DIELECTRIC STUDIES OF ORGANIC MOLECULES AND ENERGY BARRIERS FOR CONFORMATIONAL CHANGES

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SUMMARY

A bridge method has been used to measure the dielectric absorption of liquids and solutions at microwave frequencies. The dielectric data are discussed in terms of apparent dipole moments and relaxation processes contributing to the dielectric absorption.

The relaxation times of some heterocyclic compounds are shown to be dependent upon the nature of the solvent, and the degree of shielding of the heterocyclic nitrogen atom. For quinoline, isoquinoline and phthalazine the relaxation time is independent of the direction of the molecular dipole moment, and molecular re-orientation occurs mainly by rotation about the axis perpendicular to the plane of the ring.

The dipole moments of 1,4-thioxan, 1,4-dithian and 1,4-dioxan indicate a small proportion of a boat form, the dielectric absorption of the first is characterised by two relaxation times, one of which may be associated with the interconversion of two conformational isomers.

For cyclopentanone, cycloheptanone and cyclooctanone the dipole moments are smaller than those obtained from classical methods, which suggests that they are flexible rings, and for cyclopentanone a second relaxation process is identifiable with an interconversion between pseudorotational arrangements of the molecule.

A series of haloethanes have been measured in cyclohexane and p-xylene solutions and the relaxation times show them to form weak intermolecular bonds with the latter. The distribution coeficients observed, using both solvents, for the di- and trisubstituted compounds may be associated with intramolecular relaxation.

Several symmetrically substituted alkylbenzenes are found to absorb in the microwave region and possible explanations are forwarded. These results appear to offer an alternative to the hypothesis that an intramolecular relaxation process contributes to the dielectric absorption of some monoalkylbenzenes. A detailed study of the latter confirms the existence of a short relaxation time process, and the results have been used to critically examine the intramolecular process and alternative explanations are considered.

PREFACE

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INTRODUCTION

The theory and basic concept of dielectric dispersion were developed in the early part of this century. The application of this subject to the study of molecular behaviour and structure only became prominent in the 1940's, and even then the growth of the subject was retarded by the limitations of the apparatus available. The majority of workers having employed radiofrequency methods to determine dielectric constant and loss data i.e. 10^4 to 10^8 c/sec., however, for the majority of small molecules the dielectric absorption is at a maximum in the region of 10^{10} c/sec.. Over the last ten years or so Professor C.P. Smyth and his colleagues at Princeton, using an impedence method at microwave frequencies have greatly contributed to the understanding and interpretation of the dielectric absorption for a large variety of polar molecules, both in the pure liquid and in solution.

The microwave bridge technique offers the possibility of accurately measuring the dielectric constant and loss of polar molecules in non-polar solvents, which is particularly advantageous since the intermolecular effects, present in pure liquids, may then be minimized. An important requirement of dielectric dispersion studies is a sufficiently wide frequency coverage, thus the availability of up to six wave bands, covering a frequency range 6 to 70 Gc/sec., increases the value of the work carried out in this laboratory. The apparatus is described in chapter 1, together with a brief summary of the underlying theory of the method and the dielectric parameters. References to more detailed accounts are given.

The advantage of measurement of dilute solution is that a comparison of molecular relaxation time and molecular shape and size is facilitated, the internal field effect may be neglected and for many solvents the viscosities are similar. Thus the validity of an analysis, of the dielectric absorption for a particular system, may be assessed by inspection of the molecular relaxation time and comparison with values obtained for molecules of similar shape and size.

Previous students have successfully employed the method in studies of inter and intramolecular relaxation processes. For molecules containing a rotatable polar group, the dipole vector of which have a component normal to the axis of rotation, the microwave method appears to be well suited to studies of intramolecular processes in solution, a subject for which experimental data are relatively sparse. An added advantage of this technique is that dipole moments may be obtained for the polar molecules, and the values do not suffer from any approximation for the atomic polarization, and thus additional information concerning the structure of a molecule is provided. Furthermore, the method is sensitive to the measurement of very small dipole moments and this point may be used to advantage in conformational analysis and in the investigation of possible induced dipole moments for non-polar molecules.

CHAPTER 1

EXPERIMENTAL METHODS AND BASIC THEORY

A. Dielectric Constant and Loss[1,2,3]

The dielectric constant of a material may be expressed as the ratio of the field strength in vacuum to that in the substance for the same distribution of charge. Consider a simple electric condenser, consisting of two parallel plates of area A/cm.^{3} separated by a distance r, the capacity of such a condenser is given by

$$C = \frac{\varepsilon A}{4\pi r} \text{ e.s.u.} \qquad 1.1$$

Where ε is the ratio of the dielectric constant of the medium between the plates to that of free space. It is usually evaluated by measuring the capacity of a condenser with the medium between the plates (C), and with a vacuum (εC_o). Thus,

$$\varepsilon = \frac{C}{C_o} \qquad 1.2$$

and the dielectric constant expressed in this way is dimensionless.

In actual fact ε the so called dielectric constant is not a constant for polar materials, it's value being dependent on the wavelength or frequency of the externally applied field at which it is measured, and in view of this many workers prefer the word permittivity.

The dielectric constant defined above is the low frequency dielectric constant and is observed for small dipolar molecules at frequencies less than 10^8 c/sec., when the molecules are in equilibrium with the externally applied alternating field.

At higher frequencies a time-lag exists between the response of the dipole to the alternating field, and the polarization is no longer instantaneous. The charging current $E\omega\varepsilon' C_o$ at the heterodyne beat frequency of 1 Mc/sec. is inclined at an angle $\pi/2$ to the alternating potential. In a condenser in which absorptive polarization occurs the angle is $\pi/2 - \delta$. The angle δ, between the vector for the total current and that for the charging current of the wave, is the loss angle, and the tangent of this angle is the loss tangent

$$\mathrm{Tan}\,\delta = \frac{\text{loss current}}{\text{charging current}} = \frac{\varepsilon''}{\varepsilon'} \qquad 1.3$$

From this the dielectric constant becomes a complex number and is defined as:

$$\varepsilon^{*} = \varepsilon' - i\varepsilon'' \qquad 1.4$$

in which ε'' is the dielectric loss and may be related to the ability of the medium to dissipate energy. As the frequency approaches zero, ε'' approaches zero, and ε' approaches the static dielectric constant ε_o (represented in the earlier discussion by ε); and , as the frequency approaches infinity, ε'' again approaches zero and ε' approaches

ε_∞, the optical dielectric constant.

B. Dielectric Relaxation

Many chemical equilibria respond to changes in external conditions within a fraction of a second, however, a point is eventually reached where the position of equilibrium is not readjusted as soon as the external conditions are changed. Such a time-lag between changes in external and internal conditions defines relaxation. This term can be applied to many effects.

The delay in the response of small polar molecules in solution to the changes in the external field at higher frequencies is the relaxation time (τ), and may be defined as the time after the removal of the electric field for the polarization (P) to decay to $1/e$ of its original value (Po). The definition being for the case $t = \tau$ in the equation.

$$P = P_0 e^{-\frac{t}{\tau}} \qquad 1.5$$

C. Essential Equations

For molecules which can be characterized by a single relaxation time the complex dielectric constant is related to relaxation time by[4]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} = \varepsilon' - i\varepsilon'' \qquad 1.6$$

On separation of real and imaginary parts

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \qquad 1.7$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \qquad 1.8$$

where ε_0 and ε_∞ are the static and high frequency dielectric constants respectively, and ω is the angular frequency of the applied field.

The ratio $\varepsilon''/\varepsilon'$ (Tan δ) is related to the dipole moment (μ) and relaxation time by the equation:

$$\frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_0+2)(\varepsilon_\infty+2)\,4\pi c N \mu^2 \omega\tau}{\varepsilon' \, 27 kT(1+\omega^2\tau^2)} \qquad 1.9$$

where c is the concentration in moles/cc. N is the Avogadro number, T the absolute temperature and k the Boltzmann constant.

Examination of Eq. 1.8 shows that ε'' approaches zero for both small and large values of $\omega\tau$, while it is a maximum for:

$$\omega\tau = 1 \qquad 1.10$$

For this value of $\omega\tau$, (1.8) gives

$$\varepsilon''_{max} = \frac{(\varepsilon_0 - \varepsilon_\infty)}{2} \qquad 1.11$$

$$\varepsilon'_{max} = \frac{(\varepsilon_0 + \varepsilon_\infty)}{2} \qquad 1.12$$

For molecules having more than one relaxation time, Cole and Cole[5] modified Eq. 1.6 to:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} \qquad 1.13$$

in which τ_0 is the most probable or mean relaxation time, and corresponds to the frequency at which ε'' has a maximum value and α , the distribution coefficient, is a measure of the distribution of relaxation times having values between 0 and 1. This leads to the following equations:

$$\varepsilon' - \varepsilon_\infty = \frac{(\varepsilon_0 - \varepsilon_\infty)\left[1 + (\omega\tau_0)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right)\right]}{1 + 2(\omega\tau_0)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) + (\omega\tau_0)^{2(1-\alpha)}} \qquad 1.14$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)(\omega\tau_0)^{1-\alpha} \left(\cos\frac{\alpha\pi}{2}\right)}{1 + 2(\omega\tau_0)^{1-\alpha} \sin\left(\alpha\pi/2\right) + (\omega\tau_0)^{2(1-\alpha)}} \qquad 1.15$$

When $\alpha = 0$ these equations reduce to Eq. 1.7 and Eq. 1.8.

