MOLECULAR MOTION IN UREA AND THIOUREA ADDUCTS

by

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ABSTRACT

The proton magnetic resonance of tridecane and hexadecane and their urea adducts and of some thiourea adducts has been studied as a function of temperature. It has been shown that quite considerable molecular motion can occur in the adducts even at low temperatures. The results support previous conclusions obtained by other methods.
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INTRODUCTION

The term clathrate is derived from 'clathratus' (Latin, cage) and is used to describe certain compounds in which one component is trapped within the lattice of another without apparently being chemically bonded to it. Compounds of this type include the gas hydrates (1), urea adducts (2), benzene nickel ammonium cyanide clathrates (3), and the clathrates of quinol (4). The preparation, structure and properties of clathrates have been reviewed by Powell (5) (6). Structural studies indicate that the distance between the cage and the enclosed component is too great for any chemical bonding to occur hence the material must be held only by physical forces. These comparatively slight forces may allow the enclosed molecule a certain freedom of motion, thus in the sulphur dioxide-quinol clathrate the SO₂ molecule has been shown directly by X-ray Fourier analysis to reorient about one axis in its quinol cage (7). The dielectric absorption at microwave frequencies of quinol clathrates (8) and of urea adducts of long chain ketones and alkyl halides (9), and the poor X-ray scattering of gas hydrates in ice (5) lead to similar conclusions.

This investigation was concerned with the motion of the enclosed molecules in the hydrocarbon adducts of urea and thiourea.

"Wide line" Nuclear Magnetic Resonance techniques provide an excellent means of studying molecular motion in solids and are thus well suited to a problem such as this. The application of Nuclear Resonance theory to solids is briefly discussed.
(i) Introduction and theory.

The existence of nuclear spin was postulated in 1924 by Pauli (10) to account for the hyperfine structure of atomic spectra, and although molecular beam methods of observing magnetic moments (11) have been used for some time, attempts to obtain nuclear resonance signals from a condensed phase were not successful until 1946 when Bloch, Hansen and Packard (12) at Stanford, and Purcell Torrey and Pound (13) at Harvard, independently observed nuclear magnetic resonance. The initial application of the method was to the precise determination of magnetic moments and spin, but the work of Bloembergen, Purcell, and Pound (14), and of Gutowsky and Pake (15), indicated the possibilities of NMR as a tool in the investigation of the structure and properties of solids and liquids.

The phenomenon of nuclear magnetic resonance can be explained both from a classical viewpoint and by a quantum mechanical treatment. A nucleus possessing spin must also have a magnetic dipole moment associated with the non-zero spin angular momentum. Since both angular momentum and magnetic dipole moment are vectors, they are linearly related by a scalar, \( \gamma \), termed the magnetogyric ratio, such that

\[
\vec{\mu} = \gamma \vec{I}
\]

A magnetic dipole \( \vec{\mu} \) placed in an external magnetic field \( H_0 \) will experience a torque tending to turn the dipole about the direction of the field. The dipole will precess about the
Fig. 1. PRECESSION OF $\mu$ ABOUT $H_0$.

Fig. 2. LOCAL FIELD DUE TO PRECESSING NUCLEUS.
direction of $H_0$ at the Larmor frequency $w_0$ given by $w_0 = \gamma H_0$. If a small additional field $H_\perp$ is now applied at right-angles to $H_0$ and in the plane of $\mu$ and $H_0$, a further torque is experienced tending to increase $\theta$, the angle between $\mu$ and $H_0$, and if $H_\perp$ is rotating at the same frequency as $\mu$, then $\theta$ will steadily increase. If, however, the frequency of $H_\perp$ is not the same as the Larmor frequency only slight perturbations of the precession will occur. In practice it is easier to produce a linearly oscillating field than a rotating field and so $H_\perp$ is replaced by a linearly polarised field $2H_\perp$ which may be considered as two circularly polarised fields rotating with the same frequency in opposite directions. Only the field rotating in the same sense as the Larmor frequency will induce transitions; the other having negligible effect.

According to quantum mechanics the angular momentum of the nucleus must be quantised in units of $\hbar$, and may only assume certain orientations when placed in a magnetic field. Hence only certain discrete energy levels are permissible. The number of such levels is given by $(2I + 1)$, and the energy difference between adjacent levels is $\Delta E = \mu \hbar / I = \gamma \hbar \omega$. Now $\Delta E = \hbar \omega$, hence $2\pi \omega = \gamma H_0$, or in terms of angular frequency $\omega = \gamma H_0$, which is the same condition for resonance as that obtained from the classical approach.

(ii) Relaxation.

In the absence of some relaxation process by which spins may lose energy, the continued absorption of energy by the lower levels would tend to equalise the populations of the levels so that no further absorption could be detected. There must
therefore be some mechanism by which the Boltzmann distribution between the levels can be maintained during resonance absorption. Two different relaxation processes exist, the spin lattice interaction and the spin-spin interaction.

Spin-lattice relaxation. A spin-lattice relaxation time may be considered as the time constant for the system with equal populations of levels to exponentially approach to the equilibrium state, i.e. to attain thermal equilibrium with the lattice. The population of the levels at equilibrium is governed by the Boltzmann factor \( \frac{N_+}{N_-} = \exp\left(\frac{2\mu_0 H_0}{kT}\right) \) where \( N_+ \) and \( N_- \) are the number of nuclei in the upper and lower states respectively. If the probability per unit time of downward transitions is \( W_- \) and for upward transitions is \( W_+ \) then at equilibrium \( W_+ N_+ = W_- N_- \). Therefore
\[
\frac{W_-}{W_+} = \frac{N_+}{N_-} = \exp\left(\frac{2\mu_0 H_0}{kT}\right) \approx 1 + 2\frac{\mu_0 H_0}{kT}.
\]

If \( W \) is the mean of \( W_+ \) and \( W_- \) then
\[
W_- = W\left(1 + 2\frac{\mu_0 H_0}{kT}\right) \quad ; \quad W_+ = W\left(1 - 2\frac{\mu_0 H_0}{kT}\right).
\]
If the spin temperature is now altered, a change in the populations must result, if the excess of nuclei in the lower state is \( n \), then \( \frac{dn}{dt} = 2W(n_0 - n) \), where \( n_0 = N_0 H_0 / kT \). Hence \( (n_0 - n) = (n_0 - n_1)e^{-2Wt} \), where \( n_1 \) is the initial difference in population. Thus the equilibrium is approached with a characteristic time constant \( T_1 = 1/2W \).

