strong>Susceptibility Correction</strong> (c/s)</td>
</tr>
<tr>
<td>1.000</td>
<td>+10.2</td>
</tr>
<tr>
<td>.765</td>
<td>+7.6</td>
</tr>
<tr>
<td>.519</td>
<td>+5.1</td>
</tr>
<tr>
<td>.351</td>
<td>+3.4</td>
</tr>
<tr>
<td>.275</td>
<td>+2.6</td>
</tr>
<tr>
<td>.213</td>
<td>+2.2</td>
</tr>
<tr>
<td>.140</td>
<td>+1.2</td>
</tr>
<tr>
<td>.097</td>
<td>+0.9</td>
</tr>
<tr>
<td>Concentration (m.f.)</td>
<td>Susceptibility Correction (c/s)</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>1.000</td>
<td>- 2.8</td>
</tr>
<tr>
<td>.804</td>
<td>- 2.2</td>
</tr>
<tr>
<td>.716</td>
<td>- 2.0</td>
</tr>
<tr>
<td>.557</td>
<td>- 1.6</td>
</tr>
<tr>
<td>.386</td>
<td>- 0.9</td>
</tr>
<tr>
<td>.305</td>
<td>- 0.7</td>
</tr>
<tr>
<td>.239</td>
<td>- 0.5</td>
</tr>
<tr>
<td>.158</td>
<td>- 0.3</td>
</tr>
<tr>
<td>.111</td>
<td>-</td>
</tr>
</tbody>
</table>
FIG 8c DILUTION-SHIFT CURVES FOR CH$_2$CHCOOH

- CCl$_4$
- (CH$_3$)$_2$CO
- DIOXANE

SHIFT C/S

CONC m.f.
**TABLE 23c**

TEMPERATURE DEPENDENCE OF THE OH PROTON SHIFT OF METHANOL IN CCl₄

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Temperature (°C.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.0</td>
<td>139.0</td>
<td></td>
</tr>
<tr>
<td>29.0</td>
<td>138.0</td>
<td></td>
</tr>
<tr>
<td>33.5</td>
<td>136.0</td>
<td></td>
</tr>
<tr>
<td>38.0</td>
<td>134.0</td>
<td></td>
</tr>
<tr>
<td>45.0</td>
<td>132.0</td>
<td></td>
</tr>
<tr>
<td>55.0</td>
<td>128.0</td>
<td></td>
</tr>
<tr>
<td>61.0</td>
<td>125.5</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>122.5</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>111.0</td>
<td></td>
</tr>
<tr>
<td>55.0</td>
<td>99.0</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>114.0</td>
<td></td>
</tr>
<tr>
<td>39.5</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>56.0</td>
<td>80.0</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>96.0</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>78.0</td>
<td></td>
</tr>
<tr>
<td>58.0</td>
<td>55.0</td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td>45.0</td>
<td>63.0</td>
<td></td>
</tr>
<tr>
<td>54.0</td>
<td>50.0</td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>77.0</td>
<td></td>
</tr>
<tr>
<td>33.5</td>
<td>68.0</td>
<td></td>
</tr>
<tr>
<td>45.5</td>
<td>49.0</td>
<td></td>
</tr>
<tr>
<td>54.5</td>
<td>36.0</td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>55.0</td>
<td></td>
</tr>
<tr>
<td>33.5</td>
<td>42.0</td>
<td></td>
</tr>
<tr>
<td>45.5</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>54.0</td>
<td>14.5</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 23c cont'd.

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Temperature (°C.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.038</td>
<td>26.0</td>
<td>- 39.0</td>
</tr>
<tr>
<td></td>
<td>33.5</td>
<td>- 25.0</td>
</tr>
<tr>
<td></td>
<td>45.0</td>
<td>- 9.5</td>
</tr>
<tr>
<td></td>
<td>60.0</td>
<td>+ 8.5</td>
</tr>
<tr>
<td>.030</td>
<td>27.0</td>
<td>- 13.5</td>
</tr>
<tr>
<td></td>
<td>42.5</td>
<td>+ 11.0</td>
</tr>
<tr>
<td></td>
<td>47.0</td>
<td>+ 15.0</td>
</tr>
<tr>
<td></td>
<td>54.0</td>
<td>+ 22.0</td>
</tr>
</tbody>
</table>
FIG 9c TEMPERATURE-SHIFT CURVES

MeOH IN CCl₄
TABLE 24c

TEMPERATURE DEPENDENCE OF THE OH PROTON SHIFT OF METHANOL IN CHCl₃

<table>
<thead>
<tr>
<th>Concentration (m.f.)</th>
<th>Temperature (°C.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.277</td>
<td>26.0</td>
<td>-99.0</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>-96.0</td>
</tr>
<tr>
<td></td>
<td>36.0</td>
<td>-91.0</td>
</tr>
<tr>
<td></td>
<td>41.0</td>
<td>-87.5</td>
</tr>
<tr>
<td>0.163</td>
<td>29.0</td>
<td>-71.5</td>
</tr>
<tr>
<td></td>
<td>33.0</td>
<td>-68.0</td>
</tr>
<tr>
<td></td>
<td>41.0</td>
<td>-62.0</td>
</tr>
<tr>
<td></td>
<td>48.0</td>
<td>-55.0</td>
</tr>
<tr>
<td>0.090</td>
<td>25.0</td>
<td>-45.5</td>
</tr>
<tr>
<td></td>
<td>29.5</td>
<td>-40.5</td>
</tr>
<tr>
<td></td>
<td>37.0</td>
<td>-34.5</td>
</tr>
<tr>
<td></td>
<td>46.6</td>
<td>-27.5</td>
</tr>
<tr>
<td>0.073</td>
<td>27.0</td>
<td>-34.0</td>
</tr>
<tr>
<td></td>
<td>31.0</td>
<td>-31.0</td>
</tr>
<tr>
<td></td>
<td>38.0</td>
<td>-25.0</td>
</tr>
<tr>
<td></td>
<td>46.6</td>
<td>-18.5</td>
</tr>
</tbody>
</table>
TABLE 25c
TEMPERATURE SHIFTS FOR OH PROTONS
OF METHANOL

Methanol (Correction \( C_6H_{12}(l) \) to \(-OCH_3 = -76.5 \text{ c/s}\))

<table>
<thead>
<tr>
<th>Temperature (°C.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>-135.5</td>
</tr>
<tr>
<td>39</td>
<td>-130.5</td>
</tr>
<tr>
<td>61</td>
<td>-121.5</td>
</tr>
<tr>
<td>74</td>
<td>-113.5</td>
</tr>
<tr>
<td>95</td>
<td>-106.5</td>
</tr>
</tbody>
</table>

and 10c.

The measurements on pure methanol were later repeated, the temperature range being extended, and agreed well with the first set of results, being listed in Table 25c and plotted in Fig. 11c. (Fig. 11c also includes similar measurements made for water which are not strictly comparable, however, since an external cyclohexane marker was used.)

The variation of the chemical shift of the OH proton in triphenyl carbinol was examined in a 0.615 M solution in chloroform, using the aromatic proton peak as an internal reference. This shift (175 c/s) was found to remain constant over the temperature range 25° C. to 65° C.

(b) **Substituted Phenols**

The substances in Table 26c were examined.
TABLE 26c
REFERENCING PROCEDURES FOR SUBSTITUTED PHENOLS

<table>
<thead>
<tr>
<th>Compound</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Chlorophenol</td>
<td>C₆H₁₂</td>
</tr>
<tr>
<td>Salicylaldehyde</td>
<td>-CHO</td>
</tr>
<tr>
<td>Methyl Salicylate</td>
<td>-CH₃</td>
</tr>
<tr>
<td>o-Nitrophenol</td>
<td>C₆H₁₂</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>-OCH₃</td>
</tr>
<tr>
<td>o-Cresol</td>
<td>C₆H₁₂</td>
</tr>
</tbody>
</table>

All shifts have been expressed with reference to an internal cyclohexane marker.

An internal cyclohexane marker is more suitable than an external reference, since volume susceptibilities change due to density variations on rise in temperature. Also, the specific susceptibilities of hydrogen bonded substances have been shown to be temperature dependent (39). It is impossible to correct for these effects due to lack of sufficient data. However, the error involved is probably small. To test this assumption o-chlorophenol and guaiacol were studied using internal and external markers. In the case of o-chlorophenol, no change in the slope of the temperature shift curve was observed when an external cyclohexane marker was used. For guaiacol, however, a difference of 7 c/s was observed in the total shift on temperature rise, showing the temperature coefficients of the volume susceptibilities of guaiacol and cyclohexane to be appreciably different. The temperature shifts of these compounds are recorded in Tables 27c to 32c. All the shifts are plotted in Figs. 11c and 12c.
### TABLE 27c
TEMPERATURE SHIFTS FOR o-CHLOROPHENOL

<table>
<thead>
<tr>
<th>Temperature (°C.)</th>
<th>Shift (c/s; C₆H₁₂ l)</th>
<th>Shift (c/s; C₆H₁₂ E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.5</td>
<td>-201.0</td>
<td>-198.5</td>
</tr>
<tr>
<td>50.0</td>
<td>-190.0</td>
<td>-187.5</td>
</tr>
<tr>
<td>70.0</td>
<td>-182.0</td>
<td>-179.5</td>
</tr>
<tr>
<td>89.0</td>
<td>-178.0</td>
<td>-175.5</td>
</tr>
<tr>
<td>113.0</td>
<td>-174.5</td>
<td>-172.0</td>
</tr>
</tbody>
</table>

### TABLE 28c
TEMPERATURE SHIFTS FOR SALICYLALDEHYDE

**Correction**  
C₆H₁₂ (l) to -CHO = -322.5 c/s

<table>
<thead>
<tr>
<th>Temperature (°C.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>-378.5</td>
</tr>
<tr>
<td>41</td>
<td>-376.5</td>
</tr>
<tr>
<td>53</td>
<td>-375.5</td>
</tr>
<tr>
<td>68</td>
<td>-373.5</td>
</tr>
<tr>
<td>84</td>
<td>-371.0</td>
</tr>
<tr>
<td>104</td>
<td>-369.0</td>
</tr>
<tr>
<td>124</td>
<td>-366.5</td>
</tr>
</tbody>
</table>
### TABLE 29c
TEMPERATURE SHIFTS FOR METHYL SALICYLATE

**Correction**  
$C_6H_{12} (l)$ to $-OCH_3 = 95 \text{ c/s}$

<table>
<thead>
<tr>
<th>Temperature (°C.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>-376.0</td>
</tr>
<tr>
<td>53</td>
<td>-372.5</td>
</tr>
<tr>
<td>70</td>
<td>-370.0</td>
</tr>
<tr>
<td>90</td>
<td>-367.0</td>
</tr>
<tr>
<td>109</td>
<td>-364.0</td>
</tr>
</tbody>
</table>

### TABLE 30c
TEMPERATURE SHIFTS FOR $o$-NITROPHENOL

**Correction**  
$C_6H_{12} (l)$ to $C_6H_{12} (E) = -19 \text{ c/s}$

<table>
<thead>
<tr>
<th>Temperature (°C.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>-362.5</td>
</tr>
<tr>
<td>54</td>
<td>-363.5</td>
</tr>
<tr>
<td>74</td>
<td>-361.0</td>
</tr>
<tr>
<td>91</td>
<td>-361.0</td>
</tr>
<tr>
<td>121</td>
<td>-361.0</td>
</tr>
</tbody>
</table>
### TABLE 31c
TEMPERATURE SHIFTS FOR GUAIACOL

<table>
<thead>
<tr>
<th>Temperature (°C.)</th>
<th>Shift (c/s; C₆H₁₂ l)</th>
<th>Shift (c/s; C₆H₁₂ E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>- 210.0</td>
<td>- 201.5</td>
</tr>
<tr>
<td>39</td>
<td>- 203.5</td>
<td>- 195.5</td>
</tr>
<tr>
<td>52</td>
<td>- 197.7</td>
<td>- 190.3</td>
</tr>
<tr>
<td>71</td>
<td>- 192.0</td>
<td>- 185.5</td>
</tr>
<tr>
<td>95</td>
<td>- 185.0</td>
<td>- 180.5</td>
</tr>
<tr>
<td>124</td>
<td>- 179.5</td>
<td>- 178.0</td>
</tr>
</tbody>
</table>

### TABLE 32c
TEMPERATURE SHIFTS FOR o-CRESOL

<table>
<thead>
<tr>
<th>Temperature (°C.)</th>
<th>Shift (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>201.0</td>
</tr>
<tr>
<td>46</td>
<td>189.5</td>
</tr>
<tr>
<td>78</td>
<td>172.5</td>
</tr>
<tr>
<td>107</td>
<td>160.0</td>
</tr>
<tr>
<td>132</td>
<td>152.0</td>
</tr>
</tbody>
</table>
FIG I. TEMPERATURE-SHIFT CURVES

\[ \triangle H_2O \]
\[ \circ MeOH \]
\[ x \text{ Compound 1} \]
\[ \square \text{ Compound 2} \]
\[ \triangledown \text{ Compound 3} \]

\[ \text{SHIFT} \quad C/S \]

\[ \text{T} \quad ^\circ \text{C} \]
FIG 12c TEMPERATURE-SHIFT CURVES

\[ \triangle \quad \text{NO}_2 \quad \text{OH} \]

\[ \bullet \quad \text{COOCH}_3 \quad \text{OH} \]

\[ \times \quad \text{CHO} \quad \text{OH} \]

\[ -350 \quad M,P. \quad -390 \]

\[ 20 \quad T \quad \text{°C} \quad 100 \]
The o-chlorophenol, methyl salicylate and o-cresol were purified by drying with calcium sulphate and fractionating under reduced pressure. The salicylaldehyde was a technical sample and was purified by conversion to the copper chelate (40). The substance was added to a large excess of a lukewarm saturated solution of copper acetate, shaken well and allowed to stand for several hours in ice. The precipitate was filtered off and washed thoroughly with alcohol and ether. The ether was removed by distillation and the substance vacuum distilled into a sample tube. The o-nitrophenol was White Label grade and was purified by dissolving in ethanol under reflux and then adding water until a permanent milkiness was produced. The mixture was then set aside to cool. The crystals were filtered off and dried in a vacuum dessicator over P₂O₅, and afterwards melted into a sample tube (M.P. 44.9° C.). Gualacol was vacuum distilled into a sample tube, where it remained liquid at room temperature although below its M.P. of 28.2° C. All samples were sealed off in vacuo.

DISCUSSION

(a) Introduction

Three principal effects will be expected to influence the degree of hydrogen bonding in solutions of alcohols in an inert solvent such as carbon tetrachloride. These are,

(1) Electronic effects which may broadly be divided into,
    (a) Inductive effects.
    (b) Resonance effects.

(ii) Steric effects.

(iii) Other types of molecular association.