For systems having two relaxation mechanisms, Budo[6] considers the complex dielectric constant as the sum of the Debye terms,

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{\varepsilon' - \varepsilon_\infty - i\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{c_1}{1 + i\omega\tau_1} + \frac{c_2}{1 + i\omega\tau_2} \qquad 1.16$$

τ_1 and τ_2 are the relaxation times of each process and C_1 and C_2 the corresponding weight factors and

$$C_1 + C_2 = 1 \qquad 1.17$$

Separation of real and imaginary parts in Eq. 1.16 gives:

$$\eta' = \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1}{1+(\omega\tau_1)^2} + \frac{C_2}{1+(\omega\tau_2)^2} \qquad 1.18$$

$$\eta'' = \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1\omega\tau_1}{1+(\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1+(\omega\tau_2)^2} \qquad 1.19$$

η' is the reduced or normalized dielectric constant and η'' the reduced loss factor.

D. Rate Theory of Dielectric Relaxation

This subject has been extensively studied by Kauzmann[7], who considered that molecular dipole orientation involves passage over a potential energy barrier with a certain probability of jumping from one orientation to another. Thus the relaxation time τ may be related to a rate constant k' by:

$$\tau = \frac{1}{k'} \qquad 1.20$$

From transition state theory the molar free energy of activation, $\Delta G^{\ddagger}$, separating two equilibrium positions of the relaxing dipole is given by[8]

$$k' = \frac{1}{\tau} = K\frac{kT}{h}.e^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad 1.21$$

where h is Planks constant, k the Boltzmann constant, T the absolute temperature and K the transmission coefficient normally taken to be 1.

Since

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad 1.22$$

the equation may be rewritten

$$\tau = \frac{h}{kT} \cdot e^{\frac{\Delta H^{\ddagger}}{RT}} \cdot e^{-\frac{\Delta S^{\ddagger}}{R}} \qquad 1.23$$

From which

$$\ln\tau = \frac{1}{T}\,\frac{\Delta H^{\ddagger}}{R} - \ln T + \left(\ln\frac{h}{k} - \frac{\Delta S^{\ddagger}}{R}\right) \qquad 1.24$$

A linear relationship should be obtained by plotting $\ln\tau T$ against $1/T$, and $\Delta H^{\ddagger}$, the enthalpy of activation, may be evaluated from the slope of such a plot.

E. The Bridge Method[9,10]

(i) Apparatus

A block diagram of the bridge circuit is given in Fig. 1.1; the four arms of the magic T are labelled a, b, c and d. The cells were constructed from rectangular waveguide by the engineers of the Chemistry Department and the other items in the circuit were obtained from various manufacturers.

The monochromatic radiation is generated by a klystron K (to which a square-wave modulation of 1 or 3kc/sec. is applied) and propagated along the waveguide. The range of frequency which may be propagated along a particular waveguide is summarised in Table 1.1.

Fig 1.1 Block Diagram Of The Bridge Apparatus

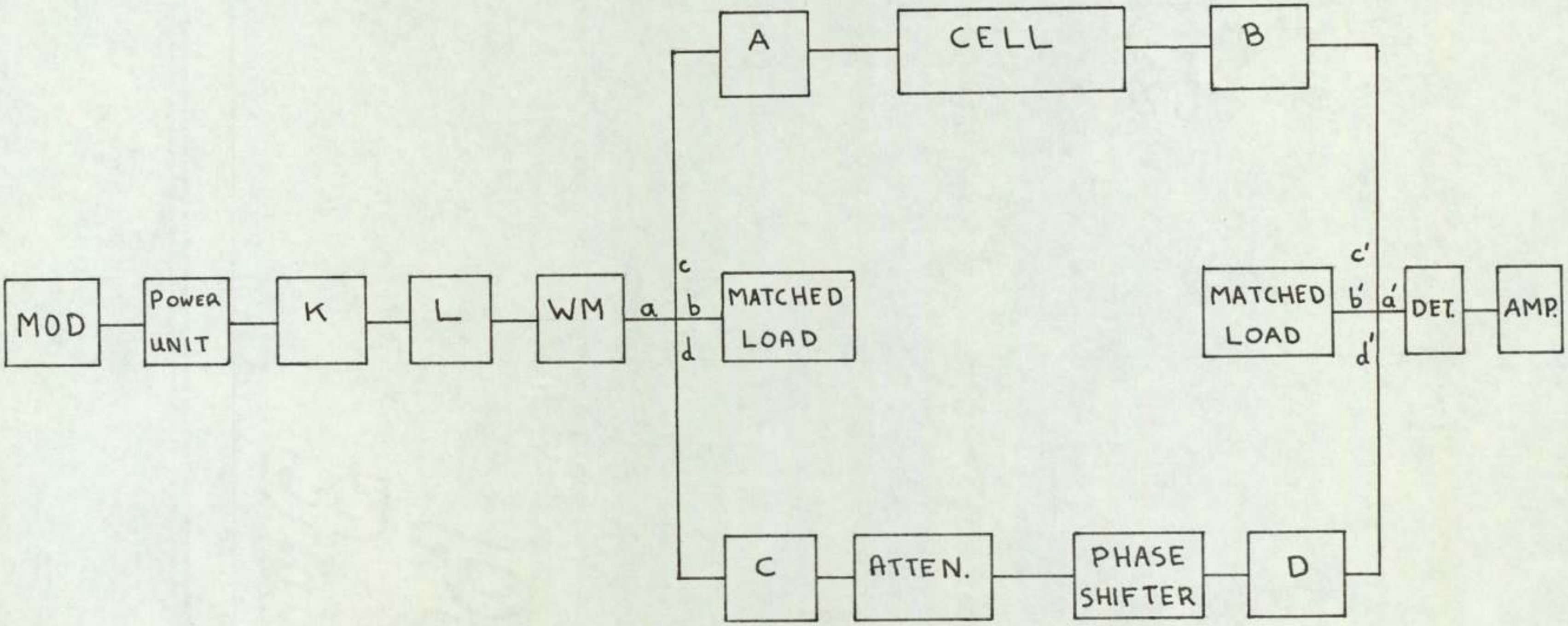


Table 1.1. Waveguide Dimensions, Frequency Range and Band Identification Letter.

Waveguide internal cross section diameter (inches)	Frequency range (Gc/sec.)	Frequency employed (Gc/sec.)	Band letter
0.122 x 0.061	60.0 - 90.0	70.00	O
0.280 x 0.141	26.5 - 40.0	34.86 35.09	Q
0.420 x 0.170	18.0 - 26.5	23.98	K
0.622 x 0.311	12.4 - 18.0	16.20	P
0.900 x 0.400	8.2 - 12.4	9.313	X
1.372 x 0.622	5.85 - 8.2	6.679	C

Although it was possible to obtain small variations in the frequency generated by the klystron, each band was only operated at the frequency specified in Table 1.1.

The attenuator or isolator (L) prevents "pulling of the klystron". The wavelength is read directly on a wavemeter (WM). At 'a' the power is split into two equal halves by the magic T, one half passing through the cell and the other half along the other side of the bridge through a calibrated variable attenuator and a phase shifter. The polar solution, in the cell, shifts the phase and attenuates the wave; hence mechanical adjustment of these two in the other arm of the bridge, the condition in which, when the waves combine, the fields have been restored to equal antiphase conditions at the junction of arms c' and d' of the output of the magic T, may be achieved. With the field so adjusted the vector sum in output in arm a' is zero and the bridge is balanced. A crystal is connected to a unit which is some form of signal detection system which can be high gain, low noise amplifier and voltmeter. At the balance point of the bridge the latter has a zero reading.

The circuit was set up on a board inclined at about 15° to the horizontal, the klystron being at the lower end.