The relaxation process has also been treated from the phenomenological viewpoint by Bloch (16). For an assembly of weakly interacting spins, the magnetisation vector, \( M \), is the vector sum of all the nuclear magnetic moments in unit volume. In the absence of the rotating magnetic field and with the spin system and lattice in thermal equilibrium then \( M_z \), the component
parallel to the steady field $H_0$, is given by $M_0 = \chi_0 H_0$. When the system is not in equilibrium, then $\frac{dM_z}{dt} = (M_0 - M_z) / T_1$. From this formulation Bloch termed $T_1$ the longitudinal relaxation time. $T_1$ from experiment is found to range from microseconds to several hours. (14).

A thorough theoretical analysis of spin lattice relaxation has been made by Bloembergen, Purcell and Pound (14).* In liquids the relaxation is due to the time varying dipolar interaction resulting from translational and rotational motion. In general a continuous spectrum of frequencies of the dipolar fields will be produced but only a narrow band of frequencies near the resonant frequency and, twice the resonant frequency, will be effective in producing spin-lattice relaxation. A similar process occurs in solids when molecular rotation and translation occur, in the absence of such motion however some other relaxation process must be present. The mechanism was shown by Bloembergen (17) to be due to paramagnetic centres present in the solid. Electron magnetic moments being of the order of $10^3$ times larger than the nuclear moments produce very large fluctuating magnetic fields in their immediate vicinity and cause rapid nuclear spin relaxation for those nuclei close by.

Spin-Spin Interaction. Apart from the interaction between the spins and the lattice, an interaction occurs between the spins themselves. According to the Bloch formulation the relaxation time $T_2$ is termed the transversal relaxation time since it is the time constant for the exponential decay of the

*Referred to as BPP.
transverse x and y components of the nuclear magnetisation vector $\frac{dM_{xy}}{dT} = -\frac{M_{xy}}{T_2}$. The physical significance of $T_2$ is the time constant for the individual spins to lose rotational phase coherence with one another. The nuclear spins will be in slightly different magnetic fields due to the magnetic dipoles of their neighbours, they will therefore precess at different Larmor frequencies and eventually become phase incoherent. The local field $H_{loc}$ due to the neighbouring dipoles consists of two components, the resultant of the static fields and the resultant of the rotating components of all local fields (Fig. 2.)

The magnitude of the field due to a dipole $\mu$ at distance $r$ is of the order of $\mu r^{-3}$. This dependence on the inverse cube infers that only nearest neighbours make any appreciable contribution. The resonance is no longer sharp but will be broadened about $H_0$, the line shape depending on the spatial configuration of the lattice and the given direction of $H_0$. For completely random distribution of a large number of near neighbours a Gaussian line shape will result. In general the line shape deviates from the pure Gaussian shape due to the ordered arrangement of dipoles in the lattice.

A second process leading to the broadening is the simultaneous exchange of energy by two antiparallel spins. One nucleus may produce a field at a second nucleus, oscillating at its Larmor frequency, resulting in reciprocal transitions. This exchange of spin energy does not result in emission or absorption of energy, but does limit the lifetime in given state. The resonance line width is thus dependent on the spin-spin interaction time or spin phase-memory time. In the notation of BPP,
$T_2$ is reserved for the specification of the line width in the general case to which $T_1$ also contributes, $T_2''$ defines the line width in the limiting case of a rigid lattice, and $T_2'$ for the case where lattice motion occurs.

There are two components of the transverse nuclear magnetisation, that in phase with the radio-frequency field $H_1$ and that $T_2$ out of phase with $H_1$. These are known as the dispersion mode or $u$-mode and absorption or $v$-mode. The magnetic susceptibilities are defined by $M = (\chi' - i\chi'') H$, where $\chi'$ is the real part and $\chi''$ the imaginary part of the complex susceptibility, $\chi'$ is associated with the dispersion mode and $\chi''$ with absorption. The dependence of $\chi'$ and $\chi''$ on $(H - H_0)$ is shown in Fig. (3).

(iii) Line Widths and Shapes.

The simplest assumption that may be made regarding line shapes is that the absorption curve corresponds to either a Gaussian or a Lorentzian distribution. In practice these simple line shapes are not found, it is in general impossible to calculate an expected line shape except in certain simple groups. Resonance line widths may be classified into two types :-

(a) Homogeneous broadened, including dipolar interaction between like spins, motional narrowing, sufficiently rapid spin-lattice relaxation such that $T_1 = T_2$.

(b) Inhomogeneous broadened due to inhomogeneous static field, anisotropic chemical shift, Knight shift, (18) Quadrupole broadening, (19) dipolar interaction between unlike spins.
(1) absorption mode.  

(2) dispersion mode.

Fig. 3. NUCLEAR SUSCEPTIBILITIES.

Fig. 4. THEORETICAL LINE SHAPE FOR STATIC DOUBLET.
Dipolar broadening. (a) Two spin group. The line shape of such a system was studied by Pake (20) in a single crystal of gypsum CaSO$_4$·2H$_2$O at room temperature, when the system is effectively rigid. Since the dipolar interaction is dependent on the inverse cube of distance, by far the largest effect is due to the neighbouring proton in the water molecule. The component of this local field parallel to the applied field $H_0$ is given by $\pm \mu r^{-3}(3\cos^2\Theta-1)$. Thus, neglecting local fields of more distant neighbours, the resultant field is $H = H_0 \pm \mu r^{-3}(3\cos^2\Theta-1)$. This results in two lines equally spaced about $H_0$. In gypsum two proton pairs occur with different values of $\Theta$, a single crystal will therefore give two pairs of symmetrically disposed resonance lines which will be broadened by the small local fields of more distant neighbours. Pake however found that resonance should occur at $H = H_0 \pm \frac{3}{2} \mu r^{-3}(3\cos^2\Theta-1)$, the term $\frac{3}{2}$ arising from the spin exchange process discussed under spin-spin relaxation processes. If the sample is polycrystalline a random distribution of individual crystals occurs and the resultant line shape is the sum of all individual spectra. The calculated line shape is shown by the broken line in fig. (4) the full line shows the broadening by other neighbours.