The electronic effects influence the polarity of the bond in ROH by providing mechanisms for electron release or withdrawal by the group R.
The polarity of the OH bond is thus determined by the effective relative electronegativities of the groups R. In aliphatic alcohols, inductive effects are of greater importance than resonance effects and the ground states of these molecules may be simply considered as a mixture of two resonance structures A and B with weights a and b respectively

\[ R - O - H \quad R - \overset{\ddagger}{O} \quad H \]

\[ A \quad B \]

The wave function of the molecule is thus of the form

\[ \psi_{ROH} = \sqrt{a} \psi_A + \sqrt{b} \psi_B \]

where

\[ a + b = 1 \]

The weight b will depend on the extent to which R can withdraw electrons from the OH bond, i.e. the greater the electronegativity of the group R, the greater the contribution of the resonance structure B. The dependence of the hydrogen bonding strength on b may be determined approximately as follows. The energy of the hydrogen bond is assumed to be largely electrostatic, which seems to be a fair approximation in the case of long hydrogen bonds, as exemplified by systems containing alcohols, the bonds being about 2.7 Å in length. Thus, for an O - H .... O hydrogen bond of length 2.65 Å, with an OH bond length of 1 Å, Coulson and Danielsson (41) have calculated by a semi-empirical wave mechanical method the weights of the electrostatic and delocalization valence bond structures C and D to be 12.6% and 2.4% respectively, assuming pure p orbitals.

\[ \overset{\ddagger}{O} \quad H .... \quad O \quad \overset{\ddagger}{O} \quad H ---- \overset{\ddagger}{O} \]

\[ C \quad D \]

For pure sp\(^3\) hybrids, the weights are 12.2% and 4.1% respectively. The delocalization contribution decreases as the O .... O distance increases...
and so the electrostatic energy seems to be the predominant term in this case. A more recent review article by Coulson (42) indicates that the electrostatic contribution may not be as important as the above calculations suggest, and that the effect of dispersion and exchange forces is appreciable in some cases, particularly for short hydrogen bonds. It will be assumed for the present, however, that a change in the value of \( b \) makes important alterations to the value of the electrostatic attraction term only.

Using a point charge approximation and assuming that only the OH bond dipole contributes appreciably to the electrostatic energy term, the following model for the hydrogen bond results.

\[
\begin{align*}
0 & \quad \text{H} \quad \cdots \cdots \quad 0 \\
- \text{be} & \quad + \text{be} & - \text{be} & + \text{be} \\
& \quad \overleftrightarrow{r_1} & \quad \overleftrightarrow{r_2} & \quad \overleftrightarrow{r_3}
\end{align*}
\]

This model requires the further assumption of free rotation about the hydrogen bond, so that the positive end of the donor molecule may be replaced by an effective charge, \(+\text{be}\), on the hydrogen bond axis as shown, at a distance \( r_3 \) from the donor oxygen atom. The electrostatic energy term, \( w \), may thus be written as

\[
w = -\frac{b^2e^2}{(r_2-r_1)^2} + \frac{b^2e^2}{r_2^2} + \frac{b^2e^2}{(r_2-r_1+r_3)^2} - \frac{b^2e^2}{(r_2r_3)^2} \quad \ldots \quad 9
\]

In this geometry, the negative attractive terms outweigh the positive repulsive terms due to their inverse dependence on the squares of the distances, i.e.,

\[
\left| \frac{1}{(r_2-r_1)^2} + \frac{1}{(r_2+r_3)^2} \right| > \left| \frac{1}{r_2^2} + \frac{1}{(r_2-r_1+r_3)^2} \right| \quad \ldots \quad 10
\]
so that a net attraction term always results. (This may easily be verified by substituting suitable values for \( r_1, r_2, r_3 \), i.e. \( r = 2.7 r_1 \) and \( r_3 > 0 \)). Thus, the electrostatic energy term may be written in the form

\[
\omega = b^2 e^2 C
\]

where \( C < 0 \). Hence,

\[
\frac{d\omega}{db} = 2 b e^2 C
\]

and so \( d\omega/db < 0 \), i.e. it appears that as \( b \) is increased, the energy of the hydrogen bond also increases. Thus, on this basis, we might expect the hydrogen bond strength in benzyl alcohol to be greater than that in methanol, due to the greater electron withdrawing power of the phenyl group as compared with the hydrogen atom (43).

Resonance effects are of importance in the case of aromatic alcohols, since when \( R \) is an aromatic ring, stabilization of the ionic structure \( B \) by resonance is possible. Thus, for phenol three possible structures contribute to \( B \) i.e.,

\[
\begin{align*}
\text{phenol} & \quad \text{OH} \\
\text{resonance forms} & \\
\text{B}
\end{align*}
\]

However, a more important factor is the possibility of the existence of resonance structures of the forms,

\[
\text{resonance forms}
\]

which are responsible for the lower value of the gas phase dipole moment of phenol (1.4 D) as compared with that of methanol (1.7 D) (44). These structures seem to be of more importance than those which stabilize the ionic structure \( B \), and would be expected to lead to a lower value of the
hydrogen bond energy.

The effects of steric interactions on hydrogen bonds will be expected to be large when \( R \) is a bulky group such as \( \Phi_3C^- \). In such a case, the approach of donor and acceptor groups necessary for hydrogen bond formation will be hindered or prevented entirely. Conceivably, these steric effects may operate in an opposite sense to the electronic effects discussed above. Thus, in the case of phenyl groups, which are inductively electron withdrawing with respect to \( H^- \) or \( CH_3^- \) groups and therefore more favourable to hydrogen bond formation, overcrowding in the region of the \( OH^- \) groups may inhibit hydrogen bond formation.

The possibility of competition between various types of molecular interaction also seems to be of importance in determining the degree of particular hydrogen bonding interactions. This point will be made clear in the discussion of acetylenic alcohols, where \( TT \) electron association is possible, and chloroethanols, where \( Cl \ldots \ldots \ldots O-H \) interactions have been postulated.

The above considerations will be used to discuss the previously mentioned hydrogen bonding phenomena observed by nuclear resonance techniques, and also to relate these phenomena to other observations concerning infrared intensities, dipole moments, acidities, etc.

(b) Methanol and related compounds

The curves of Figs. 1c and 2c indicate a marked difference in the behaviour of the \( OH \) proton shifts of the various alcohols on dilution. The curve for methanol is unique in that it exhibits a point of inflection at a concentration of \(~0.01\) m.f. which enables the limiting shift at infinite dilution and hence the total association shift* to be found with some accuracy. It seems probable that the curves for benzyl and \( dl-\alpha \)-methyl

* The difference in chemical shift between the \( OH \) proton in the pure liquid and in the liquid at infinite dilution (found by extrapolation of dilution shift curve).
benzyl alcohols also possess similar points of inflection at concentrations which are inaccessible to measurement.

In this series of compounds we should expect steric and inductive effects (resonance effects are unimportant) to operate in opposite senses. Replacing the hydrogen atoms of the CH$_y$ group in methanol by relatively electron withdrawing phenyl groups should enhance the hydrogen bond strength, since the polarity of the -OH group will be increased as discussed previously. On the other hand, this process will eventually lead to overcrowding in the neighbourhood of the -OH group and result in steric inhibition of hydrogen bond formation. The association shift of methanol is $180 \pm 2$ c/s, whereas that for benzyl alcohol is $208 \pm 5$ c/s. (This is probably an overestimate since a virtually linear extrapolation to infinite dilution was made, which results in a greater isolated molecule shielding for the OH protons of benzyl alcohol than for the similar proton of methanol. This is unlikely in view of the relative electron withdrawing powers of the phenyl and methyl groups. However, any error introduced this way is not likely to lower the above figure by more than 10 c/s.) This difference indicates stronger hydrogen bonding in the case of benzyl alcohol and shows that steric effects are unimportant. The association shift for dl-$\alpha$-methyl benzyl alcohol is $188.5 \pm 5$ which is possibly slightly greater than that found for methanol and considerably less than that found for benzyl alcohol. This is to be expected since the methyl group has a greater electron donating power than a hydrogen atom and will tend to weaken the hydrogen bond. Any steric effect due to the methyl group would also be expected to lower the association shift as compared with benzyl alcohol.

For the other three alcohols, only a limited concentration range could be studied but this was sufficient to show in all three cases that steric effects outweigh the inductive effects of the substituent groups. The slopes
of the dilution-shift curves are all considerably less than the previously discussed curves and become smaller as the number of bulky groups is increased. For triphenyl carbinol, the -OH shift is found to be virtually independent of concentration, indicating at the most only weak hydrogen bonding, a conclusion borne out by infra-red studies (45). A band at the position usually associated with the formation of polymeric species higher than dimers (i.e. 3330 cm⁻¹) was not found for triphenyl carbinol. This corroborates earlier work by Fox and Martin (46) who found that the association band decreased in the series φCH₂OH, φ₂CHOH, φ₃COH. Molecular models of triphenyl carbinol indicate that hydrogen bonding to polymeric species larger than dimers is not possible. The previously mentioned constancy of the -OH proton resonance shift of triphenyl carbinol on alteration of temperature also indicates the small degree of hydrogen bonding in this system.

The form of the dilution shift curve for methanol merits further comment. It is thought that at high concentrations methanol exists as a variety of polymeric species. X-ray scattering investigations of the pure liquid indicate that the average coordination number, C, of methanol is approximately two (47) (48) (49) and Kirkwood in his theory of the dielectric constant of associated liquids assumed that the molecules were present in the form of infinite chains. However, a value of C very close to 2 is obtained by assuming that an appreciable fraction of the polymers present are cyclic. Thus, if

\[ s = \text{Fraction of cyclic polymers} \]
\[ 1 - s = \text{"" linear ""} \]
\[ n = \text{Average no. of molecules in the polymers} \]

it can be shown that,
\[ C = \frac{2(n-2)}{n} + 2(1-s) + 2s \]  

If \( n = 4 \) (a value of 3.83 has been found by Ens and Murray (51) on the basis of infra-red investigations) and \( s = 0.8 \), then \( C = 1.90 \), so that a coordination number approaching 2 is possible for quite small values of \( n \) if cyclic polymers are considered.

It seems probable that the flat portion of the methanol curve at high concentrations represents the concentration range where interconversions of the type

\[ (\text{ROH})_n \rightleftharpoons (\text{ROH})_{n-1} + \text{ROH} \]

are occurring where \( n > 2 \). The steeply ascending portion of the curve represents the stage where the polymers are breaking down into monomers and dimers, while in the third portion (concentration < 0.01 m.f.) a monomer-dimer equilibrium largely predominates.

\[ 2 \text{ROH} \rightleftharpoons (\text{ROH})_2 \]

A justification for this view was obtained from infra-red studies on methanol at low dilutions in carbon tetrachloride (45) (52). At certain concentrations, the I.R. spectrum of the \(-\text{OH}\) group shows three distinct peaks which have been assigned to monomer (3643 cm\(^{-1}\)), dimer (3528 cm\(^{-1}\)) and polymer (~3330 cm\(^{-1}\)) respectively. By assuming that the dimer is linear, i.e. has structure I rather than structure II,

\[ \begin{align*}
  & \text{I} \\
  & \begin{array}{c}
   \text{R} - \text{O} \\
   \text{H} \\
   \text{O} \\
   \text{H} \\
   \text{R}
  \end{array} \\
  & \begin{array}{c}
   \text{R} - \text{O} \\
   \text{H} \\
   \text{O} \\
   \text{R}
  \end{array}
\end{align*} \\
\begin{align*}
  & \text{II} \\
  & \begin{array}{c}
   \text{R} - \text{O} \\
   \text{H} \\
   \text{O} \\
   \text{R}
  \end{array} \\
  & \begin{array}{c}
   \text{R} - \text{O} \\
   \text{H} \\
   \text{O} \\
   \text{R}
  \end{array}
\end{align*} 

and that the integrated absorption intensity of the dimer \(-\text{OH}\) is twice as great as the monomer \(-\text{OH}\) group intensity, the concentrations of monomer and
dimer were estimated from the total band intensities, in the region where the polymer band is of negligible intensity. A linear relation between the dimer concentration and the square of the monomer concentration was found (Fig. 13c) indicating that in the low concentration region an equilibrium defined by,

$$K = \frac{[(\text{MeOH})^2]}{[\text{MeOH}]} \sim 7$$

exists, the concentrations being expressed in mole fraction units. This value agrees well with that found by Liddel and Becker (52) who found $K \sim 3$ for a cyclic dimer and $K \sim 6$ for an open dimer. Huggins et al. (6) have related the limiting slopes of dilution shift curves to a dimer dissociation constant by making the following assumptions.

(a) The data extend to sufficiently low concentrations, $X$, to give a true limiting slope where only monomers and dimers are important.

(b) The observed shift $\delta$ is a weighted mean of $\delta_m$ and $\delta_d$, assumed characteristic values of $\delta$ for pure monomer and pure dimer respectively. If the dimers contain two distinct kinds of protons, which is the case if a linear dimer is assumed, then $\delta_d$ is the mean of the characteristic $\delta$'s of the two.

Hence, if,

$$d = \text{mole fraction of dimer}$$

$$m = \text{mole fraction of monomer}$$

$$x = \text{total moles of methanol in all forms}$$

$$m = \text{moles of monomer at equilibrium}$$

$$s = \text{moles of solvent}$$

we have,

$$\delta = \frac{m}{x} \delta_m + \frac{1}{x} (\frac{x-m}{x}) 2 \delta_d$$
FIG 13c MONOMER-DIMER EQUILIBRIUM IN MeOH/CCI₄ SOLUTIONS

\[ \text{CONC of Dimer M/l} \]

FIG 14c %H BONDED SPECIES vs %NMR SHIFT FOR MeOH/CCI₄ SOLUTIONS

- ○ % PROTONS IN DIMER + POLYMER
- × % PROTONS IN POLYMER ONLY
- * 0.32% DIMER + POLYMER PROTONS
or,

$$\delta = \delta_d - \frac{m}{x} \Delta_d$$

where $$\Delta_d = \delta_d - \delta_m$$. Hence,

$$K = \frac{X_d}{X_m^2} = \frac{(x - m)(2s + x + m)}{4m^2}$$

Then, in the limit as $$X \rightarrow 0$$ we have,

$$\delta = \delta_m$$

and,

$$\left( \frac{d\delta}{dX} \right)_{x=0} = 2K \Delta_d$$

From Fig. 2c, the value of $$\left( \frac{d\delta}{dX} \right)_{x=0}$$ for methanol is $$(-10.3 \pm 2.7) \ 0.02$$.

Using the value of $$K$$ obtained above we have,

$$\Delta_d = \frac{-10.3 \pm 2.7}{0.02 \cdot 2 \cdot 7} = -37 \pm 10 \text{ c/s} \quad 20$$

Thus if the dimer is considered to be linear, $$\delta_d = -37 \pm 10 \text{ c/s}$$

$$\delta_m = 0$$ and the decrease in shielding for the hydrogen bonded proton is $$2\delta_d$$.

Infra-red data were also used to estimate the total amount of methanol present as polymers of all kinds over the whole concentration range assuming the integrated absorption intensities of polymers higher than dimers to be ten times as large as the monomer intensity (52) (53). The percentage of total polymer was plotted against the percentage NMR shift (Fig. 14c). This resulted in a non-linear graph, indicating that all the polymeric species are not contributing equally to the association shift. The percentage of all polymers excluding dimers was then plotted, the amount of dimer being determined from the I.R. data. This plot is also shown in Fig. 14c and resulted in a curvature in the opposite sense to the previous graph. A 'best fit' curve of the form below was then drawn,
\[
\% \text{ NMR shift} = \% (\text{polymers} > 2) + C (\% \text{ dimer}) \quad \cdots \quad 21
\]

A straight line resulted from the choice \( C = 0.32 \), and is shown in Fig. 14c. This indicates that a proton involved in dimer formation contributes only one third as much to the association shift as a proton involved in polymer formation. This result is in accord with the fact that in the sterically hindered alcohols mentioned earlier where dimer formation is relatively more important at a given concentration than is the case in methanol, the total association shift is less.