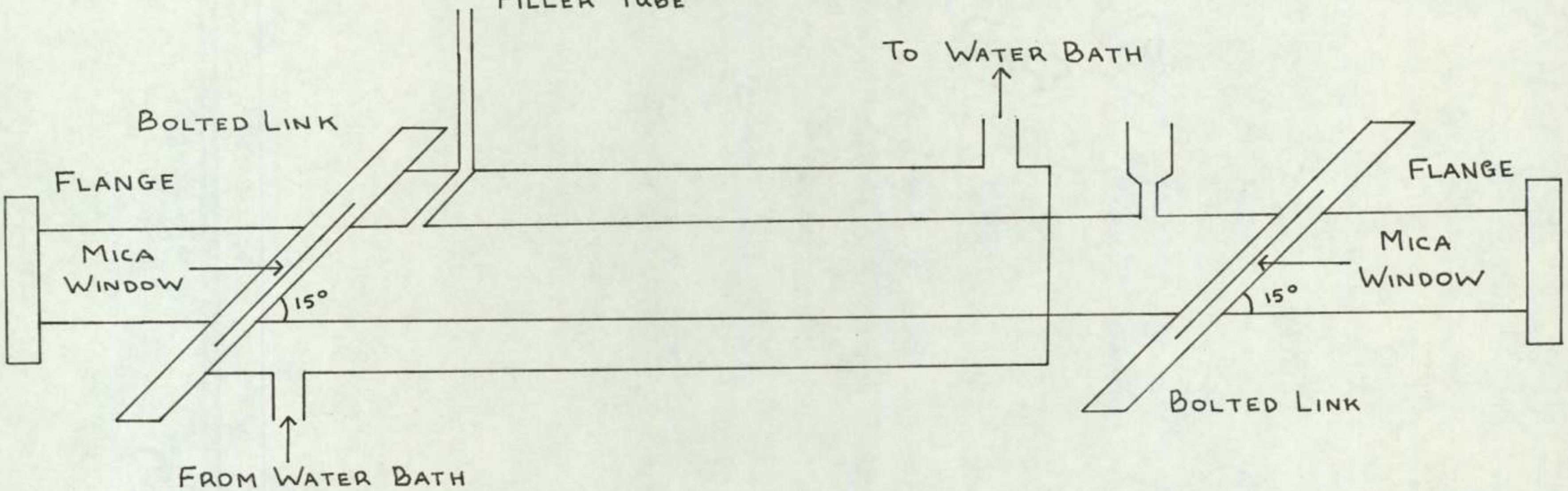
For dilute solutions, the attenuation is low and it is particularly important to minimize reflection. The magnitude of the reflections may be assessed by determining the standing wave ratio (p) which is defined as:

$$p = \frac{a_1 + a_2}{a_1 - a_2} \qquad 1.25$$

where a_1 is the amplitude of the standing wave and a_2 that of the reflected wave. It is desirable to have a standing wave ratio as near to unity as possible. The introduction of isolators at points A, B, C and D allow the above conditions to be approached, since apart from minute reflections they restrict propagation of the wave to the forward direction.

Basic details of a typical cell are given in Fig. 1.2. The mica windows are inclined at 15° to the direction of wave

Fig 1.2 DIAGRAM OF A CELL



propagation in order to minimize reflections. The Q, K and P band cells are filled through the narrow metal tube of 0.06 to 0.03 cm. i. d., which enters the cell, remaining flush with the wall, in the middle of the guide opposite the bottom window. For X and C band the additions are made through the wide ended tube at the top of the cell. Additions to the 4 m.m. cell are made by an Agla micrometer syringe, the needle of which projects at least 1" into the cell, through a hole in the centre of the waveguide at the upper end of the cell.[11] The cells are enclosed in a length of larger diameter waveguide through which water, at the required temperature, may be circulated.

(ii) a. Experimental method.

Before any series of measurements were made the klystron was allowed to stabilize for one hour. The cell was washed out with suitable solvents and finally with cyclohexane and then dried, by blowing dry air from a reciprocator pump through the cell, before it was installed in the bridge. The frequency of the propagated wave was read on the wavemeter and if necessary the klystron was suitably adjusted. The solution to be measured was stored in a tightly stoppered water jacketed container, and added to the P, X and C band cells by means of a water jacketed grade A burette. Additions to O, Q and K band cells were made from water jacketed Agla micrometer syringes.

Sufficient solution was added to completely cover the mica window, the bridge was then balanced and attenuation and phase shift readings taken. Enough solution was then added to give a phase shift of 360^o, since the phase shifter itself introduces attenuation, and the readings taken again. This proceedure was continued until sensitivity was lacking, which depends on the type of solute and it's concentration, or until the cell is full. The liquid then being drained from the cell into the container. In general measurements were made in the sequence O, Q, K, P, X and C in order to minimize any error, brought about by the evaporation of solvent, since this will be a function of the volume of the cell.

(ii) b. Attenuation and Phase Shift of a Wave.

If E_o is the electric field strength at zero time at the point which the wave enters the solution, then at time t

$$E = E_o e^{i\omega t} \qquad 1.26$$

At a distance z further down the solution the electric field intensity is diminished to:

$$E = E_o e^{i\omega t} . e^{-\nu z} \qquad 1.27$$

in which ν is known as the propagation coefficient of the solution and:

$$\nu = \alpha' + i\beta \qquad 1.28$$

Hence:

$$E = (E_o e^{-\alpha' z}) \left[\cos(\omega t - \beta z) + i \sin(2\omega t - \beta z)\right] \qquad 1.29$$

Since the term in the first bracket is the amplitude of the wave, then it follows that the amplitude of the wave has been attenuated by the factor $e^{-\alpha' z}$ in travelling through z cm. of solution. Therefore α' is known as the attenuation constant and is a measure of the diminution of electric intensity of the wave per cm. of solution. Similarly it follows from the term in square brackets that the phase of the wave has been reduced by βz radians where β is known as the phase constant and is measured in radians/cm..

(iii) Determination of ε' and ε''.

The attenuation reading in nepers was plotted against the length of liquid added in cms.. The slope being α'. The length of liquid was known from the volume added and the cross section of the waveguide.

The phase shift in radians was plotted against the length of liquid. The slope being β meas. The value of β meas is not that of the liquid however, because an equivalent volume of air has been displaced and this too has a significant phase shift. Hence:

$$\beta_{liq} = \beta_{meas} + \beta_{air} \qquad 1.30$$

β air is a constant for any waveband and

$$\beta_{air} = \frac{2\pi}{\lambda_g} \qquad 1.31$$

λ_g is the wavelength in the guide.

The slopes of the plots were evaluated from the equation

$$\text{slope} = \frac{\sum xy - \bar{y}\sum x}{\sum x^2 - \bar{x}\sum x} \qquad 1.32$$

where x = volume added

y = attenuation or phase change.

The basic equation for the evaluation of ε' and ε'' from α' and β is:

$$\alpha' + i\beta = \frac{2\pi}{\lambda_0}\left[\frac{\lambda_0^2}{(2a)^2} - \varepsilon' + i\varepsilon''\right]^{\frac{1}{2}} \qquad 1.33$$

where λ_0 is the wavelength in cm. of the radiation in vacuum as deduced from the wavemeter and "a" is the inner broad side width of the cross section of the waveguide.

From the above equation it follows:

$$\varepsilon'' = \left(\frac{\lambda_0}{4\pi}\right)^2 2\alpha'\beta \qquad 1.34$$

$$\varepsilon' = (\beta^2 - \alpha'^2)\left(\frac{\lambda_0}{4\pi}\right)^2 + \left(\frac{\lambda_0}{2a}\right)^2 \qquad 1.35$$

Hence, since α', β and λ_0 are measured and a is known ε' and ε'' values follow for a particular wavelength.

Table 1.2 lists the values of the constants in the above equations and the βair values, for the individual wavebands, for the frequencies given in Table 1.1.

Table 1.2.

Band	β air	$2\left(\frac{\lambda_0}{4\pi}\right)^2$	$\left(\frac{\lambda_0}{2a}\right)^2$
O	10.6077	0.0092862	0.47698
Q	5.82	0.037438	0.36554
K	4.0752	0.079136	0.34130
P	2.7537	0.17345	0.34318
X	1.384	0.52526	0.49579
C	1.07681	1.0145	0.41221

Static Dielectric Constant.

The static dielectric constants were measured on a heterodyne beat apparatus at 2 Mc/sec.. The instrument was a Wiss-Tech-Werkstatten Dipolmeter, Type DM01. and was calibrated, for each determination, with dry air, pure cyclohexane and pure p-xylene. The ε_0 values were reproducible to ± 0.002.

Viscosity.

Viscosities were measured by means of an Ostwald Viscometer, for which the flow time for a liquid of viscosity 1 c.p.s. was about 5 mins..

Refractive Index.

A Bellingham and Stanley refractometer of the Pulfrich type was used to determine the refractive index of solutions to five decimal places.

Density.

Densities were determined using a pyknometer of the type used by Cumper, Vogel and Walker[12]. The volume was about 10 ml. and the weighings were reproducible to 0.1 mg.

F. Treatment of Results

(i) The Cole-Cole plot[5].

Elimination of $\omega\tau$ between Eq. 1.7 and Eq. 1.8 gives the equation of a circle

$$\left[\varepsilon' - \frac{(\varepsilon_0 + \varepsilon_\infty)}{2}\right]^2 + \varepsilon''^2 = \left[\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right]^2 \qquad 1.36$$

Hence, a graph of ε' against ε'' in the complex plane gives a semicircle (Fig. 1.3a), the so-called Cole-Cole plot. If the diameter of this circle is displaced by an angle $\alpha\pi/2$ (Fig. 1.3b) in a clockwise direction from the ε_∞ point, then this suggests contributions to the dielectric absorption from more than one relaxation time. This plot provides a basis for the interpretation of dielectric relaxation phenomena.