From this the interproton distance may be calculated but the use of polycrystalline material precludes the measurement of angular disposition.

Three spin system. The resonance line shape for a triangular configuration of nuclei has been derived by Andrew and Bersohn (21). The case is considerably more complicated than the two spin system. For a single crystal, neglecting
broadening by neighbours, the spectrum consists of a central line and three pairs of lines symmetrically placed about the centre. For polycrystalline material the line shape is obtained by summation over all crystals, Fig. (5). When broadening is taken into account the line structure is smoothed out. The confirmation of the existence of $\text{H}_3\text{O}^+$ in e.g. the hydrates of $\text{HNO}_3\cdot\text{H}_2\text{O}$ (22) and $\text{HClO}_4\cdot\text{H}_2\text{O}$ (23) at $90^\circ\text{K}$ was obtained from the characteristic resonance line shape.

More complicated systems. For groups with more than three nuclei only rough predictions can be made regarding the line shape, although certain cases such as $\text{CH}_4$ and $\text{NH}_4^+$ have met with some success (24) (25).

Van Vleck (26) has derived in a rigorous manner an expression for the second moment of the absorption curve in terms of the magnetic moments, spins, and internuclear distances of the nuclei.

The second moment $\langle \Delta H_z^2 \rangle$ of the shape function $g(\text{H-H}_0)$ normalised to unit area is

$$\langle \Delta H_z^2 \rangle = \int_{-\infty}^{\infty} g(\text{H-H}_0)(\text{H-H}_0)^2 d\text{H}.$$  

Van Vleck showed that for a single crystal containing $N$ nuclei of only one magnetic species, the second moment is given by

$$\langle \Delta H_z^2 \rangle = \frac{3}{2} I(1+I)N^{-1}I_i^2 I_j^2 \sum \left(3 \cos^2 \Theta_{jk} - 1 \right)^2 r_{jk}^{-6}.$$  

Strictly, $N$ should be taken for the total number of resonating nuclei in the sample but due to the dependence on the inverse sixth power of distance $N$ may be reduced to the number in the unit cell and their nearest neighbours. $N$ may be reduced still further if the unit cell possesses symmetry such that two or more
Fig. 5. THEORETICAL LINE SHAPES FOR (a) STATIC $\Delta$ WITHOUT BROADENING, (b) BROADENED BY NEIGHBOURS.

Fig. 6. MOTION OF INTERNUCLEAR VECTOR OP ABOUT AXIS ON.
nuclei have the same environment.

If the sample is polycrystalline the angular factor may be averaged over a sphere, and if the crystal contains other magnetic species a second term must be included. The second moment now becomes

\[ \langle \Delta H_2^2 \rangle = \frac{2}{5} I (I+1) \mu_0^2 g^2 N^{-1} \sum_{j,k} m_j m_k + \frac{4}{15} \mu_0^2 N^{-1} \sum_{j} I_j (I_j+1) m_j^2 m_k^2. \]

The validity of the second moment has been amply supported and has proved extremely valuable in structural determinations.

(iv) The effect of motion on line shape and second moment.

If the motion of molecules or groups is sufficiently rapid the line width and line shape may be profoundly altered. Hindered rotation of groups of nuclei in solids often occur about one direction or axis and only a partial reduction in line width may result. Isotropic rotation is necessary for complete averaging of the dipolar fields. The limiting line width for a particular mode of motion may be calculated by averaging the appropriate angular factors.

The effect of rotation on the line shape for a two spin system has been given by Gustowsky and Pake (15), Fig.(6).

OP is the vector \( \vec{r}_{jk} \) joining nuclei \( j \) and \( k \) at an angle \( \Theta_{jk} \) to the applied field \( H_0 \). ON is the axis of reorientation making an angle \( \Theta' \) with \( H_0 \) and angle \( \gamma_{jk} \) with \( r_{jk} \). The reorientation causes \( \Theta_k \) to vary with time and it becomes necessary to take the average value of \( (3 \cos^4 \Theta_{jk}^{-1}) \) which becomes \( \frac{1}{2} (3 \cos^4 \Theta'^{-1})(3 \cos^2 \gamma_{jk}^{-1}) \). If the axis of reorientation ON is perpendicular to the internuclear vector as is commonly
the case, the absorption line has two components at 
\[ H = H_o + \frac{3}{4}\mu r^{-3}(1 - 3\cos^2\Theta'). \]
The maximum splitting is only half that of the rigid system, see Fig. (7).

A three spin system reorienting about any given axis (21) leads in the general case to a central line and three pairs of lines, as in the case of the rigid lattice. However for the special case in which the axis of rotation is perpendicular to the plane of the triangle two pairs of lines disappear, Fig.(8). This has been observed for methyl groups in a number of compounds (15).

For a single crystal the angular term in the second moment must be averaged over the motion. For a polycrystalline sample with axis of rotation randomly distributed it is necessary to average over all values of \( \Theta' \), which leads to an expression for the second moment of

\[ \langle \Delta H^2 \rangle = \frac{1}{4} \left[ \frac{6}{5} I(I+1) N^{-1} \mu_o^2 \sum_{j>k} r_{jk}^2 \left( 3\cos^2\gamma_{jk} - 1 \right) 
+ \frac{4}{15} N^{-1} \sum_{j>k} I_j(I_j+1) \sum_{j'} \sum_{j''} \left( 3\cos^2\gamma_{jj'} - 1 \right) \right] \]

If the rotational axis is perpendicular to all internuclear vectors the above expression reduces to a value one fourth of the rigid lattice value. In the more general case the factor \( \frac{1}{4}(3\cos^2\gamma_{jk}-1) \) must be applied. This factor decreases from unity at \( \gamma_{jk} = 0^\circ \) to zero at \( \gamma_{jk} = 54^\circ 44' \) and increases to \( \frac{1}{4} \) at \( \gamma_{jk} = 90^\circ \).

The effect of rotational oscillation has been considered by Andrew (27). For small angular amplitude of
Fig. 7. THEORETICAL LINESHAPES FOR A ROTATING DOUBLET.