In this connection the dilution-shift curve of methyl ethyl tert-butyl carbinol is of interest (Fig. 7c). This is expected to be a highly hindered alcohol so far as hydrogen bonding is concerned and has a low association shift of \( 66 \pm 5 \text{ c/s} \), in agreement with this prediction. The I.R. spectra of this substance in carbon tetrachloride solution (45) indicated that a monomer-dimer equilibrium is predominant to high concentrations, in contrast to the case of methanol. A plot of the dimer concentration versus the concentration of monomer squared was made and is shown in Fig. 15c, and is essentially linear over a wide concentration range, showing that polymeric species with \( n > 2 \) are present in small concentration only.

The apparent intrinsically larger association shift of higher polymeric species than dimers requires an explanation. A possible suggestion is that these species are present as cyclic forms such as,

\[
\begin{array}{c}
H \\
R \\
O
\end{array}
\begin{array}{c}
O \\
H \\
R
\end{array}
\begin{array}{c}
H \\
R
\end{array}
\begin{array}{c}
O \\
H \\
R
\end{array}
\]

In which there is a possibility of current circulation around the six-membered ring system of oxygen and hydrogen atoms. This idea is to some
FIG 15c

MONOMER-DIMER EQUILIBRIUM IN MeEt/t-BuCOH/CCl₄ SOLUTIONS
extent analogous to the π electron circulation proposed in the case of aromatics to explain the large shift to low field of aromatic protons as compared with ethylenic protons (54). In this case, however, such an explanation requires a circulation of σ electrons and the assumption that the protons are largely outside the current loop. Coulson (42) has recently estimated that the delocalization energy in a single O—H .... O bond is of the order of 8 k/cals, which is of the same order of magnitude as the exchange interaction between a pair of orbitals on the same oxygen atom (55). Hence, delocalization can embrace all six atoms and allow a circulation of π electrons around the six-membered ring system. Circulation would not be expected to occur in the σ bond system of alicyclic compounds due to the large difference in exchange energy in a C=C bond and that between orbitals on the same atom. Such an explanation thus also requires that the dimers in alcohol solutions should be linear rather than cyclic. There is little real evidence on this point at present. Matrix isolation studies of the l.R. spectra of water and methanol have been interpreted in terms of cyclic dimers (13) (56), but extrapolation of this conclusion to room temperature in a non-rigid medium seems unjustifiable.

Delocalization of the type mentioned above may also be of importance in explaining the large association shift of acetic acid (16) when forming cyclic dimers and the small shifts of chloroform in acetone or triethylamine to give linear dimers (4).

(c) Acetylenic Alcohols

The dilution shift curves of acetylenic alcohols plotted in Fig. 4c are not strictly comparable, since propargyl alcohol was studied in a chloroform solvent and the others in carbon tetrachloride. The former showed a well defined inflection point at low concentrations, which enabled
the limiting shift at low dilutions to be found precisely. The association shift was $126 \pm 2$ c/s. This is lower than the corresponding value of $145 \pm 2$ c/s found for methanol in chloroform (8), which is surprising in view of the greater electron attracting power of the $\text{HC} \equiv \text{C-CH}_2-$ group as compared with the $\text{CH}_3-$ group. The greater shielding of the $-\text{OH}$ proton in methanol at infinite dilution is evidence of the reality of this effect, the difference in shifts being $20 \pm 2$ c/s. On this basis we might expect a greater association shift for propargyl alcohol. However, the case of the acetylenic alcohols is complicated by the possibility of associations of the following types in addition to normal hydrogen bonding,

$$\begin{align*}
\text{C} & \equiv \text{C-H} \quad \text{III} \\
\text{C} & \quad \text{C} \\
\text{II} & \quad \text{H} \\
\text{-CH}_2-\text{O-H} & \quad \text{III} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H}
\end{align*}$$

Association of type I has been shown to be of importance in the case of pure acetylene (22) where the gas to liquid association shift is 56 c/s. The association shifts in solution for the acetylenic protons in these compounds are of the order of 13 c/s, a similar value being found for the acetylenic proton in propargyl acetate. Possibly, the lower association shift of propargyl alcohol is due to a certain degree of competition between normal hydrogen bonding equilibria and the equilibria whose products are represented by structures I, II and III.

The association shift of 3-butyn-2-ol is $157 \pm 5$ c/s which compares with a value of $114 \pm 5$ c/s for 2-methyl-3-butyn-2-ol. This order is to be expected in view of the larger electron donating power of the groups
attached to the $\alpha$-carbon atom in 2-methyl-3-butyn-2-ol. Also, substitution of an extra methyl group may conceivably increase the steric hindrance to hydrogen bonding. The association shift for 2-butyn-1-ol is $156 \pm 5$ c/s, i.e. there appears to be no significant difference from the shift for 3-butyn-2-ol. Apparently the methyl groups in the two isomers have a similar effect in reducing the electron attracting power of the $-\text{C} \equiv \text{C}-$ group.

Thus, in this series of alcohols, the inductive effect seems to predict the expected order of association shifts but comparison with the substituted methanols described earlier is not possible due to the presence of other types of molecular association in solutions of acetylenic alcohols.

(d) Chloroethanols

The association shifts and the chemical shifts at infinite dilution of the OH proton for these alcohols and ethanol obtained from Fig. 6c are shown in Table 33 c. The trend of the association shifts is not that to be expected from a consideration of the inductive effect which predicts an increase in hydrogen bond strength and thus an increase in association shift as the number of chlorine atoms is increased. The order of the limiting shifts at infinite dilution is as would be expected, however, since the shielding decreases as the number of chlorine atoms is increased. It would not be expected that steric effects would play a large part in determining the degree of hydrogen bonding in this series since although the $\text{CCl}_3$- group is considerably larger than a $\text{CH}_3$- group, it is sufficiently far removed from the OH- group to be unimportant sterically.

A possible explanation of the above order of association shifts is in terms of the occurrence of inter- and intramolecular associations of the type,
Associations of the type II would be expected to decrease the shielding of the OH proton in the isolated molecule, thereby lowering the association shift, the effect becoming of more importance as the number of chlorine atoms is increased. Associations of type I would become of importance at high concentrations and would also increase with increase in chlorine content. If it is assumed that the energy of the \( O - H \cdots Cl \) bond is lower than that of an \( O - H \cdots O \) hydrogen bond, which is almost certainly the case, competition between these two forms of association at high concentrations will result in an increase in the average OH proton shielding in the pure liquid. This will also reduce the association shift.

### TABLE 33c

ASSOCIATION SHIFTS AND SHIFTS AT INFINITE DILUTION FOR CHLOROETHANOLS

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Association Shift (c/s)</th>
<th>Limiting Shift (c/s from internal ( C_6H_{12} ) mkr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_3CH_2OH )</td>
<td>180 ± 2</td>
<td>+ 26 ± 2</td>
</tr>
<tr>
<td>( CH_2ClCH_2OH )</td>
<td>137 ± 5</td>
<td>- 5 ± 5</td>
</tr>
<tr>
<td>( CHCl_2CH_2OH )</td>
<td>137 ± 5</td>
<td>- 13 ± 5</td>
</tr>
<tr>
<td>( CCl_3CH_2OH )</td>
<td>132 ± 5</td>
<td>- 27 ± 5</td>
</tr>
</tbody>
</table>

Interactions of this type have recently been demonstrated in the case of \( \delta \)-haloethanols by Schleyer and West, using I.R. techniques (56a). They also showed the existence of intermolecular bonding of the type \( X \cdots H \cdots O \), where \( X \) is a halogen, between alkyl halides and methanol and phenol, the strength of the interaction being in the order \( I > Br > Cl > F \).
Further Studies on Alcohols

In Fig. 7c, the dilution shifts of propanol, allyl alcohol and methyl ethyl tert-butyl carbinol are compared. The latter has already been discussed in connection with the dilution-shift curve for methanol and the conclusion reached that there is a considerable degree of steric hindrance to hydrogen bonding in this compound.

Propanol and allyl alcohol were studied in order to determine the effect of the presence of the ethylenic linkage in the latter upon the shape of the dilution shift curve. This was found to be small and the curves gave a similar value for the limiting OH proton shift at infinite dilution. Neither curve showed an inflection point and so this quantity could not be accurately determined.

Acrylic Acid

The dilution-shift curve for acrylic acid in carbon tetrachloride (Fig. 8c) shows an initial shift to low field, indicating a decrease in the average proton shielding, until a mole fraction of ~0.1 is reached. This concentration marks a minimum in the curve and the proton shielding increases sharply on further dilution. A similar behavior was found by Reeves and Schneider (16) for acetic acid, and by Reeves (57) for trifluoroacetic acid. They interpreted the initial low field shift in terms of the presence of linear polymeric species at high concentrations, which on dilution break down into cyclic dimers. This involves the assumption that the shielding value characteristic for dimer protons is lower than that for polymer protons, which is in accord with the earlier discussion of the effect of delocalization energy on hydrogen bonding shifts. The form of the dilution shift curve for acrylic acid in carbon tetrachloride is very similar to that for acetic acid in the same solvent and so a
similar explanation for the initial low field shift on dilution probably applies. The proton shift in the pure liquid is $15 \pm 1$ c/s lower than that found for acetic acid as a result of the inductive effect of the CH$_2$ = CH- group. This difference is reflected in the greater strength of acrylic acid as compared with acetic acid.

The dilution-shift curves with dioxane and acetone as solvents show a very fast increase in proton shielding with concentration, with no initial downward trend. These solvents are capable of hydrogen bonding themselves and are able to break up the acid dimers and polymers more easily than inert solvents like carbon tetrachloride. The limiting shifts at infinite dilution in these cases give the shieldings for an acid proton hydrogen bonded to a solvent molecule.

(g) The effect of temperature on methanol OH resonances

The form of the temperature-shift curves for solutions of methanol in carbon tetrachloride (Fig. 9c) confirm the conclusions drawn from a consideration of the dilution-shift curve. The values of the slopes of the temperature-shift curves, $d\delta /dT$, under various conditions are given in Table 34c. The slope for pure methanol is constant over the temperature range investigated. On dilution, the slope increases up to a certain limit, a solution containing 0.069 mole fractions of methanol having a slope of 1.475 cycles/°C. Curves in this concentration range corresponding to the parts of the dilution-shift curve where the shift is changing rapidly with increase in concentration. At lower concentrations, e.g. 0.03 mole fractions, the temperature-shift curves become non-linear, corresponding to the region where the monomer-dimer equilibrium is of importance. The temperature-shift curves in chloroform solutions are of a similar kind (Fig. 10c). For a given concentration, the curves for carbon tetrachloride
TABLE 34c
SLOPES OF TEMPERATURE-SHIFT CURVES FOR METHANOL

<table>
<thead>
<tr>
<th>Solution</th>
<th>$\frac{d\delta}{dT}$ (cycles/°C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure methanol</td>
<td>0.370</td>
</tr>
<tr>
<td>0.092 m.f. in CCl₄</td>
<td>1.425</td>
</tr>
<tr>
<td>0.069 m.f. in CCl₄</td>
<td>1.475</td>
</tr>
<tr>
<td>0.090 m.f. in CHCl₃</td>
<td>0.780</td>
</tr>
</tbody>
</table>

Solutions have a greater slope than those for chloroform solutions (Table 34c). This is in accord with the smaller slope of the MeOH/CHCl₃ dilution-shift curve (58) as compared with the MeOH/CCl₄ curve in this concentration region. The change in shielding per degree temperature rise is less because when a methanol-methanol hydrogen bond is broken, the energy required is partially offset by the formation of a methanol-chloroform bond.

These temperature-shift curves allow the calculation of an average hydrogen bond energy in a particular solution if I.R. data are used to estimate the amount of monomer present. Suppose the equilibrium at a particular concentration is of the form,

$$n \text{ ROH} \rightleftharpoons (\text{ROH})_n$$

where $n$ is the average number of molecules in the polymers. We can then define an equilibrium constant

$$K = \frac{[(\text{ROH})_n]}{[\text{ROH}]^n}$$

The total association shift for methanol is 180 c/s, the shift for the pure compound at 20°C. with respect to an internal cyclohexane marker being 141 c/s. At 20°C. a 0.719 M (0.069 m.f.) solution has a shift of -87 c/s (Fig. 9c). Hence, the association shift at 20°C. is given by
\[ \Delta_{20} = (180 - 141) + 87 = 126 \text{ c/s} \]  

At 70°C, this solution has a shift of -27 c/s. Thus,

\[ \Delta_{70} = (180 - 141) + 27 = 66 \text{ c/s} \]

Thus, the percentage association shifts, \( \Delta' \), are

\[ \Delta'_{20} = \frac{126}{180} \times 100 = 70\% \]

\[ \Delta'_{70} = \frac{66}{180} \times 100 = 36.5\% \]

From the graph of percentage hydrogen bonded species versus percentage shift (Fig. 14c) we may obtain the percentage of methanol present as polymers. Thus, for this solution at 20°C, 81.5% of the methanol is present as polymers and at 70°C, 52%. The corresponding amounts of monomer are thus,

- 18.5% monomer at 20°C.
- 48.0% monomer at 70°C.

Hence, at 20°C, the concentration of monomer is,

\[ [\text{ROH}]_{20} = \frac{0.719 \times 18.5}{100} = 0.133 \text{ M} \]

The polymer concentration at 20°C is

\[ [(\text{ROH})_n]_{20} = \frac{0.719 \times 81.5}{n \times 100} = 0.585 \text{ M} \]

Similarly at 70°C,

\[ [\text{ROH}]_{70} = \frac{0.719 \times 48.0}{100} = 0.345 \text{ M} \]

\[ [(\text{ROH})_n]_{70} = \frac{0.719 \times 52.0}{n \times 100} = 0.373 \text{ M} \]

Thus, the respective equilibrium constants are

\[ K_{20} = \frac{0.585}{n(0.133)^n} \]

\[ K_{70} = \frac{0.345}{n(0.373)^n} \]

Integration of the van't Hoff equation between the limits \( T_1 \) and \( T_2 \) gives
\[ \log_{10} \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H}{4.576} \left( \frac{T_1 - T_2}{T_1 T_2} \right) \]

where \( R \) is in cals. deg\(^{-1}\) moles\(^{-1}\). Hence,

\[ \log_{10} \left( \frac{0.345}{n(0.373)^n} \cdot \frac{n(0.133)^n}{0.585} \right) = \frac{\Delta H}{4.576} - \frac{50}{293 \cdot 343} \]

Hence, it may easily be shown that,

\[ \Delta H = C \left[ \log_{10} A + n \log_{10} B \right] \]

where \( \Delta H \) is the average heat of formation of the polymers and \( A \) and \( B \) are constants for a particular concentration. \( \Delta H \) is thus linearly dependent on the value of \( n \). In this case,

\[ \Delta H \approx -9.197 \times 10^3 \left( 0.229 + n 0.455 \right) \]

\( \Delta H \) calculated for various values of \( n \) is given in Table 35c, along with values of hydrogen bond energies for linear and cyclic polymers defined as,

\[ \Delta H_{\text{lin}} = \frac{\Delta H}{n-1} \]

\[ \Delta H_{\text{cyc}} = \frac{\Delta H}{n} \]

All energies are in kilocalms. mole\(^{-1}\).