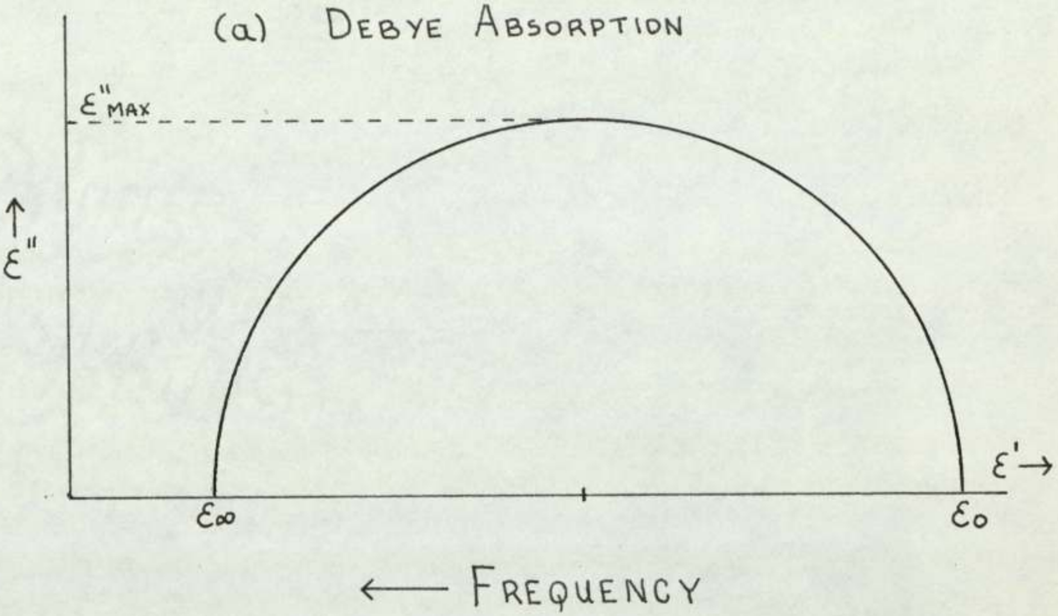
(ii) The mean (or most probable) relaxation time τ_0.

(a) An estimate of the mean relaxation time from the Cole-Cole plot may be given by Eq. 1.10. By feeding this estimate and those of ε_∞ and α, also obtained from the plot, into an Elliot 803 computer programmed to solve Eq. 1.14 and Eq. 1.15, more precise values of these parameters have been obtained.

(b) The relaxation time may also be obtained from the

Fig 1.3 COLE - COLE PLOTS

(a) DEBYE ABSORPTION



(b) NON-DEBYE ABSORPTION

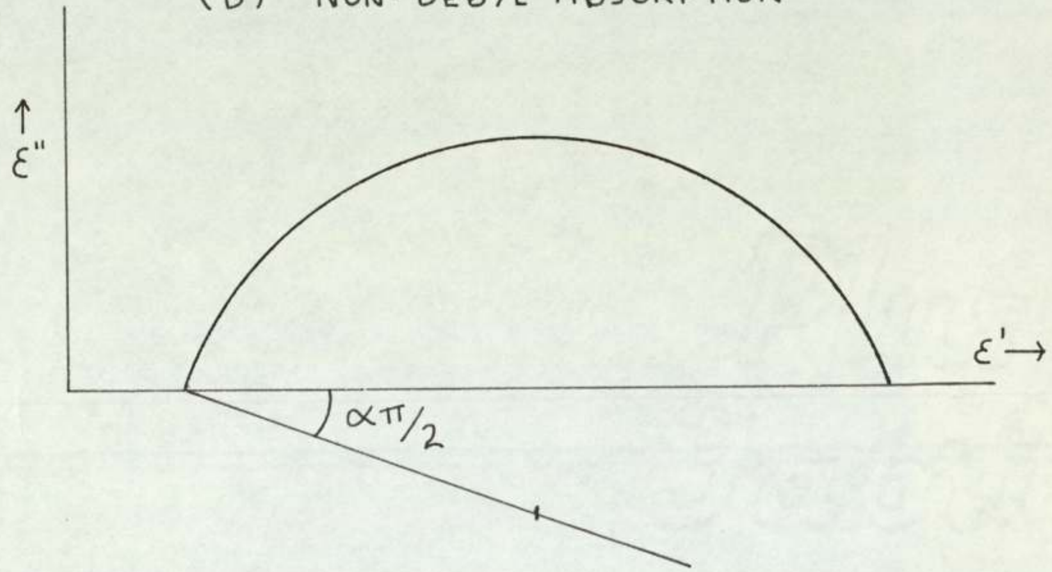
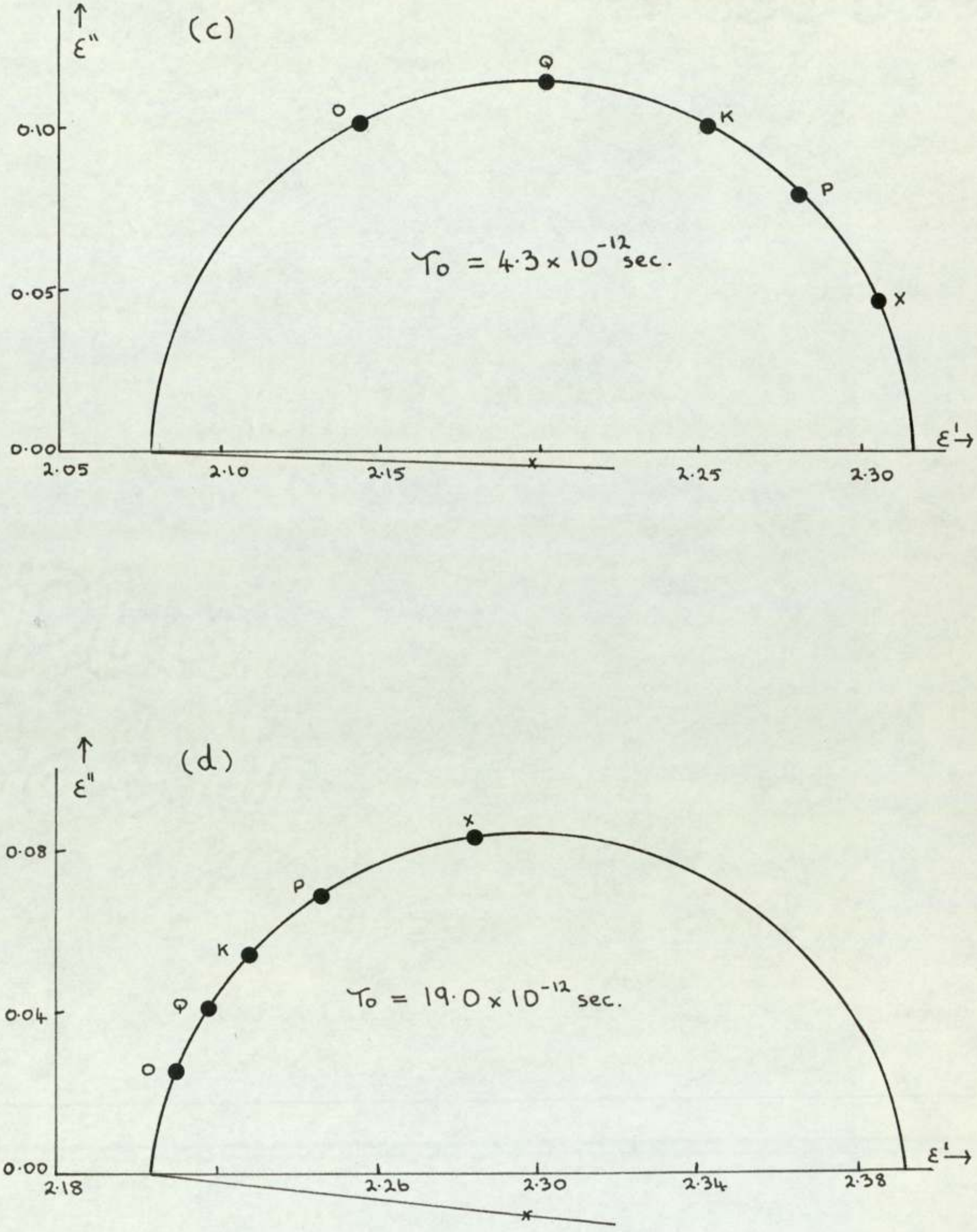


Fig 1.3 CONTINUED



relation:

$$\frac{V}{U} = (\omega\tau_0)^{1-\alpha} \qquad 1.37$$

A plot of log $\frac{V}{U}$ against log ω should give a straight line. Thus, the relaxation time will correspond to the value of log ω when log $\frac{V}{U}$ is zero, i.e. the frequency at which ε'' is a maximum and $\frac{V}{U}$ is 1. Since V is the distance on the Cole-Cole plot between ε_0 and the experimental point, and U is the distance between the point and ε_∞.