Fig. 8. LINESHAPES FOR A ROTATING Δ
(a) isolated Δ rotating about normal to plane.
(b) broadened by neighbours.
oscillation the reduction factor $\rho$ of the second moment is given by

$$\rho = 1 - \frac{3}{2} \alpha^2 \sin^2 \gamma.$$
CHAPTER 11

THE STRUCTURE OF UREA AND THIOUREA ADDUCTS

The occlusion compounds of urea and thiourea, variously referred to as inclusion compounds, adducts, channel complexes and urea complexes, can be prepared from a variety of organic molecules bearing various functional groups. The urea adducts were accidentally discovered by Bengen (2) during research on the fat content of milk. Subsequent studies have confirmed and extended Bengen's results (28) (29) (30). In general the ease of formation and stability of urea adducts are dependent on the chain length and vapour pressure of the occluded compound. Certain branched chain and cyclic compounds will adduct with urea provided there is a sufficiently long chain in the structure (31) (32).

The adducts of thiourea were discovered independently by Angla (33) and by Fetterly (34). The complexes are similar to those of urea but form with branched chain and cyclic structures (35) (36), although rather unstable complexes with straight chain hydrocarbons can be prepared (37).

The analysis of urea complexes showed a non-stoichiometric composition but that a definite ratio existed between the amounts of each component, and, for straight chain adducts, that this ratio was dependent on chain length. Debye diffraction patterns exhibited the same pattern for nearly all complexes (38) inferring that the structure of the complexes was the same, independent of the hydrocarbon.
A precise X-ray determination of the structure of urea adducts was made by Smith (39) (40). In urea itself the unit cell is tetragonal whereas in the complex it is hexagonal with six urea molecules per unit cell. \( a_0 = 8.23 \text{Å}, c_0 = 11.00 \text{Å} \), Fig. (9). The urea molecules form a hollow channel in which the hydrocarbon is enclosed. The hydrocarbon chains are in an extended planar zigzag configuration with their long axes parallel to the c axis. The time average position of the plane of the hydrocarbon molecule is randomly oriented perpendicular to the a axis and at multiples of 60° to this position. Laue and rotation photographs show continuous layer lines attributed to the hydrocarbon molecules, the distance between these lines can be used to compute the molecular length of the enclosed hydrocarbon (41).

In the complex each oxygen is hydrogen bonded to four nitrogen atoms and each nitrogen to two oxygen atoms. Two different hydrogen bonds occur (i) short, c. 2.93Å (ii) long c. 3.04Å. The bonds are essentially co-planar with the urea molecules to which the nitrogen atoms are attached. C-N-H-O angles are about 136° and 116° for the strong and weak bonds respectively. The hydrogen bonds account largely for the stability of the complex. The heat of formation of the adduct arises from (a) differences in hydrogen bond energy in urea and in the complex, (b) differences in van-der-Waals forces in tetragonal urea and hydrocarbon and in the complex. The energy associated with the observed shortening of the hydrogen bonds is of the order of magnitude of the observed heat of formation. The van der Waals forces between the oxygen of the urea and the
Fig 9  STRUCTURE OF UREA HYDROCARBON ADDUCT.

Showing position of hydrogen bonds and hydrocarbon chain.

atoms of the hydrocarbon chain, although small for each atom pair, contribute to the stability of the adduct due to the large number of such interactions.

Taking values of 1.54Å and 109°28' for the bond length and angle of the carbon chain and 2.0Å as the van der Waals radius of the methyl groups, the chain length for the extended planar zig-zag configuration is given by 1.256(n-1) + 4.0Å. From the dimensions of the urea unit cell the mole ratio of urea to hydrocarbon is 0.6848(n-1) + 2.181, which is in agreement with experiment.

The structure of thiourea adducts has been mentioned briefly by Smith (39) and also investigated by Schlenk (42). The unit cell is rhombohedral and the molecules arranged in a similar fashion to urea in urea adducts. The larger size of the sulphur atom results in a larger channel 5.8 - 6.8Å as opposed to 4.1 - 4.8Å in urea adducts. The length of the unit cell is 12.6Å. No simple relationship linking the dimensions of the enclosed component and the mole ratio exists for thiourea adducts. It is found however, for e.g. w-w' dicyclohexyl alkanes, that constant mole ratios of about 9:1 and 6:1 are obtained for certain members of homologous series. This is explained as resulting from compression of the paraffinic portion of the molecule.

The interest shown in urea and thiourea adducts has largely been confined to their technological applications in the petroleum industry (43). Apart from the structural studies of Smith and Schlenk, the only physical measurements which have been made are those of Fischer and McDowell (44), Stewart (45),
and Barlow and Corish (46) on infra red spectra, Meakins (9) dielectric measurements, and Topchiev et al. (47) differential thermal studies. The infrared studies show shifts to longer wavelengths in the N - H stretching region corresponding to increases in hydrogen bond strength. The absorptions due to the enclosed molecule show little or no change in frequency.

Meakins (9) examined the dielectric absorption at microwave frequencies of the adducts of long chain polar compounds. In all cases a large dielectric absorption was obtained and interpreted in terms of the reorientation of the long chain dipoles in the urea lattice. The presence of dielectric absorption in 1,10, dibromodecane adduct, in which the chain is known to be in an extended planar configuration, (40) and should therefore possess zero dipole moment, was assumed to result from reorientation of the C-Br dipoles independently of the main chain. The high frequency of the absorption maximum also inferred that the long chain molecules were loosely held in the urea lattice.

The thermal studies of Topchiev et al. (47) show evidence for various phase changes in the adducts of several n-paraffins in the range $C_{21} - C_{32}$. Three or four points were observed

(i) A polymorphic reversible phase change.
(ii) The melting point of the hydrocarbon.
(iii) Decomposition of the adduct.
(iv) The melting point of urea.

The existence of definite decomposition points has also been reported by Swern et al. (30) for adducts of fatty acids.
CHAPTER 111

APPARATUS AND EXPERIMENTAL PROCEDURES

(i) The Spectrometer.

The methods employed by Purcell, Torrey and Pound (4) and by Bloch, Hansen and Packard (3) differed in the instrumental technique used to observe resonance. In the spectrometer of Purcell et. al. a single coil, which acted as both transmitter and receiver, was placed in one arm of an R.F. bridge. The bridge could be balanced to obtain either the absorption or the dispersion mode. At resonance a signal appeared at the balance point of the bridge as a result of the change in the impedance of the arm containing the sample.