**TABLE 35c**

**AVERAGE HYDROGEN BOND ENERGIES IN 0.719 M MeOH/CCl\(_4\) SOLUTION**

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \Delta H )</th>
<th>( \Delta H_{\text{lin}} )</th>
<th>( \Delta H_{\text{cyc}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>-12.57</td>
<td>-8.38</td>
<td>-5.03</td>
</tr>
<tr>
<td>3.0</td>
<td>-14.67</td>
<td>-7.34</td>
<td>-4.89</td>
</tr>
<tr>
<td>3.5</td>
<td>-15.76</td>
<td>-6.30</td>
<td>-4.50</td>
</tr>
<tr>
<td>4.0</td>
<td>-17.85</td>
<td>-5.95</td>
<td>-4.46</td>
</tr>
</tbody>
</table>
Assuming a value of $n$ in the range $3.0 < n < 4.0$, these values agree quite well with others quoted in the literature (59) but do not allow a distinction to be made between linear and cyclic polymers.

(h) **The temperature coefficients of the shifts of substituted phenols**

The temperature shift curves for substituted phenols fall into two well defined groups. O-cresol, o-chlorophenol and guaiacol gave non-linear curves over the temperature range investigated, i.e. from $20^\circ\text{C}$. to $120^\circ\text{C}$. approximately. The shifts of the OH proton in all the pure substances were similar ($\approx 205$ c/s). The second group consisted of salicylaldehyde, methyl salicylate and o-nitrophenol, where the temperature shift curves were all linear over a similar temperature range, the OH proton shifts in the pure substances being in the region of $\approx 350$ c/s.

A considerable number of infra-red investigations of substances of this type have been made, and before interpreting the above data, the available evidence as to the nature of hydrogen bonding in these compounds will be discussed. O-chlorophenol was shown to have two bands in the OH fundamental region (60) the separation being $50$ cm$^{-1}$, a similar splitting of the first overtone band having previously been observed (61). Pauling had suggested that these bands arose from cis and trans forms of the compound as shown below (62),

![cis form](image1)

![trans form](image2)

the cis form being of lower energy due to the weakening of the OH bond through interaction with the chlorine atom. He estimated from intensity data that the cis form had a $10:1$ preponderance over the trans form at
room temperature, this ratio decreasing on temperature rise since the trans molecules possess a higher potential energy. Fox and Martin (63) studied methyl salicylate and found no trace of a monomeric OH band at 3600 cm\(^{-1}\) in a 0.017 M solution. The band was found to be shifted due to intramolecular association to 3200 cm\(^{-1}\), the substance existing entirely in the cis configuration.

Lüttke and Mecke (64) studied the second overtones of the OH stretching region for a variety of o- substituted phenols and divided these substances into two classes,

(a) Those having the substituents, Halogen, OH, OCH\(_3\), CN and C\(_6\)H\(_5\). These showed two sharp bands of varying intensity ratio, corresponding to the presence of cis and trans forms of the molecule.

(b) Those containing the substituents, NO\(_2\), CHO, COOR, COR. These showed a single broad band at a much lower frequency, indicating the presence of the cis form only and the presence of much stronger hydrogen bonding than in class (a).

Similar data has recently been obtained by Baker and Shulgin (64a) for o-halophenols and o-phenyl phenol. They have also shown the importance of weak interactions between OH bonds and >C = C< bonds in cases where this results in intramolecular ring formation. Such weak interactions are of more importance in these cases due to favourable entropy considerations, the entropy change being much less in the formation of an intramolecular bond than in intermolecular bond formation.

Huggins et al. (6) investigated the dilution shifts of a variety of substituted phenols including o-, m- and p-chlorophenol. The dilution shift of the ortho compound was distinguished from the others by showing a point of inflection at a concentration of 0.2 mole fractions and an
almost zero limiting slope, \((d \delta/d\chi)_{x=0}\). This was interpreted in terms of the predominance of the intramolecularly hydrogen bonded form at low concentrations. The association shift for o-chlorophenol was also considerably less than that for the other two isomers in agreement with the above interpretation.

The two groups into which the temperature shift curves fall correspond exactly to the division of these compounds made by Lüttke and Mecke on the basis of I.R. data. The smaller shielding of the OH protons in class (b), and the diminished OH stretching frequencies as compared with class (a), indicate the presence of much stronger hydrogen bonds in these compounds. For the compounds in class (b), hydrogen bond formation involves the formation of a six-membered ring as shown below,

\[
\begin{align*}
&\text{Class (b)} \quad \text{Class (a)} \\
&\begin{array}{c}
\text{OH} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \quad \begin{array}{c}
\text{OH} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \\
&\text{Class (c)} \\
&\begin{array}{c}
\text{OH} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array}
\end{align*}
\]

whereas class (a) requires a five-membered ring. This involves greater strain in the bonds concerned and a more bent hydrogen bond. The bond formed is thus weaker. Also, in the case of the six-membered chelate forms, besides the ionic and covalent forms contributing to hydrogen bonding, a further form involving delocalization of the TT electrons can contribute (65). These forms are as shown.

\[
\begin{align*}
&A \quad B \quad C
\end{align*}
\]
The non-ionic structure C may be more stable than B although its formation involves the loss of the aromatic resonance energy. (This is partially offset by the resonance energy of C. The resonance energies for comparable structures are $2.42\beta$ for styrene and $1.95\beta$ for o-quinodimethane, the difference undoubtedly being made up for in structure C by the absence of separated ionic charges (66).) This structure enhances the contribution of delocalization energy to the bond and increases its strength. Structures of type C cannot contribute to hydrogen bonding in the case of five membered ring systems appropriate to class (a). Tsubomura has found that the integrated OH absorption intensities for salicyaldehyde and methyl salicylate are less than would be expected. He plotted this quantity against the frequency of the absorption maximum, $\nu_{\text{max}}$, for a variety of hydrogen bonded substances and found an approximately linear relationship except for the above mentioned compounds and ethyl lactate which also can form an internal hydrogen bond. This drop in intensity was explained in terms of structure C, which reduces the contribution of structure B. This, as will be shown in the next section, will be expected to reduce the I.R. intensity.

The almost negligible slope of the curve for o-nitrophenol indicates that this possibly contains the strongest hydrogen bond in the compounds studied. The amount of intermolecular hydrogen bonding in compounds of class (b) is probably small, but this point will be further discussed later. For compounds of class (a) both intermolecular and intramolecular bonding are of importance, and the non-linearity of these curves seems to indicate that two competing processes are operative. The smaller non-linearity (and greater slope) of the curve for o-cresol where only intermolecular bonding can occur possibly indicates that for o-chlorophenol and gualacol, the
breakup of intermolecular bonds is more important at low temperatures.

For the strongly hydrogen bonded six-membered ring compounds of class (b) the possibility of calculating hydrogen bond energies might appear to exist if a number of assumptions are made. Let the energy difference between the cis and trans forms be \( \Delta H \). If there is no large degree of intermolecular bonding this quantity will be a rough measure of the bond energy. The fraction of molecules, \( x_T \), in the trans state at a given temperature, \( T \), should be given by a Boltzmann factor, i.e.,

\[
x_T = \exp \left( - \frac{\Delta H}{R(T - T_0)} \right) = \exp \left( - \frac{\Delta H}{RT} \right)
\]

\( T_0 \) is the melting point of the pure compound which is assumed to correspond to a state where \( x_T = 0 \), i.e. the compound is completely in the cis form. Also,

\[
x_T = 1 - x_C
\]

where \( x_C \) is the fraction of the compound in the cis form. Let \( \delta_C \) and \( \delta_T \) be characteristic shielding values for the cis and trans forms respectively. Then the observed shielding at a given temperature is,

\[
\delta = x_T \delta_T + x_C \delta_C
\]

\[
\delta = \exp \left( - \frac{\Delta H}{RT} \right) \left( \delta_T - \delta_C \right) + \delta_C
\]

Let \( \delta_T - \delta_C = \Delta \), the intramolecular association shift. Then,

\[
\delta = \Delta \exp \left( - \frac{\Delta H}{RT} \right) + \delta_C
\]

Considering the specific case of salicylaldehyde, \( \delta_C \) may be obtained by extrapolating the temperature shift curve to a temperature representing the melting point of the compound, i.e. -70°C. This can be done accurately since the curve is linear in this temperature range, and gives a value of
\( \delta_c = -383 \text{ c/s} \). The determination of \( \delta_T \) involves a greater approximation. However, one would expect the limiting shift of the OH proton in an isolated trans molecule to be slightly less than the similar shift for phenol, due to the electron attracting power of the -CHO group. The pure liquid shift of phenol is \(-245 \text{ c/s}\), and its association shift is \(120 \text{ c/s}\) (58) (10). Hence the isolated molecule shift is \(-245 \text{ c/s} + 120 \text{ c/s} = -125 \text{ c/s}\). We will suppose that the similar figure, \( \delta_T \), for salicylaldehyde is \(-140 \text{ c/s}\).

Hence,

\[
\Delta = -140 \text{ c/s} + 383 \text{ c/s} = 243 \text{ c/s} \quad . . . . . . . . \quad 40
\]

Substituting these values in Eqn. 39, using the shift of \(-370.5 \text{ c/s}\) at 93°C gives,

\[
-370.5 = 243 \exp \left( -\frac{\Delta H}{200} \right) - 383 \quad . . . . . . . . \quad 41
\]

with \( R = 2 \text{ deg}^{-1} \cdot \text{mole}^{-1} \cdot \text{cal} \). This gives a value of \( \Delta H \) of 0.6 kilocal. \text{mole}^{-1}. This is very much smaller than would be expected for a hydrogen bond of this type which should have an energy of \( 7 \pm 2 \) kilocal. \text{mole}^{-1}.

Two possible explanations of this low figure present themselves.

(a) That 0.6 kilocal. \text{mole}^{-1} represents the difference between an intramolecularly hydrogen bonded molecule and the same molecule intermolecularly bonded.

(b) That the assumption of \( x_T = 0 \) at the melting point is invalid. Possibly the compound crystallises in the trans form giving a network of hydrogen bonds. An analogous case would be acetic acid which seems to contain polymeric species higher than dimers at high concentrations (16) (67).

A further difficulty lies in the linearity of the temperature-shift curves for compounds of group (b). From Eqn. 37, since \( x_T \) and \( x_c \) are exponentially dependent on the temperature, we should not expect a linear relation.
between the shift and the temperature. Possibly this linearity is only apparent due to the investigation of too small a temperature range.

(i) **The Relation of Association Shifts to other properties**

Attempts were made to correlate various other properties of the alcohols studied with their association shifts.

Integrated absorption coefficients of I.R. stretching bands are related to the dipole moment derivatives of the bond concerned by the expression (53),

\[
\frac{du}{dQ} = \pm \left[ \frac{3c^2 \cdot 1000}{N_{TT}} A \right]^{\frac{1}{2}}
\]

where,
- \(u\) = Bond dipole moment.
- \(Q\) = Normal coordinate describing the vibration.
- \(A\) = Integrated absorption intensity.

The quantity \(A\) has been measured by Brown and Rogers (68) (69) for a number of the alcohols discussed in this thesis. They measured the intensity at low dilutions (0.01 to 0.09 M) where the alcohols are present largely as monomers. Their results for aliphatic alcohols may be interpreted in terms of contributions due to the resonance structures I and II,

\[
\begin{align*}
\text{I} & & \text{II} \\
R - O - H & & R - O + H \\
\end{align*}
\]

as discussed previously in connection with hydrogen bonding strengths. One might therefore expect some degree of correlation between the values of \(A\) and the association shifts found for these alcohols. These quantities are listed in Table 36c, the values of \(A\) being in units of \(1 \times 10^4\) mole\(^{-1}\). litre. cm\(^{-2}\). Since the integrated absorption intensity appears to depend on the weight \(b\) of the ionic structure II, and according to the initial discussion, the hydrogen bond strength is linearly dependent on \(b^2\), the integrated
absorption intensities should be proportional to the hydrogen bond strength or association shift. From Table 36c it can be seen that for intensities measured in a carbon tetrachloride solvent, the association shifts and integrated intensities are in the order shown for the following series of alcohols.

\[
\begin{align*}
  t - BuOH & \quad n - PrOH & \quad MeOH & \quad C_6H_5CH_2OH \\
  0.891 & \quad 1.33 & \quad 1.75 & \quad 4.88
\end{align*}
\]

This is the order of the electron attracting powers of the groups R, as evidenced by the values of the thermodynamic dissociation constants of the corresponding acids (70) which are given below each alcohol in units of

\[
\begin{array}{llll}
\text{TABLE 36c} \\
\text{INTEGRATED ABSORPTION INTENSITIES} \\
\text{AND ASSOCIATIONayar Shifts OF ALCOHOLS} \\
\hline
\text{Alcohol} & \text{Integrated} & \text{Association} & \text{Shift (c/s)} \\
& \text{Intensity} & \text{In CCl}_4 & \text{In CHCl}_3 \\
\hline
t-Butyl alcohol & 0.39 & 152 \pm 2^* & - \\
n-Propyl alcohol & 0.52 & 180 \pm 5 & - \\
Methyl alcohol & 0.54 & 180 \pm 2 & 145 \pm 2^+ \\
Allyl alcohol & 0.58 & 180 \pm 5 & - \\
2-Methyl-3-butyn-2-ol & 0.59 & 113 \pm 5 & - \\
Benzyl alcohol & 0.66 & 208 \pm 5 & - \\
3-Butyn-2-ol & 0.66 & 157 \pm 5 & - \\
Propargyl alcohol & 0.69 & - & 126 \pm 2 \\
2-2-2-Trichloroethanol & 0.92 & 132 \pm 5 & - \\
Phenol & 0.99 & 120 \pm 2^* & - \\
\end{array}
\]

* Taken from Saunders and Hyne, J.C.P. 29, 1319, 1958.

1 x 10^5. Allyl alcohol possibly also fits into this scheme. Alcohols of different types to the above do not show a similar correlation, e.g. the acetylenic alcohols, trichloroethanol and phenol. However, it can be seen that for the two acetylenic alcohols for which intensity data are available (in a CCl₄ solvent) the magnitudes of the association shifts and absorption coefficients are in the expected order. The lack of correlation between the association shifts and intensities for different types of alcohols may be ascribed to the reasons already discussed in connection with the relative magnitudes of the association shifts.

The magnitudes of the intensities and association shifts for phenol and methanol are of interest. The lack of correlation is possibly connected with the resonance stabilization of the ionic structure C₆H₅-O⁻ in the case of phenol, an effect which is non-operative in methanol. However, it would seem that contributions due to the previously mentioned resonance structures involving a positive charge on the oxygen atom should reduce the integrated intensity. Thus the situation with regard to the relative magnitudes of the absorption intensities of methanol and phenol is not clear from this viewpoint. The ratio of the expected association shifts may be roughly compared in the following way. Considering an electrostatic model of the bond as previously described we may calculate the ratio of the bond energies by using the experimental dipole moments to obtain the weight b of the ionic structures. Assuming the dimensions shown below in both cases,

```
O H O
```

1.0 Å  1.7 Å

and vapour phase dipole moments of 1.7 D for methanol and 1.4 D for phenol we find (44),

The fractional charge, be, for MeOH = \( \frac{1.7e}{4.8} \) = 0.354e
The fractional charge, \( b' e \), for \( \Phi OH = \frac{1.4e}{4.8} \) is 0.292e.