(c) On elimination of ε_∞ from equations 1.7 and 1.8:

$$\varepsilon' = \varepsilon_0 - \omega\tau\varepsilon'' \qquad 1.38$$

Hence, τ_0 may be evaluated for systems, showing Debye behaviour, from the slope of a plot of ε' against $\varepsilon''\omega$.

(iii) Analysis of the dielectric data in terms of two discrete relaxation times.

Consider Eq. 1.18 and Eq. 1.19 when either C_1 or C_2 is zero, a plot of η' against η'' is a semicircle centre (0.0, 0.5) and radius 0.5. When C_1 and C_2 are both non-zero, points are obtained within these circles. Bergmann[13, 14] developed a graphical method of analysis, using such plots, to obtain values of two mutually independent relaxation times.

Estimates of τ_1, τ_2 and C_1 obtained by this chord method have been fed into an Elliot 803 computer, programmed to minimize the square of the differences between the experimental points at any frequency and the calculated values, from variable τ_1, τ_2 and C_1 values and the constants ε_0 and ε_∞ obtained from Eq. 1.18 and Eq. 1.19 at the same frequency. The accuracy of the analysis was then checked by comparison of the calculated and measured points when minimization was complete.

Purcell, Fish and Smyth[15] have employed Eq. 1.38 to give an indication of a second process, for systems showing a non-zero distribution coefficient. For such systems, provided τ_1 and τ_2 are sufficiently different in magnitude, the plot is a curve, the limiting slopes of which are roughly $-\tau_1$ and $-\tau_2$, where the latter is the shorter relaxation time. However, the procedure tends to yield τ_1 values too short and τ_2 values too long, though comparison of the former with the τ_0 value has proved useful in the interpretation of the dielectric data.

(iv) Dipole Moment Determination.

For high weight fraction (w_2) solutions the apparent dipole moments (μ) have been evaluated from the Debye equation:

$$\mu = 0.012812\left[\frac{3T(\varepsilon_0-\varepsilon_\infty)M_2}{(\varepsilon_0+2)(\varepsilon_\infty+2)\,w_2\,d_{12}}\right]^{\frac{1}{2}} \qquad 1.39$$

where M_2 is the molecular weight of the solute and d_{12} the density of the solution.

For dilute solutions this equation has been modified by extrapolation to infinite dilution:

$$\mu = 0.012812 \left[\frac{3T(\varepsilon_0 - \varepsilon_\infty) M_2}{(\varepsilon_1 + 2)^2 d_1 w_2} \right]^{\frac{1}{2}} \qquad 1.40$$

in which ε_1 is the dielectric constant of the solvent and d_1 is it's density.

G. Preparation and Purification of Materials.

(i) Solvents.

Cyclohexane and p-xylene were obtained from commercial sources. The solvents were dried over and refluxed from sodium, followed by distillation from sodium through a two foot column packed with glass rings. They were stored in well closed amber bottles over sodium.

(ii) Preparation.

1,4-Dithian was prepared from sodium sulphide and ethylene dibromide[16]: the product was twice recrystallised from ethanol and dried in vacuum over phosphorous pentoxide. The m.p. was 115° C..

(iii) Purification of Solutes.

The purification of the commercially available materials is summarised in Table 1.3. Liquids were dried over suitable drying agents, and distilled on a 30 theoretical plate spinning band column, the second fraction being collected. Solids were recrystallised from suitable solvents and dried in a vacuum oven over a drying agent.

The purity of all materials was checked by gas-liquid chromatography, the purity of the haloethanes was further confirmed by examination of their N.M.R. spectra.

Table 1.3

Solute	Solid		Liquid	
	Solvent	m.p.	Drying agent	b.p.
	Chapter 2.			
Quinoline	-	-	Potassium hydroxide	237
Isoquinoline	-	-	"	243
Phthalazine	Cyclohexane	90.0	-	-
Acridine	"	111.0	-	-
5,6-Benzoquinoline	"	93.0	-	-
4-Methylpyridine	-	-	Potassium hydroxide	143
	Chapter 3.			
1,4-Thioxan	-	-	Sodium	147
1,4-Dioxan	Eigenberger's method[17]			101
Tetrahydropyran	-	-	Sodium	88
Pentamethylene sulphide	-	-	Sodium	142

continued

Table 1.3 continued.

Solute	Solid		Liquid	
	Solvent	m.p.	Drying agent	b.p.
S-Trioxan	Cyclohexane	63.5	-	-
Chapter 4.				
Cyclopentanone	-	-	Potassium carbonate	129
Cyclohexanone	-	-	"	155
Cycloheptanone	-	-	"	179
Cyclooctanone	-	-	"	200
Chapter 5 and 6.				
1,1-Dichloroethane	-	-	Calcium chloride	56
1,1-Dibromo-	-	-	"	107
1,2-Dichloro-	-	-	"	84
1,1,1-Trichloro-	-	-	"	74
1,1,2-Trichloro-	-	-	"	112

continued

Table 1.3 continued.

Solute	Solid		Liquid	
	Solvent	m.p.	Drying agent	b.p.
1,1,1,2-Tetrachloro-	-	-	Calcium chloride	129
1,1,2,2-Tetrachloro-	-	-	"	146
1,1,2,2-Tetrabromo-	-	-	"	dist. at 2-5 mm.
Pentachloroethane	-	-	"	dist. at 2-5 mm.
Chapter 7 and 8.				
Toluene	-	-	Purified by Vogel's method[18]	111
Ethylbenzene			Purified by the method of Cumper, Vogel and Walker[19].	136
Isopropylbenzene				152
t-Butylbenzene				169
Benzene				80
p-Cymene				176
Benzocyclobutene	Pure sample prepared by J.B.F. Lloyd[20].			
Phenyltrimethylsilane	Pure sample prepared by W.F. Hassell[21].			

continued

Table 1.3 continued.

Solute	Solid		Liquid	
	Solvent	m.p.	Drying agent	b.p.
Indane	-	-	Sodium	117
Tetralin	-	-	"	206
Styrene	-	-	Calcium sulphate	(10mm.)33°
Allylbenzene	-	-	Sodium	-
Phenylacetylene	-	-	distilled at 5-10mm.	
Mesitylene	-	-	Sodium	164
Durene	p-Xylene	79	-	-
Hexamethylbenzene	p-Xylene	164	-	-
4-Methylcyclohexene	-	-	Sodium	102
Benzotrichloride	-	-	Calcium chloride	220

H. Experimental Results

(i) Corrections.

The absorption of 1,4-dioxan is discussed in Chapter 3 and that of p-xylene in Chapter 3 and 7. When these two have been employed as solvents the results have been corrected for their absorption:

$$\varepsilon''_{corr} = \varepsilon''_{meas} - \varepsilon''_{solvent}$$
$$\varepsilon'_{corr} = \varepsilon'_{meas} + \left[\varepsilon_{0\,solvent} - \varepsilon'_{solvent}\right]$$

At regular intervals cyclohexane was measured at each wavelength. These measurements revealed that no correction of the loss factor was necessary, however, very small corrections were found to be necessary to ε' for O, Q and K bands.

(ii) Assesment of the bridge method.

Previous workers[22,23,24] in this laboratory had made a critical assessment of the method, and the errors involved in the dielectric parameters. The ensuing discussion is a summary of their findings.

(a) Assignment of ε_∞.

The most important source of error in η' and η'' is ε_∞. This is not directly measured by dielectric absorption techniques in the microwave region, and must be regarded as another unknown. The error in the assigned value of ε_∞ can be considered by comparing the high-frequency intercept, with the static dielectric constant ε_1 of the solvent for dilute solutions of strongly polar solutes. As a second check, there is the dipole moment determined by conventional methods. If the moment is not in good agreement with such values, the discrepancy must be capable of being explained by an anomalously high atomic polarization contribution, or the assigned ε_∞ must be reconsidered.

(b) Errors in dielectric constant and loss.

Experience has shown that the reproducibility of ε' is not better than 0.003 and approaches 0.5% for dilute solutions except for O band where it tends to about 1%. For ε'' the reproducibility is not better than 0.002 for a large number of cases. These errors compare favourably with the impedance method of Smyth for which the quoted errors are 2% in ε' and 5% in ε'' for low loss solutions.

(c) Errors in relaxation parameters.

The dielectric data obtained from mixtures of chloroform and bromobenzene in cyclohexane, and of chlorobenzene and bromobenzene in cyclohexane have been examined[25]. Since the relaxation time of each component in cyclohexane, and the mole fractions of each in the mixtures (and hence the C_1 and C_2 values) were known, a critical appraisal of the errors in the parameters was permitted. These workers considered that their results justified the resolution of systems with two relaxation times into their component parts.

(iii) Presentation of results.

The static dielectric constant, high frequency dielectric constant, distribution coefficient, dipole moment, relaxation times and weight contributions are listed in tabular form in the relevant chapter.

Calculated and measured dielectric constant and loss data for all the solutions are listed in the appendix, in which tables 1 and 6 refer to results discussed in chapters 2 to 8 respectively.

The relaxation times (τ_0, τ_1 and τ_2) tabulated in the following chapters are all given x 10^{12} sec..