The nuclear induction method of Bloch employed a second coil, acting as a receiver, which was placed orthogonally to the transmitting coil and to the steady magnetic field. On passage through resonance an e.m.f. was induced into the receiver coil. The magnetic coupling (leakage) between the coils was controlled by the geometry of the system and by movable paddles, which caused the flux lines to deviate from axial symmetry and thus compensated for slight departures from orthogonality.

The spectrometer used in these investigations was a Varian V4200/4300B Dual purpose spectrometer (48) operating on the Bloch or crossed coil principle. A block diagram is given in Fig. (10). For proton resonance the spectrometer was operated at 40/Mc/s and 9400 gauss. The R.F. power was supplied
Fig. 10. BLOCK DIAGRAM OF VARIAN "WIDE-LINE" SPECTROMETER.
by a 10 Mc/s crystal oscillator followed by two frequency
doublers. The induced signal in the receiver coil appeared
as a modulation of the coupling between the coils. This
signal was fed to a low noise preamplifier in the probe and
then, after further amplification, was demodulated to audio
frequencies by a tuned R.F. amplifier-detector. In order to
calibrate signals, provision was made for audio frequency
modulation of the R.F. power.

The polarising magnetic field was modulated at audio
frequencies by sweep coils in the probe, enabling A.C. amplifiers
to be used in the spectrometer. The output from the detector
was converted to direct current by a phase sensitive detector
and recorded as the derivative of the absorption signal. The
signal could be presented on a Dumont persistent screen
oscilloscope by driving the X-axis by the sweep oscillator and
applying the signal to the Y-axis. In recording the signal,
filters placed after the phase sensitive detector allowed much
of the noise to be integrated. The sweep modulation was
reduced to a value low compared with the line width in order
to avoid spurious broadening of the signal.

Certain minor modifications were made which improved
the performance of some components of the spectrometer but did
not substantially alter any aspects of its operation.

(i) The V2100 Magnet Power Supply was modified to exclude
the V2101B Voltage Regulator (as per instructions from Varian
Associates).

(ii) The drive shafts from the synchronous motors in the
V4280 A Field Scanning Unit were replaced by a single spindle.
This prevented the drive slipping at an Allen nut connection in the original mechanism.

(iii) To prevent lateral movement of the scanning motors, which allowed the gears to disengage, the springs holding the unit were replaced by a clamp.

(ii) Variable temperature systems.

Two designs of variable temperature equipment were used. In design I, fig. (11), cooling was achieved by a stream of dry nitrogen controlled by a reduction valve, needle valve and flowmeter. The gas was cooled by passing through a copper coil immersed in refrigerant (liquid nitrogen or CO₂/acetone). For temperatures above room temperature a Nichrome wire heater wound on a quartz rod was inserted in the gas stream.

The system labelled Design II, shown in fig. (12) and described by Connor (49) was also used for some measurements. Although of limited temperature range (-60°C to +120°C) this apparatus had the advantage of an improved filling factor and the sample could be easily changed. It was possible to examine different samples at the sample temperature without dismantling the entire apparatus.

Temperatures were measured with a copper constantan thermocouple connected to a "Rubicon" potentiometer.

(iii) Calibration of signals.

The resonance line derivatives were recorded on either a Varian G-10 or a Leeds Northrup "Speedomax". These recorders were calibrated in terms of gauss per cm of chart paper. The method of calibration entailed the measurement of the distance
Fig. 11.

DETAILS OF DEWAR INSERT.

... to fit Varian 15mm insert.

Design 1
Fig 12. DEWAR INSERT AND DEWAR LEAD.

Design II
between the sidebands on a signal from water. The sidebands were produced by modulating the R.F. power with the output from a Hewlett Packard Audio Oscillator.

Experimental second moments were obtained from the derivative curves in the usual manner. The correction for finite modulation was applied (50). Line widths were measured in terms of the width between points of maximum slope.

(iv) Preparation of Samples.

Samples were contained in 5mm pyrex tubes of which the bottom 3cm were thinned to improve the filling factor.

(a) Urea adducts. According to Smith's X-ray data (40) the mole ratio of urea to hydrocarbon is given by

\[ 0.6848(n-1) + 2.181 \]

which is in agreement with the observed composition. In preparing urea adducts the theoretical amount of hydrocarbon was added to a saturated solution of urea in methanol or isopropanol. The solution was warmed until the precipitated adduct had dissolved and then allowed to cool in a preheated lagged Dewar.

Deuterated urea and thiourea were prepared by repeated recrystallisation from D\(_2\)O. Most solvents polar enough to dissolve urea also exchange with it, therefore deuterated methanol was prepared by decomposing magnesium methylate in D\(_2\)O.

(b) Thiourea Adducts. The values given by Redlich et.al. (35) were used and the same experimental procedure followed as for urea adducts.

A list of reagents, their source and purity is given in the Appendix.
CHAPTER IV

RESULTS AND DISCUSSION

(i) Normal Paraffins.

Results.

(a) Tridecane \( n-C_{13}H_{28} \). At 77°K, the lowest temperature of measurement, the line width was 15.6 gauss and the second moment 21.5 gauss\(^2\). At about 200°K a narrow line of 5 gauss appeared and fine structure was present in the centre of the resonance line. This fine structure become more pronounced as the temperature increased. The second moment decreased smoothly to 16.3 gauss\(^2\) at 255°K when it fell to 4.0 gauss\(^2\). The wide line narrowed to 12.7 gauss at 255°K and then disappeared. The line width and second moment then remained constant from 255°K to the melting point 268°K. Resonance line shapes are shown in fig. (13), the variation of second moment and line width with temperature in fig. (15 a,b.).

(b) Hexadecane \( n-C_{16}H_{34} \). At 77°K the second moment was 23.5 gauss\(^2\) and decreased smoothly to 15.4 gauss\(^2\) at the melting point 289°K. The line width fell from 15.4 gauss at 77°K to 12.3 at 289°K. The fine structure observed in tridecane was also present in hexadecane. No discontinuities in second moment or line width occurred. Resonance line shapes at different temperatures are shown in fig. (14) and the temperature variation of second moment and line width in fig. (16 a,b.)
Fig. 13. LINE SHAPE DERIVATIVES OF TRIDECANE.
Fig 14. LINE SHAPE DERIVATIVES OF HEXADECANE.
(ii) Discussion.