The electrostatic energies are,
\[
W_{MeOH} = e^2b^2 \left[ -\frac{1}{(1.7)^2} + \frac{1}{(2.7)^2} \right]
\]
\[
W_{\Phi OH} = e^2b'^2 \left[ -\frac{1}{(1.7)^2} + \frac{1}{(2.7)^2} \right]
\]

Thus,
\[
\frac{W_{MeOH}}{W_{\Phi OH}} = \frac{b^2}{b'^2} = \left( \frac{0.354}{0.292} \right)^2 = 1.467
\]

The ratio of the association shifts is,
\[
\frac{\Delta MeOH}{\Delta \Phi OH} = \frac{180}{120} = 1.50
\]

The close agreement is perhaps to some extent fortuitous in view of the simple model assumed.

In his theory of the dielectric constant of associated liquids, Onsager assumed that the ionic character of the OH bond was considerably increased (71). Recently, Barrow has attempted to explain the integrated absorption intensities of alcohol OH bonds in terms of the change in ionic character of the bonds on stretching. Hydrogen bonding considerably enhances these intensities (53), and from the experimentally determined values of \( \Delta \) it is possible to calculate the dipole moment derivatives in the free and hydrogen bonded states, since,
\[
\frac{du}{dr} = \left( \frac{1}{m_H} + \frac{1}{m_O} \right)^{-\frac{1}{2}} \frac{du}{d\Phi}
\]

where \( r \) is the OH bond length and \( m_H \) and \( m_O \) are the masses of hydrogen and oxygen atoms respectively. This assumes that the vibration is purely an OH stretching mode. Combining Eqn's. 42 and 46 and using the values of \( \Delta \) found by Liddell and Becker (52) for methanol, i.e. 0.47 x 10⁻⁴ litre.mole⁻¹.cm⁻²
for the monomer and $5.4 \times 10^{-4}$ litre.mole$^{-1}$.cm$^{-2}$ for the polymer, one
arrives at values of,

$$\left(\frac{du}{dr}\right)_M = 1.023 \times 10^{-10} \text{ e.s.u. cm}^{-1}$$

$$\left(\frac{du}{dr}\right)_P = 3.468 \times 10^{-10} \text{ e.s.u. cm}^{-1}$$

From Eqn. 42 it is seen that the sign of the dipole moment derivatives is not determined, but there seem reasonable grounds for assuming that they are positive (53). Thus, for a given acceptor molecule the intensities always increase as the strength of the donor increases. (This is not true for very strong hydrogen bonds such as are present in crystals, but is the case for the type of system considered in this thesis.) In the free alcohol, a decrease in intensity would be expected if the contribution due to hydrogen bonding was added to any initially negative value of $du/dr$. This reasoning depends on regarding the formation of the hydrogen bond as leading to incipient ionization of the hydrogen atom.

Attempts were made to try and relate the values of $du/dr$ to the shielding of the proton, by interpreting the supposed change in ionicity in terms of a reduction in the electron density around the proton. These were not successful. A large number of assumptions are involved and it seems likely that this type of approach will be quantitatively unsuccessful since the shielding of the proton is so greatly dependent on the detailed shape of the electron distribution round about it. A further difficulty lies in the interpretation of the quantities $du/d\Omega$. Coulson and Burnelle (72) have calculated dipole moment derivatives for the OH bonds of the water molecule. They come to the conclusion that it is a simplification to regard these bonds as straight and calculate the longitudinal and transverse components of the bond dipole moment. The transverse component turns out
to be the larger, indicating the danger of relying on intuitive pictures of bond properties.

The changes in the values of $d\mu/dr$ have been interpreted by Tsubomura (65) in terms of contributions due to the covalent structure, $\overset{\circ}{O} \ H \rightarrow \overset{\circ}{O}$, where there is considerable delocalization of the electrons of the donor oxygen atom. The dipole derivative was expressed as,

$$\frac{du}{dr} \sim \frac{d\mu_0}{dr} + \frac{d\mu_T}{dr}$$

where $d\mu_0/dr$ is the derivative for the free OH group and $d\mu_T/dr$ is the derivative of the contribution due to donor atom electron delocalization. Using values for the weight of this covalent contribution as calculated by Coulson and Danielsson (41), a value of $d\mu_T/dr$ of $0.9 \times 10^{-10}$ e.s.u. cm$^{-1}$ was obtained. Although the weight of the covalent structure is small, the dipole moment associated with it is large ($\sim 13$ D) and so its contribution to $d\mu/dr$ is not negligible. The assumption of a change in ionicity of the OH bond on formation of a hydrogen bond should mean that the OH bending modes should be dependent on concentration. Although experimental data on this point is scanty (73) it seems probable that there is no strong concentration dependence of these modes. This finding would not be at variance with the idea of a contribution to $d\mu/dr$ as a result of delocalization since the intensity of the bending mode would not be expected to show a large change under these circumstances. Charge delocalization may thus play a role in explaining both the enhanced I.R. intensities and the large association shifts found for alcohols and other hydrogen bonded substances.

(j) Suggestions for further work

(1) The study of the temperature coefficients of the OH proton shifts of methanol and ethanol at sufficiently low concentrations (where a monomer-
dimer equilibrium exists) would enable a better defined bond energy to be determined, since one would be able to assume an equilibrium of the form,

\[ 2 \text{ROH} \rightleftharpoons (\text{ROH})_2 \]
rather than,

\[ n \text{ROH} \rightleftharpoons (\text{ROH})_n \]
as was done in this discussion.

(2) Infra-red investigations of acetylenic alcohols and chloroethanols might provide evidence for the other types of molecular association postulated in discussing their dilution shift curves.

(3) Studies of the concentration dependence of the OH bending modes in hydrogen bonded compounds would enable a more clear-cut distinction to be made between the effects of possible changes in bond ionicity and electron delocalization on the integrated intensities of the stretching modes of hydrogen bonded OH groups.

(4) The temperature shift curves of compounds such as 2-hydroxy-3-t-butyl benzaldehyde, where there is additional hindrance to free rotation of the OH group, might provide information which would aid in the interpretation of similar curves obtained for ortho-substituted phenols.

(5) Theoretical calculations of the shielding to be expected for the OH proton in a molecule such as methanol would be of interest. Recently, a variational method for calculating such shieldings has been developed by Stephen (74). This employs simple molecular orbitals type wave functions of the form,

\[ \phi_o = N (\phi_A + \lambda \phi_B) \]
to describe the bond AB, where \( \lambda \) is a parameter describing the bond ionicity. The change in shielding with variation of \( \lambda \) would be of interest in the case
of OH bonds, in view of the postulated change in ionic character on hydrogen bonding. Also, the change in shielding with alteration of bond length could be determined, to enable the contribution to the association shift that the small stretching of the OH bond on hydrogen bond formation makes.

NOTE

Recent work by Shubalova (Optics and Spectroscopy, 1959, 696) on the I.R. spectra of solutions of acetylene in various solvents indicates that there is a considerable shift of the C-H stretching vibration to lower frequencies (200 cm\(^{-1}\)) in donor solvents such as acetone or pyridine. This provides further evidence for the formation of hydrogen bonds between acetylenic hydrogen atoms and donor atoms such as O or N, which was postulated to explain the magnitude of the dilution shifts of acetylenic alcohols.
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63. Fox and Martin. T.F.S. 36, 897 (1940).


CHAPTER IV

THE NMR SPECTRA OF TRIARYL CARBONIUM IONS

INTRODUCTION

Triaryl carbinols are known to ionize in strongly acidic solutions to give carbonium ions

\[ \text{Ar}_3\text{COH} + 2\text{H}^+ \rightleftharpoons \text{Ar}_3\text{C}^+ + \text{H}_3\text{O}^+ \]

whose stability depends mainly on the extent of resonance interaction between the central carbon atom and the aromatic rings. Substituents which can aid this charge dispersal, e.g. CH\(_3\), CH\(_2\)OH, are known to have a large stabilizing effect on the carbonium ions. Thus, the equilibrium constant for the ionization of tri-p-anisyl carbinol is larger by a factor of 3 x 10\(^7\) than that of the unsubstituted triphenyl carbinol (1). Meta substituents have a smaller effect since direct resonance interaction with the central carbon atom is not possible.

Two steric factors also influence this electronic interaction. First is the effect of bulky ring substituents such as tert-butyl in inhibiting ring solvation (2), and second, the steric interactions of the ortho positions. The interaction depends on the actual structures of these ions, which are in doubt, three types of configuration having been suggested.

(1) A completely planar ion. Symmetry D\(_{3h}\)

(2) Symmetrical propellor. Symmetry D\(_3\)

(3) One or two rings conjugated. No symmetry elements.

The first can be ruled out on steric grounds, due to the large interactions at the ortho positions (3). Deno et al. measured thermodynamic equilibrium constants for the reaction,
\[
R^+ + H_2O \rightleftharpoons ROH + H^+ \quad \text{(2)}
\]
and interpreted their results in terms of the third structure involving one or two ring conjugation only. Sharp and Sheppard have studied the infra-red spectra of these ions in the solid state (4) as salts of complex fluoroacids. They discussed their results in terms of the vibrational levels postulated by Karagounis (5) for various configurations of the triphenylmethyl free radical, and concluded their results were consistent with D$_3$ symmetry or a symmetrical propellor shape. Applications of molecular orbital theory to the electronic spectra of these ions also favour D$_3$ symmetry (6).

The NMR spectra of some substituted triaryl carbonium ions was investigated in an attempt to shed some light on their electronic structures and configurations. The spectrum of 1,1,Di-p-anisyl-ethylene was also investigated, since it forms a diaryl carbonium ion in acid solution. The only spectra of carbonium ions reported to date are those of some protonated aromatic hydrocarbons (7) and the tropylium cation (8).

**EXPERIMENTAL SECTION**

In order to compare the chemical shifts with those of neutral compounds containing similar groups a solvent was required which was sufficiently acidic to cause complete ionisation of the triaryl carbinols, which would dissolve such compounds as toluene and anisole and which was free from proton resonances in the region to be studied. A solution of 1.5 M trifluoroacetic acid in trifluoroacetic anhydride was chosen. In each case, the sample* consisted of a 10% solution of the carbinol, sealed off in vacuo.

* The samples were prepared or supplied by Dr. R.B. Moodie. Preparations were by conventional Griguard synthesis and melting points agreed well with the literature values (9).
The diamagnetic properties of the solvent were not changed appreciably over the range 1.5 to 3 M. acid, as shown by the fact that the positions of the proton resonances of toluene did not change. This fact was of interest since in two cases a small amount of water was added to the solvent to facilitate solution of the carbinol, and in another case, a triarylchloromethane was used instead of the carbinol. The NMR measurements were made at 40 Mc. in the usual way using an external water marker. Some spectra of the aromatic protons were also recorded at 60 Mc. (These measurements were made at the Chemistry Department, University of Washington, Seattle.) Since all the solutions were dilute and the volume susceptibilities of the triarylmethyl cations are expected to be similar, the bulk susceptibility corrections are negligible and so the measured shifts can be compared directly.

The visible spectra of some of these compounds have been investigated (9) and seems to indicate complete ionization at the concentrations employed. Triphenyl carbinol ($\lambda_{\text{max}} = 410 \mu\lambda; \varepsilon = 43,500. \lambda_{\text{max}} = 425 \mu\lambda; \varepsilon = 42,200$) at a concentration $3 \times 10^{-4} \text{ M}$ and $1.5 \times 10^{-4} \text{ M}$ tri-p-anisyl carbinol ($\lambda_{\text{max}} = 478 \mu\lambda; \varepsilon = 87,000$) were investigated in a 0.1 cm. cell using a Cary Model 14 recording spectrophotometer. The spectra appeared unchanged in a $10^{-3} \text{ cm. cell}$ (about $4 \times 10^{-2} \text{ M}$), but solvent volatility prevented precise determinations. These spectra are similar to those found for carbonium ions in sulphuric acid. ((a) Triphenyl methyl cation (2) $\lambda_{\text{max}} = 404 \mu\lambda; \varepsilon = 40,000. \lambda_{\text{max}} = 431 \mu\lambda; \varepsilon = 40,000.$ (b) Tri-p-anisyl methyl cation (10) $\lambda_{\text{max}} = 433 \mu\lambda; \varepsilon = 91,000.$)

It was assumed that complete ionization also occurred in the slightly more concentrated solutions used for the NMR measurements. These spectra would not necessarily reveal the presence of a small amount of unionized triarylmethyl trifluoroacetate, since in the equilibrium
$\text{CF}_3\text{CO}_2\text{C Ar}_3 \rightleftharpoons \text{Ar}_3\text{C}^+ + \text{CF}_3\text{CO}_2^- \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad 3$

the rate of interconversion of the ionized and unionized forms may be too fast for separate proton resonances to be observed.

The NMR and visible spectra of $m$-methoxyphenyl diphenyl carbinol and tri-$m$-methoxyphenyl carbinol in this solvent were found to be quite different from the other carbinols studied, indicating possibly that some reaction with the solvent had occurred.

**RESULTS AND DISCUSSION**

Table 1d records the chemical shifts of the aromatic and substituent protons measured from an external water marker at 40 Mc. In the case of the aromatic protons, these measurements were made to the largest peak except in the case of the tri-$p$-anisyl methyl cation where the measurement is to the centre of the symmetrical quartet.

(a) **The Substituent Protons**

In no case was a multiple substituent proton peak observed. In the case of the trisubstituted ions it might be expected that multiple peaks might be observed if the degree of conjugation of the aromatic rings with the central carbon atom was different. However, as the splitting expected would only be of the order of a few cycles per second, and since the rate of twisting of the rings in and out of conjugation with the central carbon atom would undoubtedly occur at a faster rate than this, only one peak should be seen, representing a time average of all the possible degrees of conjugation with the central carbon atom. The samples of tri-$p$-anisylmethyl and tri-$p$-tolylmethyl cations were cooled to $-80^\circ\text{C}$ in a dry ice-acetone bath and the appearance of the substituent peaks noted as the sample warmed up. No splitting was observed at any temperature.

Greater shielding of the substituent protons was observed in the
### CHEMICAL SHIFTS OF AROMATIC AND SUBSTITUENT PROTONS

<table>
<thead>
<tr>
<th>Compound from which cation was derived</th>
<th>Aromatic Shifts (c/s)</th>
<th>Substituent Shifts (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenyl carbinol</td>
<td>- 101.0</td>
<td>-</td>
</tr>
<tr>
<td>p-Tolyl diphenylcarbinol</td>
<td>- 98.0</td>
<td>+ 102.5</td>
</tr>
<tr>
<td>Di-p-tolyl phenyl carbinol</td>
<td>- 94.75</td>
<td>+ 104.5</td>
</tr>
<tr>
<td>Tri-p-tolylcarbinol</td>
<td>- 93.5</td>
<td>+ 105.5</td>
</tr>
<tr>
<td>m-Tolyl diphenylcarbinol</td>
<td>- 95.5</td>
<td>+ 112.5</td>
</tr>
<tr>
<td>Tri-m-tolylcarbinol</td>
<td>- 89.0</td>
<td>+ 112.5</td>
</tr>
<tr>
<td>p-Anisyl diphenylcarbinol</td>
<td>- 96.0</td>
<td>+ 42.0</td>
</tr>
<tr>
<td>Tri-p-anisylcarbinol</td>
<td>- 87.5</td>
<td>+ 47.0</td>
</tr>
<tr>
<td>p-tert-Butylphenyl diphenyl chloromethane</td>
<td>- 101.0</td>
<td>+ 151.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aromatic Shifts (c/s)</th>
<th>Substituent Shifts (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tert-Butylbenzene</td>
<td>- 76.0</td>
<td>+ 161.5</td>
</tr>
<tr>
<td>Anisole</td>
<td>- 68.0</td>
<td>+ 59.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>- 69.0</td>
<td>+ 124.0</td>
</tr>
</tbody>
</table>

Carbonium ions substituted in all three para positions compared with those with only one para substituent. In the latter case, greater stability would be expected for a structure in which the substituted ring occupies a position of greater conjugation than the other two rings. This effect should be less marked with meta substituents, where no direct resonance interaction with the substituent is possible, and in fact no difference was observed in the shielding of the substituent protons for m-tolyl diphenyl methyl and tri-m-tolylmethyl cations.
A greater difference was observed between the shifts of the substituent resonances for toluene and the tri-p-tolylmethyl cation (18.5 c/s) than between anisole and the tri-p-anisylmethyl cation (12.5 c/s). Since the methoxy group has a greater stabilizing effect on the triphenyl methyl cation than the methyl group (1) one might expect these differences to be in the reverse order. However, hyperconjugation is only possible in the case of the methyl substituents, and provides a mechanism whereby positive charge can be transferred directly to the substituent protons, thus reducing their shielding.