For many of the compounds studied in this thesis the mean relaxation time is invaluable for indicating contributions to the dielectric absorption from processes other than molecular re-orientation. The data listed in Table 1.4 were obtained from the normalized Cole-Cole plots drawn through the theoretical points obtained by substitution of the τ_1, τ_2, C_1 and C_2 values given in Table 1.4 into Eq. 1.18 and 1.19 for the frequencies used in this work was evaluated from the plot of $\log \frac{V}{v}$ against $\log \omega$ and was measured on the normalized Cole-Cole plots. Significant contributions by a short or long relaxation process, compared with molecular relaxation time, result in short or long τ_0 values respectively, and hence τ_0 provides a means of detecting significant contributions to the overall dielectric absorption by processes other than molecular re-orientation.

It is evident from this table that when τ_1 and τ_2 are of similar magnitude and when C_1 or C_2 is large, the value of α is almost zero.

The plots of ε'' against $\log \omega$, Fig. 1.4 using $\varepsilon_0 - \varepsilon_\infty =$ 0.10, for a range of relaxation time and weight contributions, provide a means of assessing the contribution to the dielectric loss made by each process at a particular frequency.

Thus inspection of Table 1.4 and Fig. 1.4 will enable a critical assessment of the results presented in this thesis.

Table 1.4 τ_0 and α Data For The Theoretical Cole-Cole Plots Of The Dielectric Absorption Of Two Relaxation Processes τ_1 and τ_2 With The Respective Weight Contributions C_1 and C_2. (All Relaxation Times Are Given x 10^{12} sec..)

$\tau_1 = 2.0 : \tau_2 = 10.0$				$\tau_1 = 3.0 : \tau_2 = 10.0$				$\tau_1 = 4.0 : \tau_2 = 10.0$			
C_1	C_2	τ_0	α	C_1	C_2	τ_0	α	C_1	C_2	τ_0	α
1.0	0.0	2.0	0.00	1.0	0.0	3.0	0.00	1.0	0.0	4.0	0.00
0.9	0.1	2.2	0.04	0.9	0.1	3.3	0.04	0.9	0.1	4.3	0.02
0.8	0.2	2.5	0.10	0.8	0.2	3.7	0.06	0.8	0.2	4.7	0.05
0.7	0.3	3.0	0.12	0.7	0.3	4.1	0.08	0.7	0.3	5.2	0.06
0.6	0.4	3.7	0.15	0.6	0.4	4.8	0.10	0.6	0.4	5.7	0.06
0.5	0.5	4.5	0.16	0.5	0.5	5.5	0.11	0.5	0.5	6.3	0.07
0.4	0.6	5.5	0.14	0.4	0.6	6.3	0.10	0.4	0.6	6.9	0.06
0.3	0.7	6.7	0.12	0.3	0.7	7.3	0.08	0.3	0.7	7.6	0.06
0.2	0.8	7.9	0.08	0.2	0.8	8.2	0.06	0.2	0.8	8.4	0.04
0.1	0.9	9.1	0.04	0.1	0.9	9.1	0.03	0.1	0.9	9.2	0.02
0.0	1.0	10.0	0.00	0.0	1.0	10.0	0.00	0.0	1.0	10.0	0.00

Table 1.4 Continued.

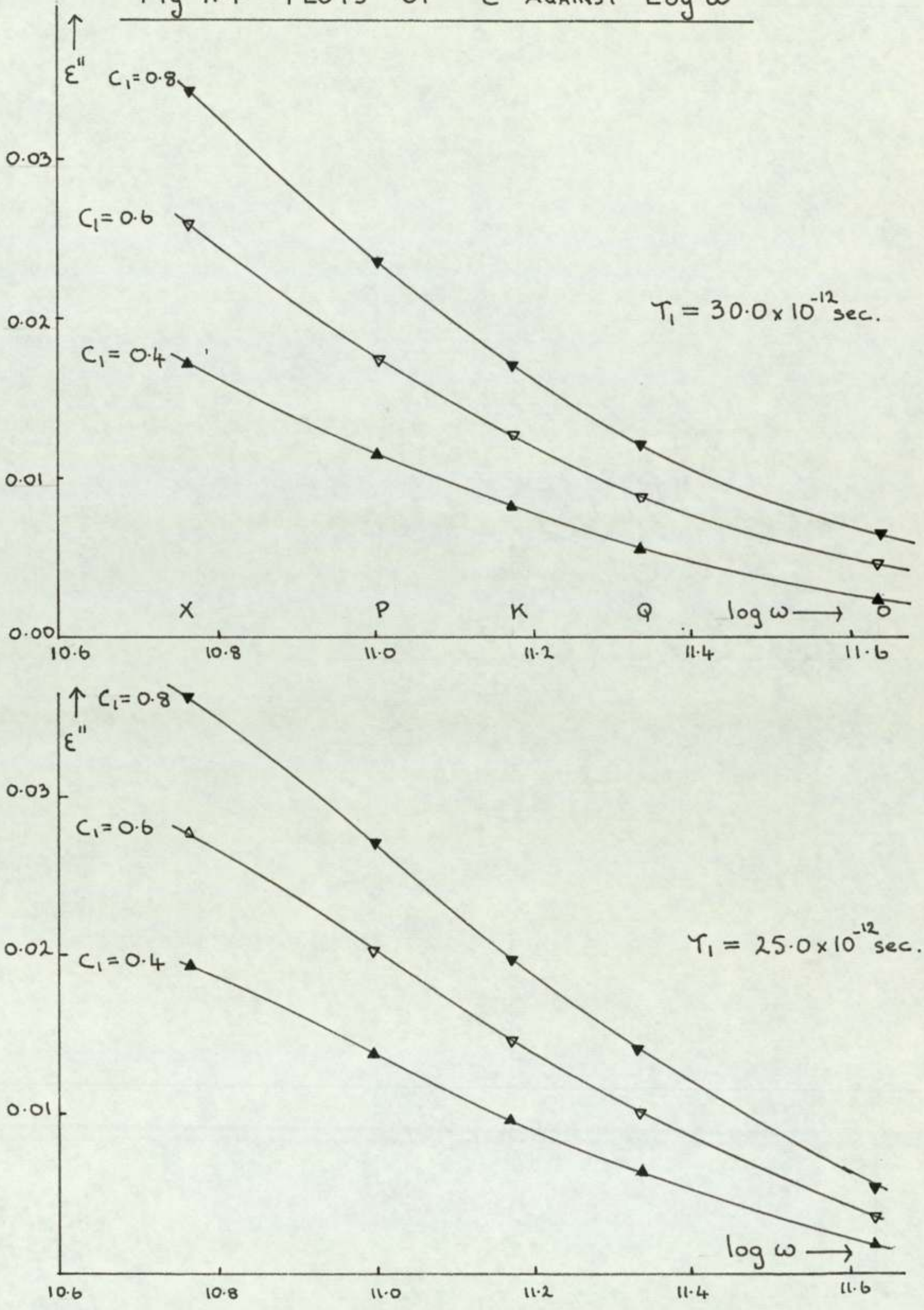
$\tau_1 = 6.0 : \tau_2 = 10.0$

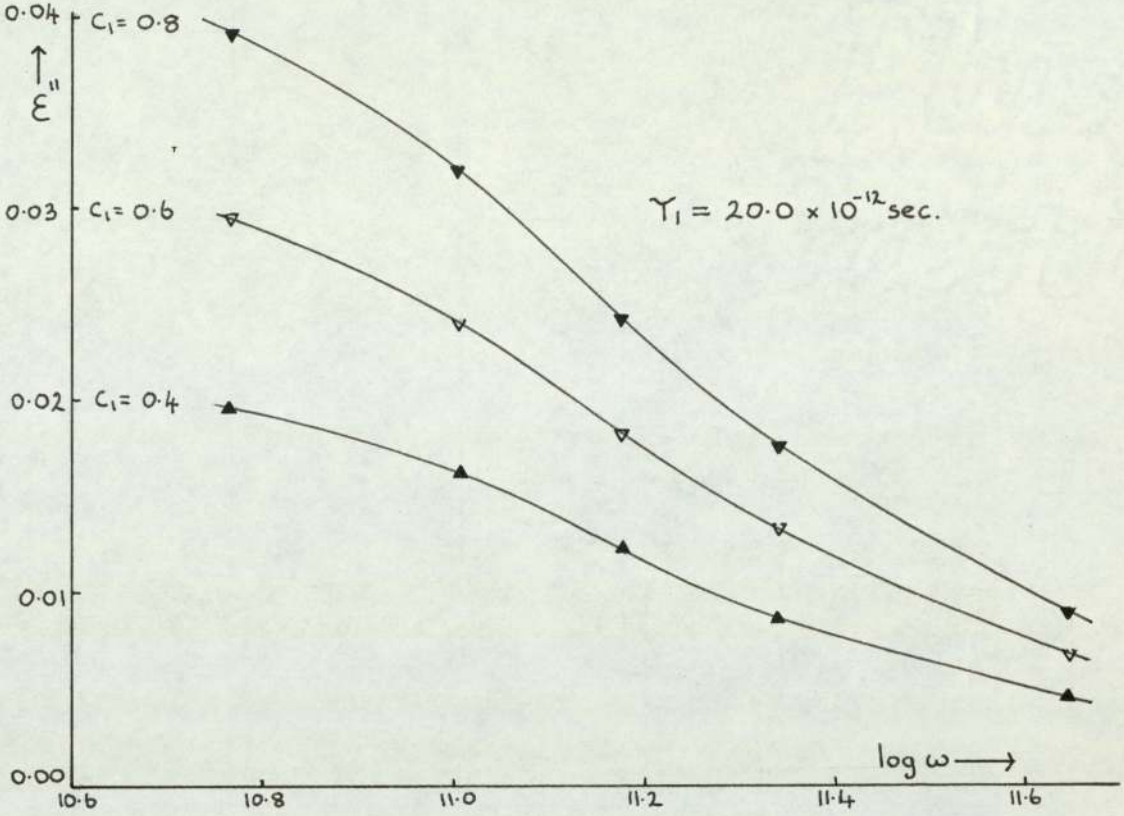
c_1	c_2	τ_0	α
1.0	0.0	6.0	0.00
0.9	0.1	6.3	0.01
0.8	0.2	6.6	0.01
0.7	0.3	7.0	0.02
0.6	0.4	7.4	0.02
0.5	0.5	7.8	0.02
0.4	0.6	8.2	0.02
0.3	0.7	8.6	0.02
0.2	0.8	9.0	0.01
0.1	0.9	9.5	0.01
0.0	1.0	10.0	0.00