The behaviour of tridecane and hexadecane follows a similar pattern as that discussed by Andrew (27) for octadecane, octacosane and dotriacontane. The theoretical intra- and inter-molecular second moments were calculated by Andrew on the basis of Müller's X-ray structures for the n-paraffins (51). For the general member, \( \text{C}_n \text{H}_{2n+2} \), the intra-molecular rigid lattice second moment (26) is given by \( (18.5 + 19.1/n+1) \). The inter-molecular contribution was based on the structure of nonacosane, \( \text{C}_{29}\text{H}_{60} \), for which the structure was completely determined and calculated to be 7.8 gauss\(^2\). Andrew's experimental second moments for octacosane and dotriacontane at 95\(^\circ\)K agreed with the theoretical rigid lattice values and this was taken as evidence for the absence of molecular motion at this temperature. In octadecane the calculated second moment was much higher than the experimental value at 95\(^\circ\)K, suggesting that some form of motion was present. In tridecane and hexadecane the experimental second moments of 21.5 gauss\(^2\) and 23.5 gauss\(^2\) at 77\(^\circ\)K are well below the calculated rigid lattice values of 27.7 gauss\(^2\) and 27.3 gauss\(^2\) respectively.

The type of motion most likely to occur is that of rotation or at least rotational oscillation. Using the formula derived by Gutowsky and Pake (15) for the reduction in second moment due to rotation the intra-molecular contribution becomes \( (6.8 - 11.6/n+1) \) gauss\(^2\) and the inter-molecular contribution reduces to 2.6 gauss\(^2\). If all the molecules
Fig. 15(a)
LINE WIDTH vs TEMPERATURE
TRIDECANE.

Fig. 15(b)
SECOND MOMENT vs TEMPERATURE
TRIDECANE.
Fig. 16 (a).
LINE WIDTH vs TEMPERATURE
HEXADECANE.

Fig. 16 (b).
SECOND MOMENT vs TEMPERATURE
HEXADECANE.
rotate the theoretical second moments for tridecane and hexadecane would be \(8.5 \text{ gauss}^2\) and \(8.7 \text{ gauss}^2\) respectively. The experimental value for hexadecane just below the melting point is \(15.4 \text{ gauss}^2\), which is too high for complete rotation of all the molecules. If however, rotational oscillation occurred, the reduction factor for the second moment would be much less, and dependent on the angular amplitude. Andrew (27) derived an expression for this reduction factor in terms of the angular amplitude of oscillation and the orientation of the internuclear vector to the axis of oscillation. Applying Andrew's treatment, an angular amplitude of \(30^\circ\) at \(77^\circ K\) and of \(45^\circ\) at \(250^\circ K\) would be necessary to reduce the second moment by the required amount.

An alternative explanation, suggested by Andrew, involved a form of co-operative motion in which the hydrocarbon chains behaved as a set of meshing gears such that some molecules rotated while others remained stationary.

The large change in second moment in tridecane at \(255^\circ K\) corresponds to the phase transition reported by Finke et al. (52) from heat capacity measurements. The phase changes which occur in n-paraffins a few degrees below the melting points are attributed to the onset of rotation about the long axis of the molecule (51) and a change in crystal structure from monoclinic or triclinic to orthorhombic (53). In tridecane the second moment above \(255^\circ K\) of \(4.0 \text{ gauss}^2\) is lower than the calculated \(8.5 \text{ gauss}^2\) for complete rotation. A similar behaviour was found by Andrew in octacosane and dotriacontane, Andrew suggested that other forms of motion such as torsional
oscillation, longitudinal and lateral motion and flexing were responsible. Although the change in second moment at 255°K is fairly sharp, the changes in line shape are definitely not, the narrow 5 gauss component is evident nearly 50° below the transition point and increases in intensity as the broad line decreases both in width and intensity. This suggests that some form of motion must be present at about 200°K and is increasing as the temperature rises. From thermal and dielectric data on long chain compounds Hoffman (54) assumed that the onset of rotation is a co-operative effect but that the chains do not twist severely during rotation in the solid state.

According to Smith (55) the addition of a few percent of neighbouring homologues is sufficient to alter the triclinic and monoclinic forms to rhombohedral. The presence of impurities capable of motion themselves or producing centres in the lattice which allow the hydrocarbon itself a higher degree of motion, could be responsible for the low value of the second moment. Although the hydrocarbons were claimed to be 99 mole percent minimum purity the influence of small amounts of impurity on the resonance line shape has been adequately demonstrated (56).

In calculating the inter-molecular second moment, Andrew used the structure of nonacosane. The differences in packing and changes in lattice dimensions with temperature between nonacosane and hexadecane and tridecane will lead to different values of second moment. However this should not be of sufficient magnitude to account for the discrepancies between the experimental and theoretical second moments.
The fine structure occurring in the centre of the resonance signal was discussed by Andrew in terms of the rotation of the terminal methyl groups independently of the main chain. Andrew suggested that the central component of the resonance line shape arising from a triangular three spin system (22) becomes observable when rotation occurs since the broadening due to neighbours is partly removed. A similar narrow line in methyl chloroform was shown by Powles and Gutowsky (57) to be due to an impurity capable of rotation at fairly low temperatures. No adequate experimental evidence exists to prove impurities are responsible for all or part of the fine structure, or for the low second moment in tridecane, but the possibility cannot be entirely ruled out at the present moment.

(ii) Urea-d₄ Adducts of Tridecane and Hexadecane.

Urea adducts of n-paraffins C₇-C₁₃ and C₁₆ were studied. All showed a narrow line due to the hydrocarbon and a broad line of 7.1 - 7.3 gauss due to the protons of the urea lattice. The temperature dependence of the line width and second moment of tridecane and hexadecane - urea d₄ adducts was examined.

(a) Tridecane Adduct. The resonance line shape of the tridecane adduct showed a complicated temperature dependence. At 77°C the resonance derivative curve, fig(17d), consisted of a broad line of 9.8 gauss and a narrower line of 3.0 gauss. The two lines narrowed and appeared to merge as the temperature increased until, at 119°C, a single line was obtained, fig.(17c). At 150°C the signal separated into two components of widths 6.8 and 1.8 gauss respectively. As the temperature increased the
Fig. 17. LINE SHAPE DERIVATIVES OF TRIDECANE ADDUCT.
broader line decreased in intensity, and a narrow spike appeared in the centre of the resonance signal, Fig. (17b). Above about 225°K the broad component vanished leaving the narrow line, which decreased slowly in width to 1 gauss at 268°K, when it disappeared. The resonance now consisted of a sharp line of about 30 milligauss wide.