A considerable decrease in shielding was also observed going from tert-butylbenzene to the p-tert-butylphenyl methyl cation (10.5 c/s). However, it is not possible to say whether this is a purely inductive effect or whether carbon-carbon hyperconjugation is involved, i.e. if structures of the type,

\[
\begin{align*}
\text{CH}_3^+ & \quad \text{C} \quad \text{C(C}_6\text{H}_5)_2 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

contribute.

(b) The Ring Protons

The effect of the substituents was to increase the shielding of the ring protons, as can be seen by comparison with the triphenyl methyl cation (Table 1d). In the monosubstituted compounds this effect in the substituted ring is partly offset by its presumed greater conjugation with the central carbon atom. The result was overlap of signals from substituted and unsubstituted rings.

Fig. 1d shows the spectrum of the triphenyl methyl cation at 40 and 60 Mc. A spectrum of this ion was also recorded in 96% sulphuric acid at
FIG 1d NMR SPECTRA OF $\phi_3 C^+$

40 Mc.

60 Mc.

-169 $\rightarrow$ -147

-114.5 $\rightarrow$ -101

H C/S $\rightarrow$
40 Mc (5% solution) and gave a similar spectrum although the resolution was poor.

Resonance theory predicts, from a consideration of simple valence bond structures, that the meta protons should be more shielded than the ortho or para protons, if one assumes that shielding is proportional to the electron density on the adjacent carbon atom. This assumption in the case of azulene gives a spectrum whose assignments and relative shifts agree well with those found experimentally (11). The corresponding charge densities for the triphenyl methyl cation are shown in Fig. 2d. This argument does not apply to molecules like nitrobenzene for which it has been shown that the ortho protons are least shielded (12), with the meta and para proton peaks superimposed at higher field. The proximity of the latter is reasonable since the Hammett sigma values (13) for meta and para nitro groups are close, i.e. resonance is of minor importance in nitrobenzene. Complete identification of the proton signals from the triphenyl methyl cation was not found to be possible. The group of peaks at low field (Below - 157 c/s on the 60 Mc. spectrum) can, however, be assigned to the para protons since they occupy the theoretical value of one-fifth of the area of the curve. This finding agrees well with Pople's calculations of the electron densities in this ion (14) using self-consistent molecular orbital methods, which take account of inter-electron repulsions. A simple Hückel molecular orbital treatment which does not consider electron correlations predicts the largest shielding for the meta position, as does the resonance picture mentioned above, and equal shielding for the ortho and para positions. These charge densities are also shown in Fig. 2d. The NMR spectrum of protonated pentamethyl benzene is similar in that the para substituent is least shielded (7).
FIG 2d

RESONANCE STRUCTURES

HUCKEL M.O.s

S.C.M.O.s

CHARGE DENSITIES IN THE TRIPHENYLMETHYL CATION
Using these S.C.M.O. results leads to a figure of 5.75 \( \alpha \) electrons per aromatic ring, 0.75 electrons occupying the vacant \( \pi \) orbital on the central carbon atom. Using Pople's ring current theory one may estimate the expected shift to high field as compared with a ring containing 6 \( \alpha \) electrons. Since the experimentally determined shift between ethylene and benzene protons is 56 c/s (15), the shift expected for 5.75 \( \alpha \) electrons is \( 56 \times \frac{5.75}{6} \) or 54 c/s. Hence, the relative shift to high field is 56 - 54 = 2 c/s. Since the triphenyl methyl ion resonance was shifted considerably to low field as compared with benzene, the effect of decreasing ring current is evidently small compared with the decrease in shielding caused by the lower \( \alpha \) electron density.

A factor which one may term ortho-electrostatic interaction may be important in determining the charge distribution in these compounds. The propellor form of the ion will be of lowest energy when the three rings are folded close to one another to enable maximum overlap to occur with the central \( \pi \) orbital. The ortho carbon atoms are very close in this configuration, however, and electrostatic repulsion between the partial positive charges on these atoms may influence the configuration and electronic structure of these ions to some extent.

The spectrum of the mono-p-methyl ion (Fig. 3d) resembles that of the unsubstituted triphenyl methyl cation, with the single peak due to the substituted ring superimposed on the main peaks. The peaks at low field are probably due to the protons in the para positions in the unsubstituted rings since the area under the peaks below - 154 c/s is approximately one-seventh of the total area.

The spectrum of the tri-p-anisylmethyl cation at 40 Mc. (Fig. 4d) shows a well resolved quartet due to coupling between the ortho and meta
NMR SPECTRA OF AROMATIC PROTONS

FIG 3d
60 Mc

FIG 4d
40 Mc

$\text{CH}_3\text{C}_\phi_2$

$(\text{MeO}_\text{C}_\phi)_3^+$
positions. Assuming negligible cross-ring coupling, this quartet may be considered as a superposition of two AB cases (16). One may calculate the absolute value of the spin-spin coupling constant, $J$, and the chemical shift, $\delta$, between the ortho and meta protons. $J$ is given directly by the separation of the right or left hand pair of lines, which is 8.9 c/s and the separation of the inner pair of lines, $\delta_1$, (7.1 c/s) is given by,

$$\delta_1 = 2C - J$$

where,

$$C = \frac{1}{2} (\delta^2 + J^2)^{1/2}$$

This gives a value of $\delta = 13.3$ c/s. Values of $J$, the ortho coupling constant, found by other authors range from 8.2 c/s to 8.6 c/s (16) (17). This value may also be compared with a value of $8.0 \pm 0.5$ c/s found for protonated 1,1 dianisylethylenes in sulphuric acid, whose spectrum will be described shortly. In the case of the tri-p-tolyl ion, this quartet is unresolved even at 60 Mc., the aromatic protons giving a single sharp peak.

The spectra of the aromatic protons of the p-anisyl diphenyl methyl and p-tert-butylphenyl diphenyl methyl cations were recorded at 60 Mc. (Fig. 5d). A well resolved fine structure was observed, but no definite assignments could be made.

The meta methyl substituted ions illustrate an interesting point. Table 1d shows that a meta methyl substituent shields the ring protons to a greater extent than does a para methyl substituent. This is because the electron donating properties of the methyl group function to donate negative charge to the electron deficient ring, but because of its meta location, it is unable to interact directly by resonance with the central electron deficient carbon atom.
FIG 5d NMR SPECTRA OF AROMATIC PROTONS

(CH₃)₃C⁺φ₂

MeO⁻C⁺φ₂
(c) **The spectrum of 1,1 Di-p-anisylethylene**

The spectrum of this compound (6.7% solution) was recorded in 96% sulphuric acid and in the trifluoroacetic acid/trifluoroacetic anhydride solvent (10% solution). In both cases a carbonium ion is formed, the spectra being shown in Fig. 6d. Anomalous visible spectra for this compound in a solvent consisting of trichloroacetic acid in benzene have been reported by other workers (10) (19) (18) and it has been suggested that a transition from a classical carbonium ion to a TT-complex may occur subsequent to protonation, as shown below.

\[
(p-CH_3OC_6H_4)_2 C = CH_2 + H^+ \rightleftharpoons (p-CH_3OC_6H_4)_2 C \equiv CH_3 \\
\text{CLASSICAL CARBONIUM ION} \\
\downarrow \quad \uparrow \\
(p-CH_3OC_6H_4)_2 C \equiv CH_2 \\
\text{TT - COMPLEX}
\]

However, solutions in 96% sulphuric acid show only those peaks which would be expected for a classical carbonium ion.

The NMR spectrum in sulphuric acid showed a well resolved quartet, apparently due to the aromatic protons, the chemical shift between the doublet centres being 32 c/s and the coupling constant 8.0 ± 0.5 c/s. (Considering the spectrum as a superposition of two AX cases.) The methyl group occurred - 85 c/s from an external cyclohexane marker, this large shift to low field being possibly due to the spread of the positive charge to the methyl protons by a hyperconjugative mechanism. Alternatively, an equilibrium may exist where there is rapid interconversion between the ethylenic form and the classical carbonium ion, the signal seen being a weighted time average of the two.

The spectrum in the trifluoroacetic acid/trifluoroacetic anhydride solvent did not provide any unequivocal information since decomposition or
FIG 6d NMR SPECTRUM OF 1,1-DIANISYL ETHYLENE AT 40 Mc

(H₂O(E) to C₆H₁₂ = +143.5 C/s)
reaction of some kind was clearly occurring as evidenced by the unassigned peaks at low field. A quartet due to the aromatic protons was obtained as before, the chemical shift between ortho and meta protons being much smaller in this case. The peak due to the protons attached to the ethylenic carbon atoms occurred on the low field side (−12.5 c/s) of the methoxy signals, in distinction to the spectrum in sulphuric acid. This might indicate that these protons are more ethylenic in character than before and that the third proton is loosely bonded in a TT-complex and is able to exchange readily with the solvent protons. The relative intensities of these two high field peaks were measured to try and substantiate this idea. An average of eight traces was taken, both height and weight ratios being compared.

\[
\text{Weight Ratio} = \frac{2\text{MeO}}{1\text{Me}^1} = \frac{0.2936}{0.1143} = 2.567
\]

\[
\text{Height Ratio} = \frac{2\text{MeO}}{1\text{Me}^1} = \frac{88.67}{34.47} = 2.564
\]

These values are consistent and intermediate between the expected ratios of 1:2 (\(\text{C} - \text{CH}_3 : 2\text{CH}_3\text{O} - \)) and 1:3 (\(\text{C} = \text{CH}_2 : 2\text{CH}_3\text{O}-\)) and so it is difficult to draw any definite conclusions on these grounds.

(d) Suggestions for future work

A more detailed study of 1,1 Di-p-anisylethylene should throw further light on the nature of the carbonium ion formed in acidic solutions. In particular, the dependence of the shifts on solvent acidity would be of interest. Investigations of triaryl methyl carbonium ions might be extended to those containing ortho substituents, conjugation with the central carbon atom thus being highly hindered, and to the apparently anomalous meta methoxy substituted compounds. A related class of compounds, the triphenylmethane dyes, might also prove of interest.
BIBLIOGRAPHY FOR CHAPTER IV

CHAPTER V

SOLUTIONS OF IODINE IN OLEUM

THE POSSIBLE EXISTENCE OF THE I⁺ ION

INTRODUCTION

The idea of the existence of positive halogen ions originated from the supposed behaviour of the halogens on hydrolysis (1)

\[ X_2 \rightarrow X^+ + X^- \]
\[ X^+ + OH^- \rightleftharpoons XOH \]
\[ X^- + H^+ \rightleftharpoons XH \]

However, there is no evidence for I⁺ being any more than a transitory species in aqueous solution, since hypoiodous acid, HOI, is labile and disproportionates as follows (2)

\[ I^+ + OH^- \rightleftharpoons HOI \]
\[ 2HOI + IO^- \rightarrow IO_3^- + 2I^- + 2H^+ \]

It seems though that the I⁺ ion can be stabilized in the presence of a suitable electron donor and also that it may be an important intermediate in iodination reactions. Its existence in solutions of iodine in 65% oleum has been postulated (3). The various lines of research leading to these conclusions will be discussed briefly.

CHEMICAL AND PHYSICAL EVIDENCE FOR THE EXISTENCE OF I⁺

(a) Stabilization of I⁺ by electron donors

Hypoiodous acid also has the properties of a labile base, the equilibria below lying to the left, i.e. in favour of basic ionisation (4).

\[ I^+ + OH^- \rightleftharpoons HOI \rightleftharpoons H^+ + IO^- \]
The $\text{l}^+$ ion can be stabilized by coordination, e.g. with an amine such as pyridine, a series of salts of the hypothetical bases $\text{l(py)} \cdot \text{OH}$ and $\text{l(py)}_2 \cdot \text{OH}$ having been prepared in non-aqueous media (5). Examples are the following.

$$\text{l(py)} \cdot \text{NO}_3; \text{l(py)}_2 \cdot \text{NO}_3; \text{l(py)}_2 \cdot \text{ClO}_4 \text{ etc.}$$

$\text{l(py)}^+$ salts of some 30 organic acids.

These salts have characteristic chemical properties such as the ability to dissolve noble metals with liberation of iodine (6),

$$3 \text{l(py)}_2 \cdot \text{NO}_3 + \text{Au} \xrightarrow{\text{CHCl}_3} \text{Au}^{3+} + 3\text{NO}_3^- + 3/2 \text{I}_2$$

and the liberation of iodine at the cathode on electrolysis.

Apparently no X-ray structural determinations on these salts have been made although Hassel and coworkers (7) have investigated the 1:1 complex of pyridine and iodine monochloride and some related halogen complexes with amines and ethers. In all cases they have found that the groups,

$$0 \cdots \cdots X - X \quad \text{and} \quad N \cdots \cdots X - X$$

are linear, in contrast to suggestions made by Reid and Mulliken (8) concerning this type of complex in pyridine solution. However, it is not inconceivable that the structure of loosely bound complexes of this sort may be very different in the liquid and solid states.

Numerous spectroscopic studies of these salts have been made and also of solutions of iodine in pyridine, a series of equilibria of the type shown having been proposed in the latter case (8)

$$\text{py} + \text{l}_2 \xrightleftharpoons{\text{fast}}^\text{fast} \text{py.l}_2 \text{ ('Outer complex')} \text{)}$$

$$\text{py.l}_2 \xleftarrow{\text{fast}}^\text{fast} (\text{py}) \text{l}^+ \text{l}^- \text{ ('Inner complex')} \text{)}$$

It was concluded that the predominant species was the 'outer complex', a
small concentration of the ions being present, as evidenced by conductivity measurements (9).

The above system has been compared directly with solutions obtained by dissolving I(py)$^+$ salts in pyridine (10) (11). A band at 320 μm was found in all the solutions and attributed to the I(py)$^+$ ion, formed in the case of the iodine-pyridine solution through establishment of the equilibria,

$$2I_2 + py \overset{\text{fast}}{\rightarrow} I_2 + py \cdot I_2 \overset{\text{slow}}{\rightarrow} I(py)^+ + I^-$$

The situation is complicated by changes in the spectra in the course of time, presumably due to side reactions.

(b) Transport Studies

The positive charge of the I$^+$ ion has been used as the basis of experiments whose object was to prove its existence.