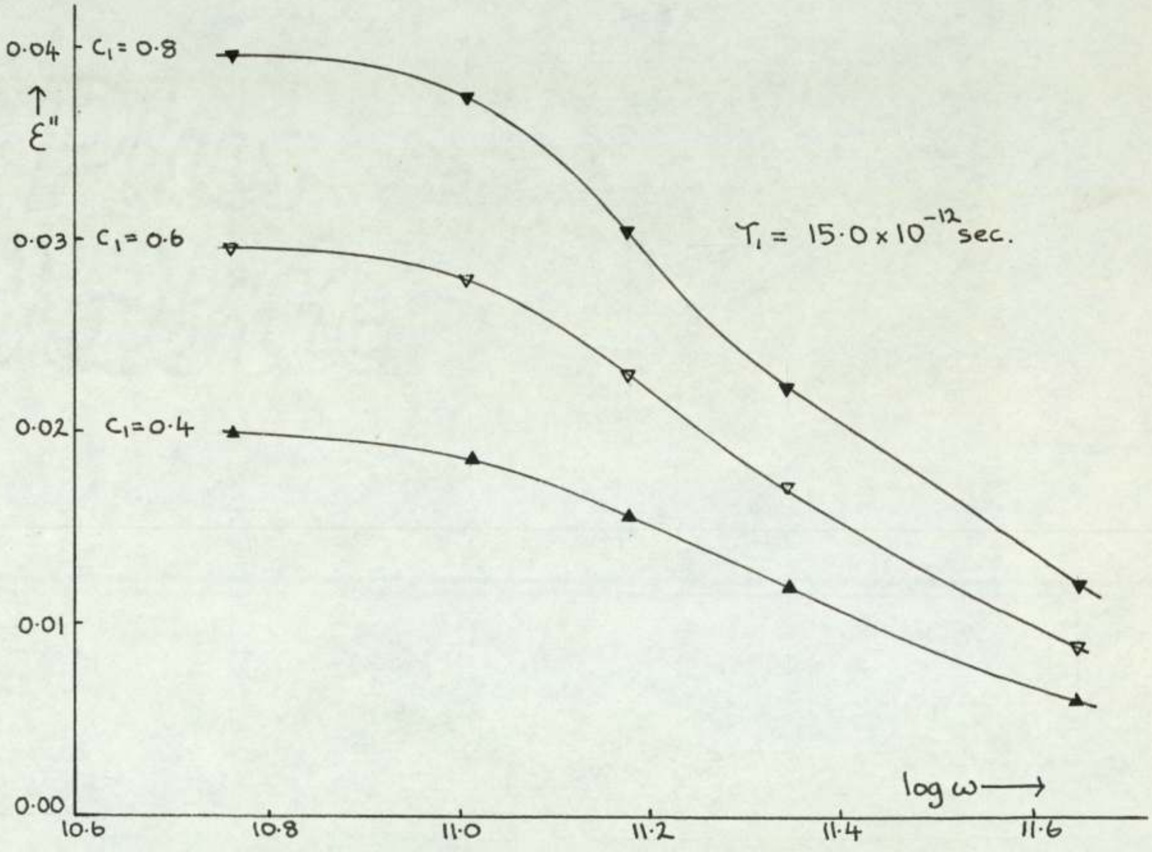
$\tau_1 = 8.0 : \tau_2 = 10.0$

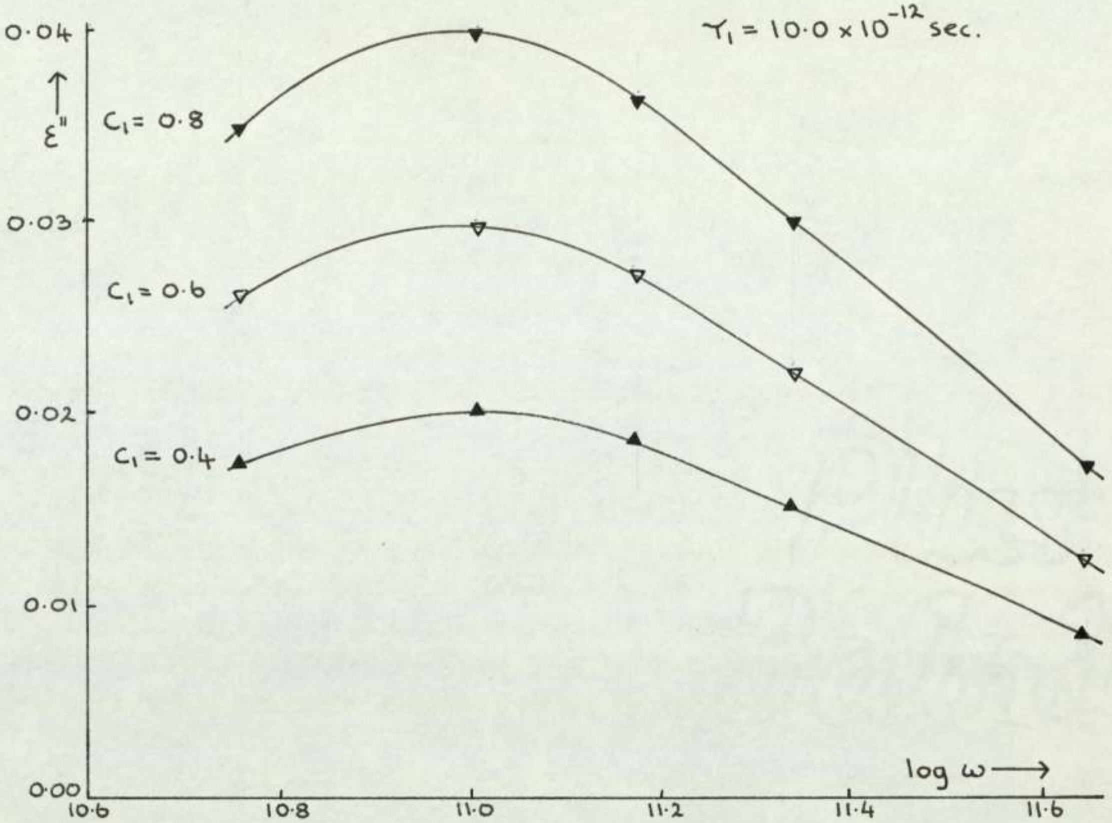
c_1	c_2	τ_0	α
1.0	0.0	8.0	0.00
0.9	0.1	8.1	0.00
0.8	0.2	8.3	0.00
0.7	0.3	8.5	0.01
0.6	0.4	8.7	0.01
0.5	0.5	8.9	0.01
0.4	0.6	9.1	0.01
0.3	0.7	9.4	0.01
0.2	0.8	9.7	0.00
0.1	0.9	9.9	0.00
0.0	1.0	10.0	0.00