The variation with temperature of the second moment is shown in Fig. (18). The second moment decreased from 12.6 gauss$^2$ at 77°K to 2.8 gauss$^2$ at 160°K and then decreased only slowly 2.1 gauss$^2$ at 225°K, when it fell to 0.7 gauss$^2$. At 268°K the second moment fell from 0.4 gauss$^2$ to zero.

(b) Hexadecane Adduct. The behaviour of the hexadecane adduct was very similar. The second moment at 77°K was 15.5 gauss decreasing to 2.6 gauss$^2$ at 160°K and to 1.3 gauss$^2$ at 220°K. In the range 220°K - 230°K the second moment decreased to 0.7 gauss$^2$ and at 289°K fell to zero. The temperature variation of the second moment is shown in fig. (19).

Two components were observed in the line shape, a narrow line of 2.2 gauss at 77°K decreasing to 0.9 gauss at 289°K and a broader line of 11.9 gauss at 77°K which decreased to 5.5 gauss at 217°K and vanished in the range 220-230°K.

Discussion.

The second moment of the resonance line in the urea adducts should consist of the following contributions

(i) intramolecular, from the hydrocarbon chain.

(ii) intermolecular, from terminal methyl groups at the end of chains in the same channel.
Fig. 18. SECOND MOMENT vs TEMPERATURE.
TRIDECANE UREA-d₄ ADDUCT.

Fig. 19. SECOND MOMENT vs TEMPERATURE.
HEXADECANE UREA-d₄ ADDUCT.
(iii) intermolecular, from chains in different channels.
(iv) contribution from unexchanged protons in the urea lattice.
(v) contribution due to other atoms possessing spin eg H\(^2\), C\(^{13}\), N\(^{14}\), N\(^{15}\).

The second moment is dependent on the inverse sixth power of distance thus (iii) may be neglected since the minimum possible distance between chains is at least 5 Å. The contribution from (iv) is also sufficiently small to be neglected. The second moment contribution due to other nuclei will certainly be less than 0.2 gauss\(^2\). The distance apart of the terminal methyl groups is of the order of 2.0 Å, the van der Waals radius. The second moment for two rigid methyl and methylene groups at this distance is 1.2 gauss\(^2\). The total calculated second moments for the rigid hydrocarbon adducts will be 21.1 gauss\(^2\) for the tridecane adduct, and 20.8 gauss\(^2\) for the hexadecane adduct, which are much greater than the experimental values. The graphs of second moment vs temperature show that the second moment is still increasing at 77°K and obviously the hydrocarbon cannot be rigid at this temperature. Free rotation of the terminal methyl groups about their C\(_3\) axes will reduce the intramolecular second moment by 3.8 gauss\(^2\), and the intermolecular contribution to zero. The calculated values now become 16.1 gauss\(^2\) for tridecane adduct and 15.8 gauss\(^2\) for the hexadecane adduct. The experimental value for hexadecane is 15.5 gauss\(^2\) and, from the temperature dependence of the second moment, appears to be approaching a limiting value. The chain length of hexadecane is 22.84 Å which is slightly greater than
twice the urea repeat distance of 11.01Å. According to Smith (40) the chain is shortened slightly in order to fit into two unit cells. This shortening will be either a twisting of the chain or a flexing. The distance between certain protons will thus be decreased while others will be further apart, however, since the second moment is dependent on the inverse sixth power of distance, the second moment will be increased slightly by about 0.3 gauss$^2$. The result of the observed shortening will be a restriction of rotational or torsional oscillation but will still presumably allow the methyl groups to rotate. If the methyl group rotation alone is responsible for the reduction in second moment, then Andrew's (27) explanation of the narrow spike in the resonance line of hydrocarbons in terms of methyl rotation must be incorrect. The reduction of second moment can be explained alternatively in terms of rotational oscillation, but in the case of the hexadecane adduct at this temperature, this does not seem to be the most probable mechanism. It has already been mentioned that the dielectric absorption studies of Meakins favour the rotation of the terminal groups in 1.10 dibromodecane. In hydrocarbons the removal of the bulk effect of the bromine atom would leave the methyl groups even less hindered.

In the tridecane adduct the experimental second moment of 12.6 gauss$^2$ at 77$^0$K is too low to be explained in terms of methyl group rotation alone. The graph of second moment vs temperature does not cover a sufficient range to justify extrapolation to what might be a limiting value.

The second moment of both adducts decreased over the range 77$^0$K - 160 K to between 2.5 and 3.0 gauss$^2$. For complete
rotation the calculated intramolecular second moments for tridecane and hexadecane are 6.3 and 6.6 gauss$^2$ respectively. There is no break in the second moment versus temperature curves to suggest that only pure rotation occurs. From the temperature variation from 197°K to 293°K of the frequency maximum of dielectric absorption, Meakins (9) has obtained estimates of the barrier heights involved in dipolar reorientation. In octadecyl bromide and 1,10 dibromodecane the energy barriers are 2.4 kcal/mole and 2.3 kcal/mole respectively. In pure crystalline long chain compounds of similar molecular weight the barriers would be of the order of 10 - 30 kcal/mole (9). The energy barriers are thus very low and together with the high frequency of the absorption indicate that the molecules are very loosely held in the lattice.

The decrease in the second moment can at least be qualitatively accounted for by assuming that the chains undergo oscillations of increasing amplitude as the temperature rises until complete rotation occurs. At the same time the hydrocarbon chain becomes capable of lateral and longitudinal motion within the channel. The fact that the narrow spike in the centre of the resonance line seems to increase with the disappearance of the wide line may be significant in this respect.

The line of about 3 gauss wide present in the signal from both adducts at 77°K and narrows to about 1 gauss at the melting points of the hydrocarbons may be due to free or only partially adducted hydrocarbon. The samples were prepared by crushing selected single crystals of adduct into the sample tube, decomposition due to abrasion is possible but not likely.
Alternatively this line may be due to occluded solvent molecules of methanol or isopropanol which have been dragged into the lattice during adduct formation. That the line is due to hydrocarbon however, is supported by the change in line width and second moment at the melting points of the hydrocarbons.