Transport measurements have been made on solutions of iodine monochloride in nitrobenzene (12) and were thought to show the existence of the equilibrium:

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

However, I$^+$, if present, would undoubtedly iodinate nitrobenzene, which might then protonate to give m - I \( \not\) NO$_2$H$^+$. Alternatively, the positive ion might be the species I$^+$, formed thus,

$$ICl + I^+ \rightleftharpoons I_2Cl^+$$

or $$2ICl \rightleftharpoons Cl^- + I_2Cl^+$$

(c) Kinetic Studies

The kinetics of the iodination of aniline were studied by Berliner (13) using solutions containing varying quantities of iodide ion and phosphate buffer. The reaction was found to be independent of the hydrogen ion
concentration and was base catalysed. The concentrations of \( l^- \) and \( l_2 \) were calculated from the equation,

\[
(1) \quad l^3 = l_2 + l^- \quad \text{........... } K_1
\]

and the following equations were considered in determining the nature of the iodinating species

\[
(2) \quad l_2 + H_2O \rightleftharpoons HOI + H^+ + l^- \quad \text{........... } K_2
\]

\[
(3) \quad HOI \rightleftharpoons l^+ + OH^- \quad \text{........... } K_3
\]

\[
(4) \quad HOI \rightleftharpoons 10^- + H^+ \quad \text{........... } K_4
\]

\[
(5) \quad l_2 \rightleftharpoons l^+ + l^- \quad \text{........... } K_5
\]

\[
(6) \quad H^+ + \phi NH_2 \rightleftharpoons \phi NH_3^+ \quad \text{........... } K_6
\]

All the underlined species are potential iodinating agents. \( l^- \) and \( l_3^- \) are, however, ruled out at once since it was found that the rate of the reaction decreased as the concentration of \( l^- \) was increased. \( l_2 \) and \( 10^- \) give rate expressions at variance with experiment. If \( l^+ \) is the iodinating agent,

\[
k_{obs} = \frac{k_3 k_1 k_2 k_3}{K_w [l^-]^2} = \frac{k_5 k_1 k_5}{[l^-]^2}
\]

which is in agreement with experiment. If HOI reacted with \( \phi NH_3^+ \) to give iodoaniline, a similar rate expression would be obtained. But \( \phi NH_3^+ \) is meta-directing and experimentally it was found that 64% of the product was the para-compound. A similar ambiguity had previously been found by Soper and Smith (14) who were not able to distinguish between HOI and \( l^+ \) as iodinating agents in a like manner. It was considerd that the \( l^+ \) ion was probably hydrated, its outer electron shell thereby being made up to eight, i.e.,
(d) **Studies of solutions of iodine in oleum**

Properties of the $I^+$ ion whose study might be expected to lead to less ambiguity than the above investigations are

(a) Magnetic properties.

(b) Electronic spectra.

The iodine atom has an electronic structure [Core] 5$s^2$ 5$p^5$ and so the $I^+$ ion will have a structure [Core] 5$s^2$ 5$p^4$ containing two unpaired electrons in the 5$p$ shell and should hence be paramagnetic. Susceptibility, magnetic resonance and spectral measurements would appear to be profitable methods of studying the $I^+$ ion and have all been employed by Symons (3) (15) for this purpose. It was thought that solutions of iodine in 100% sulphuric acid might contain the $I^+$ ion, paralleling the successful study of the nitronium ion, $NO_2^+$, in aromatic nitration (16). However, spectroscopic measurements of solutions of iodine in 100% sulphuric acid indicate an essentially similar spectrum to that found for iodine in the gaseous phase (17) (18), and show that a more powerful electrophilic agent is required to liberate $I^+$ from $I_2$ than $H_2SO_4$

$$A + I_2 \rightarrow Al^- + I^+$$

Sulphur trioxide is apparently such a reagent. On its addition to $I_2$ $H_2SO_4$ solutions, sulphur dioxide is evolved and the following series of colour changes are observed,

Violet $\rightarrow$ Brown $\rightarrow$ Green $\rightarrow$ Blue

100% $H_2SO_4$ (20–30% oleum) (65% oleum)

The blue solutions are stable for months at ordinary temperatures and on heating to 200°C, no loss of iodine occurs. The solubility of iodine is increased a hundred fold as compared with 100% sulphuric acid. On
addition of water only 80% of the iodine is recovered as such, 20% of it being converted to iodate ion, which is simply explained by postulating a unipositive valence state.

\[ 5 I_2 \rightarrow 10 I^+ \rightarrow 4 I_2 + 2 I^- \]

Gouy balance measurements showed these solutions to be paramagnetic, the following values of the magnetic moment being reported, assuming that all the iodine was present as $I^+$

(a) $1.90 \pm 0.1$ B.M. (0.1 M solution)
(b) $2.50 \pm 0.4$ B.M. (0.01 M solution)

If $I$ atoms are present, which is unlikely in view of the analytical data, a value of 1.73 B.M. would be expected using the 'spin only' formula,

\[ \mu = 2 \left[ S(S + 1) \right]^{1/2} \]

The 'spin only' value for two electrons is 2.83 B.M. and assuming a $^3P_2$ spectroscopic state for $I^+$

\[ \mu = g \left[ J(J + 1) \right]^{1/2} = 3.68 \text{ B.M.} \]

where (19),

\[ g = \frac{1 + [J(J + 1) + S(S + 1) - L(L + 1)]}{2J(J + 1)} \]

The experimental value is lower than the reasonable theoretical values, presumably due to the fact that not all the iodine is present as $I^+$, the concentration being lowered by various competing equilibria, the following being most likely,

\[ \begin{align*}
I^+ + HSO_4^- & \rightleftharpoons IHSO_4 & \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTS
\]
\[ \begin{align*}
I^+ + HSO_4^- & \rightleftharpoons IHSO_4 & \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTS
I^+ + HS_2O_7^- & \rightleftharpoons IHS_2O_7 & \cdots \cdots \cdots \cdots \cdots \cdOTS
I^+ + SO_3 & \rightleftharpoons ISO_3^+ & \cdots \cdots \cdOTS
SO_3 + HSO_4^+ & \rightleftharpoons HS_2O_7^+ & \cdots \cdots \cdOTS
\end{align*} \]
In the first three instances, diamagnetic products will result. At first sight 3 seems unlikely in view of the strongly electrophilic nature of the reactants. There is a parallel, however, between $\text{SO}_3^+$ and $\text{S}_2\text{O}_3^-$

formed in solutions of sulphur in oleum (20), which are isoelectronic. The competing equilibrium (4) reduces the effectiveness of $\text{I}$ as the $\text{SO}_3^-$ concentration increases. The apparent moment is reduced by addition of potassium hydrogen sulphate, $\text{KHSO}_4$, which shifts $\text{I}$ to the right and hence decreases the concentration of $\text{I}^+$.

The following mechanism was proposed for the formation of $\text{I}^+$,

$$\text{SO}_3^- + \text{I}_2 \rightleftharpoons \text{I}^+ + \text{SO}_3^-$$
$$\text{SO}_3^- + \text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3\text{H} + \text{HSO}_4^-$$
$$\text{SO}_3\text{H} + \text{SO}_3 \rightleftharpoons \text{I}^+ + \text{HSO}_4^- + \text{SO}_2$$

**Spectroscopic Evidence**

The $\text{I}^+$ ion has been identified in the spark spectrum of iodine in an excited state, by Murakawa (21), who calculated the energies of the low lying excited states relative to the ground state. He obtained four transitions from the $3\text{P}_2$ ground state, all of which are forbidden by atomic selection rules,

1. $3\text{P}_2 \rightarrow 3\text{P}_1$ $\quad 1410 \text{ mJ}$
2. $3\text{P}_2 \rightarrow 3\text{P}_0$ $\quad 1550 \text{ mJ}$
3. $3\text{P}_2 \rightarrow 1\text{D}_2$ $\quad 728 \text{ mJ}$
4. $3\text{P}_2 \rightarrow 1\text{S}_2$ $\quad 310 \text{ mJ}$

The first allowed transition lies at $< 200 \text{ mJ}$ and is thus not observable in oleum solutions. For elements of high atomic number, singlet $\rightarrow$ triplet transitions become partly allowed and the line at 728 mJ should result in a blue solution. The solutions of iodine in oleum are in fact characterized
by a strong band at 650 \( \mu \) (15) which is postulated to be the 728 \( \mu \) band shifted to lower wavelengths by solvent interaction. Other bands appear at 470, 400 and 300 \( \mu \) and are shown not to be directly related to the 650 \( \mu \) band. The 650 and 400 \( \mu \) bands are not observed in the brown solutions of iodine in oleum (20 \( \rightarrow \) 30% free \( \text{SO}_3 \)), whereas the bands at 300 and 470 \( \mu \) are. Addition of free \( \text{SO}_3 \) causes a decrease in the intensity of these bands while those at 650 \( \mu \) and 400 \( \mu \) are increased. On heating the blue solutions the 650 \( \mu \) band increases in intensity at the expense of the 400 \( \mu \) band, the effect being reversed on cooling and it was therefore concluded that these bands must be due to two distinct species.

**Magnetic Resonance Measurements**

Attempts have been made to detect an electron spin resonance spectrum from these solutions (3), without success however, although a small line which was not reproducible was found in one instance at 20\(^\circ\)K. This result might be expected if there is strong spin-orbit coupling in the \( \text{I}^+ \) ion, resulting in a large broadening of the resonance signal which would reduce its intensity below an observable value. Similar attempts to observe resonances from triplet states, e.g. naphthalene in its phosphorescent state have been unsuccessful except in the case where the naphthalene molecules were oriented in a durene matrix, a resonance occurring at four positions, the outermost peaks being separated by 2100 gauss (22).

However, it has been shown by Bloembergen, Purcell and Pound (23) and by Dickinson (24) that paramagnetic ions dissolved in proton containing media have a marked effect on the proton resonance, broadening it and in general shifting it to higher values of the applied field. It was thought therefore that an examination of the proton resonance of iodine-oleum solutions at various concentrations might throw some light on the nature
of the species contained in these solutions.

RESULTS

The proton nuclear resonance spectra of solutions of iodine in 65% oleum were measured at 40 Mc. with a Varian 4300 high resolution spectrometer, as described previously. Two external reference capillaries were included with each sample, one containing 65% oleum and the other distilled water, enabling the shifts and broadening of the oleum resonances to be found by interpolation. The validity of this referencing procedure has been demonstrated by Bothner-By and Glick (25) who have shown experimentally that the absolute position of an external marker does not depend on the magnetic susceptibility of the medium surrounding the capillary marker tube. Owing to the width of some of the oleum signals, this was a more convenient method of measuring shifts than the usual side-band technique, although this was used to measure the distance between the two reference capillaries. This was found to be 218 c/s, the oleum resonance lying on the low field side. The same pair of reference tubes was used for all the measurements to eliminate any possible discrepancies due to 'shape factor' effects.

The oleum was not specially purified. The line width of the signal was about 2 c/s (at half-height) indicating the absence of any appreciable amount of paramagnetic impurities. The iodine was 'AnalaR' grade.

The broadening and chemical shifts of the oleum resonances are shown as a function of iodine concentration in Table 1e, and typical spectra obtained at various concentrations in Fig. 1e. The proton resonance spectra of the brown solutions obtained by dissolving iodine in 20 and 30% oleum were also examined, and showed no appreciable broadening or shift. It was concluded that these solutions do not contain paramagnetic species,
a result in accordance with previous findings (3) (15). The broadening due to paramagnetic ions was determined by subtracting the line width due to pure oleum (2 c/s) from the line width at half-height found for the solutions. The shift and broadening are approximately proportional to the iodine concentration as shown in Figs. 2e and 3e, although the broadening falls off at high iodine concentrations.

**TABLE 1e**

**BROADENING AND CHEMICAL SHIFT OF PROTON RESONANCE OF OLEUM DUE TO THE PRESENCE OF I$_2$**

<table>
<thead>
<tr>
<th>Concentration of I$_2$ (mole/l.)</th>
<th>Line-width at $\frac{1}{2}$-height (c/s)</th>
<th>Broadening (c/s)</th>
<th>Shift from 65% oleum (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure oleum</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.0098</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>0.0197</td>
<td>4</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>0.0281</td>
<td>7</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>0.0985</td>
<td>14</td>
<td>12</td>
<td>14.5</td>
</tr>
<tr>
<td>0.2003</td>
<td>24</td>
<td>22</td>
<td>29</td>
</tr>
<tr>
<td>0.3136</td>
<td>34</td>
<td>32</td>
<td>43</td>
</tr>
<tr>
<td>0.4010</td>
<td>41</td>
<td>39</td>
<td>56</td>
</tr>
<tr>
<td>Saturated</td>
<td>75</td>
<td>73</td>
<td>104</td>
</tr>
</tbody>
</table>

Measurements were also made on a saturated solution of sulphur in oleum, a similar broadening phenomenon being observed, the shift in this case being to low field. This system has been shown to give a well defined electron spin resonance spectrum (20)(26).

An attempt was made to dissolve a paramagnetic transition metal ion in 65% oleum to compare the effect of a known paramagnetic species.
FIG 1. NMR SPECTRA OF SOLUTIONS OF I$_2$ IN 65% OLEUM

[Diagram showing spectra for different concentrations of solutions.]
SHIFT OF PROTON RESONANCE IN OLEUM

FIG 2e

SHIFTING C/S

CONC I₂ M/1 → 0.4

FIG 3e

BROADENING OF PROTON RESONANCE IN OLEUM

BROADENING C/S

CONC I₂ M/1 → 0.4
Ni$^{2+}$ ion suggested itself, having the electronic structure \([\text{Core}]\) 3s$^2$ 3p$^6$ 3d$^8$ and thus two unpaired electrons in the 3d shell. However, neither this ion nor any other transition metal ion was sufficiently soluble in this medium for useful comparison.

**DISCUSSION**

**The shifts of the oleum resonances**

Dickinson has shown (24) that the variation of chemical shift with concentration is given by,

\[
\frac{d\delta_S}{dc} = -\frac{2}{3} \frac{\chi H_0}{c}
\]

where $\delta_S$ is the chemical shift in cycles/second, $c$ is the concentration in moles/cc. and $\chi$ is the susceptibility of a particular solution. $H_0$ is the field in the magnet gap, 9400 gauss in this case. This expression requires that,

(a) The sample shape approximates to an infinite cylinder. (A good approximation in this case since sample dimensions are 60 mm. x 3.5 mm.)

(b) The field of the remaining ions in the Lorentz cavity is zero (27).

Dickinson found deviations from Eqn. 1 which he interpreted in terms of a non-zero Lorentz cavity field. One might expect the field to be zero, since the interaction energy is of the type $\mu \cdot H$ averaged over a sphere. In this case the field will be assumed to be zero. Since,

\[
\chi = N \frac{\alpha^2 \mu^2}{3kT}
\]

where $\alpha$ is the Bohr magneton and $\mu$ is the effective magnetic moment of $1^+$, the slope $d\delta_S/dc$ can be expressed in terms of $\mu$.

From Fig. 2d the experimental slope is found to be - 72 cycles/mole/litre, which gives a value of $\mu = 1.5$ B.M. on the arbitrary assumption that
all the iodine is present as $I^+$, i.e. that the reaction

$$1_2 \rightarrow 2 I^+ + 2e$$

goes to completion. (The slope of the graph in Fig. 2d is positive since the measured shift is the positive increase in the field $H_0$ which compensates the negative term $H''(24)$, which is the magnetisation due to added paramagnetic species.) This result may be compared with the value of 1.9 B.M. found for a 0.1 M solution using a conventional Gouy balance. Using the 'spin only' value of 2.83 B.M. a theoretical slope of $-281$ cycles/mole/litre is obtained.