The decrease in second moments of both adducts in the region of 225°C are unlikely to be of a similar nature to the polymorphic phase changes reported by Topchiev et.al. (47). The hydrocarbons examined were in the range C_{21}-C_{32} and the phase changes occurred within 10 - 20°C of their melting points. No results on low temperatures has been reported. In view of the coincidence in temperature of these transition points it is possible that the urea lattice itself has altered. Definite conclusions cannot be drawn on the basis of only two adducts. An examination of other adducts and possibly a dilatometric study would be useful.

(iii) Thiourea Adducts.

Results.

The resonance line derivatives of some of the thiourea adducts investigated are shown in figs (20) (21). The curves have been reduced to the same scale. In all cases the width of the broad line, attributed to the protons of the thiourea lattice, was 8.5 - 8.7 gauss. The line widths of the hydrocarbon resonances are given in table 1. The adducts of durene (1,2,4,5, tetramethyl benzene) and decalin (decahydronaphthalene) showed a composite line shape of two broad lines and sometimes a narrow spike. Cyclopentane and
Fig. 20. LINE SHAPE DERIVATIVES OF THIOUREA ADDUCTS.
Fig. 21. LINE SHAPE DERIVATIVES OF THIOUREA ADDUCTS.
dicyclohexyl showed only narrow lines of modulation width.

Cyclohexane  1.6 Gauss  
Cyclohexene  0.65 "  
Cyclopentane  - "  
Me.cyclohexane  0.95 "  
Me.cyclopentane  1.4 "  
Dicyclohexyl  - "  
Durene  2.2, 6.0 "  
Decalin  1.7, 5.5 "

Table 1. LINE WIDTHS OF THIOUREA ADDUCTS.

A brief temperature dependence study of the adducts of cyclohexane and cyclopentane was made. The line width and second moment of the cyclohexane thiourea-\(d_4\) adduct at 77\(^{\circ}\)K were 4.6 gauss and 2.7 gauss\(^2\) respectively. The line width at 298\(^{\circ}\)K was 1.6 gauss and the second moment 0.3 gauss\(^2\). From 177\(^{\circ}\)K to 400\(^{\circ}\)K the line width remains constant but begins to decrease irreversibly in intensity above 350\(^{\circ}\)K. The cyclopentane adduct showed the same decrease in intensity above about 310\(^{\circ}\)K.

Discussion.

With the exception of durene all the compounds studied were liquid at room temperature in the pure state. The occurrence of a finite line width and second moment would therefore indicate a restriction of motion in the adduct. Schlenk (42) has pointed out that the larger size of the sulphur atom and the greater dimensions of the channel results effectively in a periodicity of the van der Waals forces along the length of the channel. The N.M.R. evidence supports the idea that the adducted
compounds is trapped in some potential minimum such that, while rotational or oscillatory motion may be quite unrestricted, translational motion is hindered.

Andrew and Eades (59) have examined the proton magnetic resonance spectrum of cyclohexane from 95°K to the melting point. Below 150°K the lattice was effectively rigid with a second moment of 26.0 gauss$^2$, falling to 6.4 gauss$^2$ in the range 150° to 186°K. This reduction is quantitatively accounted for by reorientation of the molecule about its triad axis. The discontinuous change in second moment at 186°K to 1.4 gauss$^2$ is caused by almost isotropic reorientation which reduces the intramolecular second moment to zero. Since the centres of mass remain fixed the intermolecular contribution does not average to zero. In the cyclohexane thiourea adduct at 77°K the second moment of 2.7 gauss$^2$ is too low to be anything except intermolecular in origin. The motion must be isotropic reorientation. If, as was suggested for the urea adducts, there is a change in the dimensions of the thiourea channel at some temperature, then the adducted molecule would be allowed more freedom of translational motion which would reduce the second moment still further. The lack of sufficient experimental data again makes any definite deductions impossible.

At higher temperatures the irreversible decrease in the intensity of the resonance signal is obviously due to decomposition.

The composite line shapes of durene and decalin and the narrow lines of cyclopentane and dicyclohexyl adducts are difficult to explain. The smaller molecular size of cyclopentane
may allow it considerable freedom of motion in the channel, this explanation will not suffice for the dicyclohexyl adduct. An investigation of the series of W-W' dicyclohexylalkanes might clear up this point. It is possible that the larger more complex molecules of durene and decalin have trapped appreciable numbers of solvent molecules in the channel and that this is responsible for the line shape.

The change in hydrogen bond energy on isotopic substitution may significantly alter the structure and properties of the lattice. It is not suggested that the protonated adducts will necessarily exhibit the same behaviour as the deuterated species.

It is difficult at the present stage to arrive at any definite general conclusions regarding the behaviour of the adducts. The mechanism by which the long chain molecules are retained in the urea channel obviously differs from the situation in the thiourea adducts. Some suggestions have been made as to future work which may lead to a better understanding of the interaction between the cage and the enclosed material.
# APPENDIX

## SOURCE AND PURITY OF COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>Eastman Kodak, White Label</td>
<td></td>
</tr>
<tr>
<td>Thiourea</td>
<td>May and Baker, &quot;Analar&quot;</td>
<td></td>
</tr>
<tr>
<td>Tridecane</td>
<td>Phillips Petroleum Co.</td>
<td>99 mole Percent</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>Humphrey and Wilkinson</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Eastman Kodak, Spectro grade</td>
<td></td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>Phillips Petroleum Co.</td>
<td>99 mole Percent</td>
</tr>
<tr>
<td>Methyl cyclohexane</td>
<td>Eastman Kodak, Spectro grade</td>
<td></td>
</tr>
<tr>
<td>Methyl cyclopentane</td>
<td>Phillips Petroleum Co.</td>
<td>99 mole Percent</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>&quot; &quot;</td>
<td>99.98 &quot;</td>
</tr>
<tr>
<td>Durene</td>
<td>Eastman Kodak, White Label</td>
<td></td>
</tr>
<tr>
<td>Dicyclohexyl</td>
<td>Light and Co.</td>
<td></td>
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