This result is in qualitative agreement only with that found from susceptibility measurements. Deviations from Eqn. 1 are often found and have been explained in two ways, apart from the possibility of a non-zero Lorentz cavity field. Bloembergen and Dickinson (28) have developed an expression which takes into account possible magnetic anisotropy of the paramagnetic ion of the form,

$$\frac{d\delta_S}{dc} = - \frac{2 \pi T \chi H_0}{3} + \frac{4}{15} \left(g_\|^2 - g_\perp^2\right) \frac{\beta^2 H_0 S(S + 1)}{C d^3 \frac{3 kT}{\beta}}$$

where $\chi$ is the number of ligands in the coordination sphere of the paramagnetic ion, $d$ is the separation between the paramagnetic species and the ligand nuclei, $C$ is the molar concentration of the ligand and the remaining symbols have their usual significance. Since the $I^+$ ion has a $3P_2$ state one might expect strong spin orbit coupling resulting in $\delta_{\perp} \neq \delta_{\parallel}$ and a deviation from Eqn. 1 on this account.

The second possibility is that covalent bonding between the paramagnetic species and the compound containing the resonating nucleus may occur and lead to a finite density of unpaired electrons at the resonating nucleus (29), which has the effect of shifting the resonance to low field. This effect
has been invoked by Phillips et al. (30) to explain their results on solutions of cobaltous ions in n-propanol, where covalent bonding between the OH groups and the paramagnetic ions is possible. This results in the OH group resonance initially being shifted to higher fields until a concentration of about 0.7 M CoCl$_2$ is reached when the signal moves to lower field strength. A deviation from the slope expected from Eqn. 1 thus results for the OH protons and also for the protons on the $\alpha$ and $\beta$ carbon atoms. The deviation found for I$^+$ is small and probably this type of mechanism does not play an important role. If this is the case, certain protonated paramagnetic species such as HI$^+$ or Hl$_2$$^{2+}$ can be eliminated.

**Broadening of the oleum resonances**

For a Lorentzian line shape, the line width at half-height in c/s is related to the spin-spin relaxation time, $T_2$, by the expression (31)

$$\delta_B = \frac{1}{T_2}$$

For liquids, $T_2$ and $T_1$, the spin-lattice relaxation time, can normally be assumed to be equal (31). To test this assumption $T_1$ for a 0.4 M solution of iodine in oleum was measured directly using spin-echo techniques* (32), and found to be $7 \pm 1.5$ millisec., which compares with a value of 8.15 millisec. for $T_2$ calculated from the line-width at this concentration. The assumption thus appears to be justified in this case.

Bloembergen, Purcell and Pound's original expression relating $T_1$ to the magnetic moment of the paramagnetic ions (23) has been modified by Abragam (33) to

* Thanks are due to Dr. Myer Bloom of the Physics Department, U.B.C., for making this measurement.
where \( N_{\text{ion}} \) is the concentration of paramagnetic ions in moles/cc., \( \gamma \) is the gyromagnetic ratio for the proton and \( \eta \) is the viscosity. From Eqn. 4 and since \( T_1 = T_2 \), we may rewrite Eqn. 5, giving,

\[
\delta_0 = \frac{16 \pi}{15 kT} N_{\text{ion}} \gamma^2 \beta^3 \eta
\]

The viscosity was measured at 25°C. to see if there was any appreciable change over the concentration range investigated. A Fisher F 1779 Ostwald type viscometer was used, fitted with P\(_2\)O\(_5\) tubes to avoid access of atmospheric moisture. The viscometer was immersed in a thermostatically controlled bath at 25°C. and a value of 44.5 centipoise was taken for the viscosity of 65% oleum (34). A small increase in viscosity was found which would slightly accentuate the deviation from linearity of the graph of broadening against iodine concentration. The results are shown in Table 2e.

**TABLE 2e**

**THE VISCOSITY OF IODINE 65% OLEUM SOLUTIONS**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Flow Time (sec.) (Average of 4 readings)</th>
<th>Viscosity (centipoise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65% oleum</td>
<td>238.6</td>
<td>44.5</td>
</tr>
<tr>
<td>0.208 M.-l(_2)</td>
<td>244.8</td>
<td>45.6</td>
</tr>
<tr>
<td>0.402 M.-l(_2)</td>
<td>259.6</td>
<td>48.4</td>
</tr>
</tbody>
</table>

Using Eqn. 6 and the previously calculated value of \( \mu = 1.5 \) B.M. gives an inverse relaxation time of \( 7.35 \times 10^3 \text{ sec}^{-1} \) for a 0.4 M solution. The experimental value of \( 1.2 \times 10^2 \text{ sec}^{-1} \) is a factor of 60 less than that
predicted by Eqn. 6.

However, Eqn. 6 is derived by making a number of assumptions of which the most important in this case is that one supposes that the cause of the variation of the magnetic field produced by the ion at the proton position is the relative displacement of the ion and the proton. It is necessary to add the variation due to electronic relaxation of the spin of the ion characterized by a time $\Theta$, and it can be shown that the effect of $\Theta$ becomes appreciable for,

$$\Theta \lesssim \frac{d^2}{2D} \sim 10^{-10} \text{ sec.}$$

where $d$ is the diameter of the ions and the proton containing molecules (assumed equal) and $D$ is their diffusion coefficient. Hence, the effect may become important for solutions very much more viscous than water, as is the case for these solutions.

Kozyrev and Rivkind (35) have compared the magnetic moments of transition metal ions calculated from static susceptibility data, $u_{\text{stat}}$, and derived from $T_1$ measurements, i.e. using Eqn. 6, giving $u_{\text{eff}}$. In the particular case of $\text{Co}^{2+}$ they find $u_{\text{stat}}$ to be 5.0 B.M. and $u_{\text{eff}} \approx 0.74$ B.M., i.e. the inverse relaxation time calculated using $u_{\text{stat}}$ is a factor of,

$$\left(\frac{u_{\text{stat}}}{u_{\text{eff}}}\right)^2 = \left(\frac{5.0}{0.74}\right)^2 \sim 46$$

larger than the observed inverse relaxation time. The theoretical reasons for the non-equivalence of $u_{\text{stat}}$ and $u_{\text{eff}}$ have been discussed by Abragam (33) and Van Vleck (36). Only for ions in $S$ states having no orbital magnetism, e.g. $\text{Mn}^{2+}$ and $\text{Fe}^{3+}$ which both have the term symbol $^6S_5/2$ is $u_{\text{eff}} = u_{\text{stat}}$. For ions such as $\text{Co}^{2+} ({}^4F_9/2)$ which has energy levels lying
near the ground state, $\mu_{\text{eff}} \neq \mu_{\text{stat}}$, and it is also these ions which will be expected to have the shortest electronic relaxation times. These short relaxation times decrease the correlation time of the fluctuating field of the ion and result in a diminution of $1/T_1$ for the protons and of $\mu_{\text{eff}}^2$.

Hence, the large discrepancy between the experimental and theoretical inverse relaxation times for the iodine solutions is not surprising in view of their high viscosity and also since the $I^+$ ion is in a $^3P_2$ spectroscopic state. Thus, Eqn. 6 is not a satisfactory representation in this case.

Another approach is to compare the results with similar data for other systems. Morgan et al. (37) measured $T_1$ for protons in aqueous solutions of chromic ions bonded to a variety of ligands. The viscosity of the solutions was varied by addition of glycerol. Interpolating their data for $\text{Cr(en)}_3^{3+}$ ions gives $T_1 = 0.53$ millisec. for a solution 0.4 M in chromic ions and having a viscosity of 48 centipoise. Using 3.9 B.M. for the magnetic moment of the ions (38) in the ethylene diamine complex, the moment of the paramagnetic species in oleum can be estimated from the relation,

$$\frac{T_1 (I)}{T_1 (\text{Cr})} = \frac{\mu^2 (\text{Cr})}{\mu^2 (I)}$$

This gives $\mu (I) = 1.1$ B.M., a result in qualitative agreement with the previous one, suggesting possibly that the paramagnetic species are affecting the protons of the solvent in similar ways in these two solutions. The main conclusion drawn by Morgan et al. (37) was that direct proton exchange between the $\text{Cr(en)}_3^{3+}$ ion and the solvent is not occurring. Applied to the $I^+$ solution, this means that species such as
HI⁺ can again be rejected, but that the postulate that I⁺ cations are present is in accord with the results.

**Suggestions for future work**

A more complete understanding of this system will result if it becomes possible to identify spectroscopically the various species present in these solutions so that a quantitative estimate of the I⁺ concentration can be made. Work on these lines is at present in progress (39).

It has been suggested (40) that the nuclear Overhauser effect (41) might be employed to detect the presence of paramagnetic species in these solutions. A similar experiment has been performed by Codrington and Bloembergen (42) who detected an enhancement of the proton resonance of Mn²⁺ solutions when the electron resonance of the Mn²⁺ ions was saturated at its resonant frequency.
BIBLIOGRAPHY FOR CHAPTER IV

PUBLICATIONS

FIG 1a

$\bar{H}_0(Z)$

PRECESSION OF $\bar{u}$

IN A FIELD $\bar{H}_0$
FIG. 2a

SIMPLIFIED NMR SPECTROMETER CCTS.

R.F. OSC.

R.F. BRIDGE

RECEIVER

R.F. BRIDGE CCT.

NUCLEAR INDUCTION CCT.
FIG 3a

BLOCH SUSCEPTIBILITIES
(IN UNITS OF $\frac{1}{2} \chi_0 \omega_0 T_2$)

ABSORPTION

\[ \chi'' \]

\[ (\omega - \omega_0) T_2 \]

DISPERSION

\[ \chi' \]

\[ (\omega - \omega_0) T_2 \]
FIG 4a

LOW RESOLUTION E\textsuperscript{1}OH SPECTRUM

FIG 5a

HIGH RESOLUTION E\textsuperscript{1}OH SPECTRUM
FIG 1b

BLOCK DIAGRAM OF SPECTROMETER
CRITERIA OF FIELD HOMOGENEITY

FIG 2b

OVERCYCLED

IDEAL CASE

UNDERCYCLED

FIG 3b

'WIGGLES'

'WIGGLES BEATS'

\[ \text{DISTANCE} \]

\[ H_0 \]
FIG 4b

DESIGN I
HEATER & SPINNER

GAS INLET ASSEMBLY

TAPERED DEWAR

TUNGSTEN ROD

TEFLON CAP

SAMPLE TUBE

TEFLON BEARINGS
DESIGN II. GAS INLET SYSTEM

- Quickfit Thermometer
- Glass Bellows
- Thermocouple Entry
- Heating Element

FIG 6b
DILUTION-SHIFT CURVES

- \( \text{CH}_3\text{OH} \)
- \( \phi \text{CH}_2\text{OH} \)
- \( \phi \text{C(CH}_3\text{)HOH} \)
FIG 2c  DILUTION-SHIFT CURVES

- CH₃OH
- CH₂OH
- (CH₃)₂OH
- C₂H₅OH
- C₃H₇OH

SHIFT C/S

CONC. m.f.
FIG 3c NMR SPECTRA

a) PROPARGYL ALCOHOL

b) PROPARGYL ACETATE
FIG 4c DILUTION-SHIFT CURVES

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Graph Line Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃C≡CCH₂OH</td>
<td>Solid line</td>
</tr>
<tr>
<td>HC≡C(CH₃)OH</td>
<td>Dashed line</td>
</tr>
<tr>
<td>HC≡C(CH₃)₂OH</td>
<td>Dotted line</td>
</tr>
<tr>
<td>CH₃C≡CCH₂OH</td>
<td>Chain-dashed line</td>
</tr>
</tbody>
</table>

SHIFT C/S vs CONC. m.f.
FIG 6c DILUTION-SHIFT CURVES

- CH₂CICH₂OH
- CHCl₂CH₂OH
- CCl₃CH₂OH
- C₂H₃CH₂OH

CONC. m.f.

SHIFT C/5
FIG 5c DILUTION-SHIFT CURVES

- $\text{HC:CCH}_2\text{OH}$
- $\text{HC:CC(CH}_3\text{)OH}$
- $\text{HC:CC(CH}_3\text{)}_2\text{OH}$
FIG 7c DILUTION-SHIFT CURVES

- CH₃CH₂CH₂OH
- CH₂CH CH₂OH
- Me Et t-Bu COH
FIG 8c DILUTION-SHIFT CURVES FOR CH\_2CHCOOH

- \( \text{CCl}_4 \)
- \( (\text{CH}_3)_2\text{CO} \)
- DIOXANE
FIG 9c TEMPERATURE-SHIFT CURVES
MeOH IN CCl₄

SHIFT C/S

0.030
0.038
0.047
0.069
0.092
0.108
0.170
0.262
1.000

20 T °C 70
FIG 10c TEMPERATURE-SHIFT CURVES
MeOH IN CHCl₃
FIG 11c TEMPERATURE-SHIFT CURVES

- H$_2$O
- MeOH
- X
- Cl
- OCH$_3$

SHIFT C/S

T °C

M.P.
FIG 12c TEMPERATURE-SHIFT CURVES

$\Delta$ \hspace{1cm} \begin{array}{c} \text{OH} \\ \text{NO}_2 \end{array}$

$\circ$ \hspace{1cm} \begin{array}{c} \text{OH} \\ \text{COOCH}_3 \end{array}$

$\times$ \hspace{1cm} \begin{array}{c} \text{OH} \\ \text{CHO} \end{array}$

![Graph showing temperature-shift curves with data points for three different compounds.](image)
**FIG 13c** MONOMER-DIMER EQUILIBRIUM IN MeOH/CCI$_4$ SOLUTIONS

**FIG 14c** %H BONDED SPECIES vs %NMR SHIFT FOR MeOH/CCI$_4$ SOLUTIONS

- ○ %PROTONS IN DIMER + POLYMER
- × %PROTONS IN POLYMER ONLY
- • 0.32 %DIMER + POLYMER PROTONS
FIG 15c

MONOMER-DIMER EQUILIBRIUM IN MeEt-t-BuCOH/CCl₄ SOLUTIONS
FIG 1d NMR SPECTRA OF \( \phi_3C^+ \)
FIG 2d

RESONANCE STRUCTURES

HUCKEL M.O.s

S.C.M.O.s

CHARGE DENSITIES IN THE TRIPHENYLMETHYL CATION
NMR SPECTRA OF AROMATIC PROTONS

FIG 3d

\[ \text{CH}_3\text{C}^+\text{C}^+\phi_2 \]

FIG 4d

\[ (\text{MeO} \text{C})_3^+ \]
FIG 5d NMR SPECTRA OF AROMATIC PROTONS 60 Mc
FIG 6d NMR SPECTRUM OF 1,1-DIANSYL ETHYLENE IN H₂SO₄
FIG 2. Shift of proton resonance in oleum.

FIG. 1. NMR SPECTRA OF SOLUTIONS OF I\textsubscript{2} IN 65\% OLEUM

0.401 M/l

H\textsubscript{2}S\textsubscript{2}O\textsubscript{7}, H\textsubscript{2}S\textsubscript{2}O\textsubscript{7}+I\textsubscript{2}

0.0925 M/l

H\textsubscript{2}S\textsubscript{2}O\textsubscript{7}, H\textsubscript{2}S\textsubscript{2}O\textsubscript{7}+I\textsubscript{2}
FIG6d NMR SPECTRUM OF 1,1- DIANISYL ETHYLENE AT 40 Mc