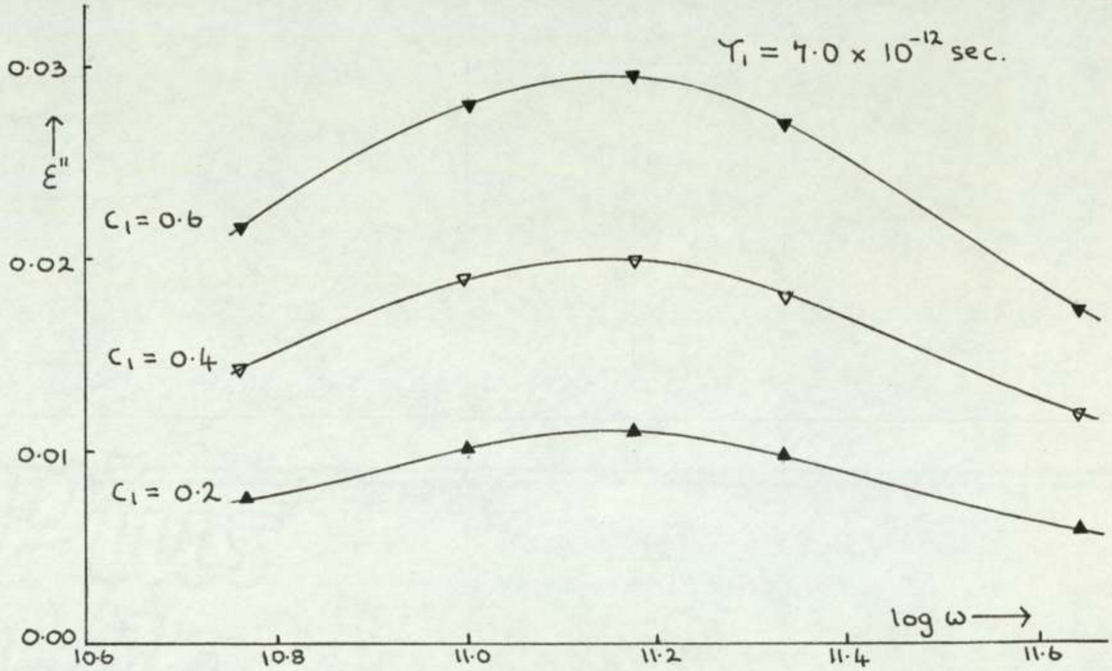
Fig 1.4 Plots Of ε'' against Log ω

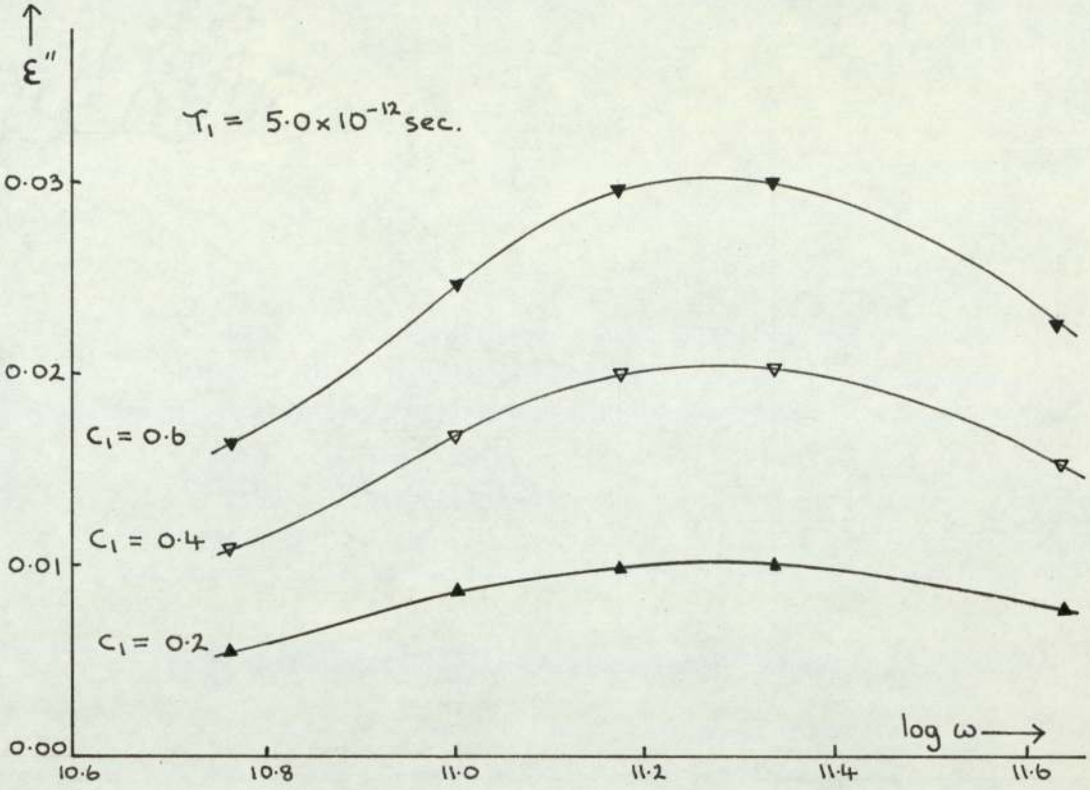


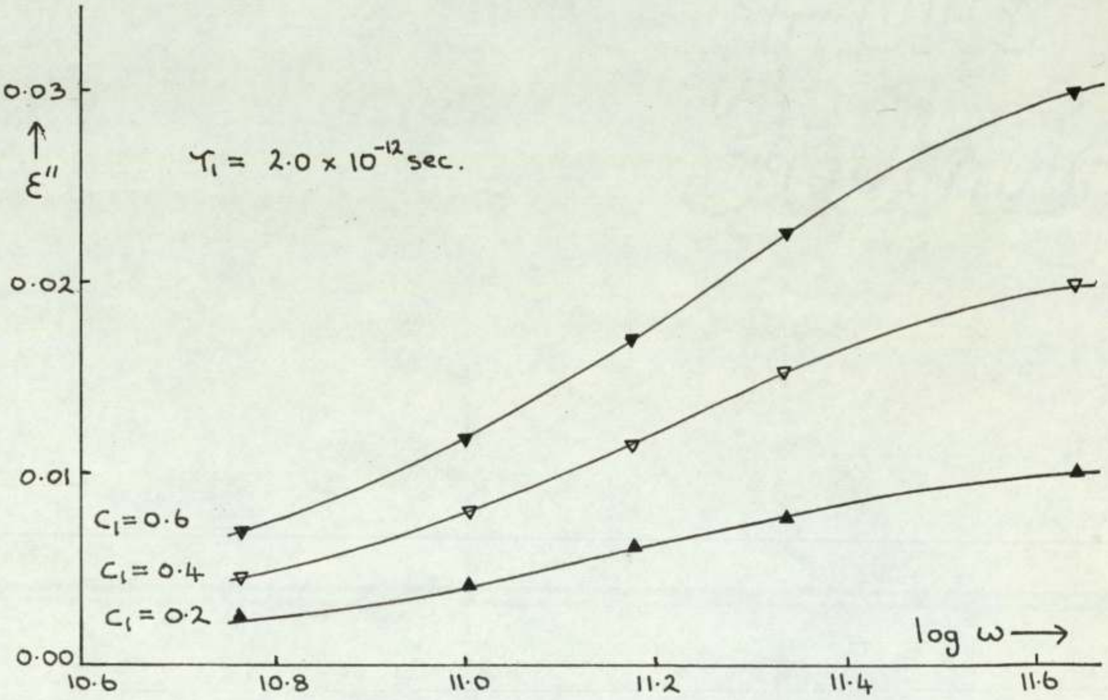

0.04
0.03
0.02
0.01
0.00
ε''
$C_1 = 0.8$
$C_1 = 0.6$
$C_1 = 0.4$
$\tau_1 = 20.0 \times 10^{-12}$ sec.
log ω
10.6
10.8
11.0
11.2
11.4
11.6


0.04
0.03
0.02
0.01
0.00
ε''
$C_1 = 0.8$
$C_1 = 0.6$
$C_1 = 0.4$
$\tau_1 = 15.0 \times 10^{-12}$ sec.
log ω
10.6
10.8
11.0
11.2
11.4
11.6


$\tau_1 = 10.0 \times 10^{-12}$ sec.
ε''
$C_1 = 0.8$
$C_1 = 0.6$
$C_1 = 0.4$
0.04
0.03
0.02
0.01
0.00
log ω
10.6
10.8
11.0
11.2
11.4
11.6


$\tau_1 = 7.0 \times 10^{-12}$ sec.
ε''
$C_1 = 0.6$
$C_1 = 0.4$
$C_1 = 0.2$
0.03
0.02
0.01
0.00
log ω
10.6
10.8
11.0
11.2
11.4
11.6


ε''
τ₁ = 5.0×10⁻¹² sec.
0.03
0.02
0.01
0.00
C₁ = 0.6
C₁ = 0.4
C₁ = 0.2
log ω ⟶
10.6
10.8
11.0
11.2
11.4
11.6


0.03
ε''
τ₁ = 2.0 × 10⁻¹² sec.
0.02
0.01
0.00
C₁ = 0.6
C₁ = 0.4
C₁ = 0.2
log ω ⟶
10.6
10.8
11.0
11.2
11.4
11.6

CHAPTER 2

THE MOLECULAR RELAXATION OF SOME RIGID MOLECULES IN DILUTE SOLUTION

Introduction.

The analysis and interpretation of dielectric data in terms of one or more relaxation times is facilitated, and is more valid, if the molecular relaxation time can be predicted with reasonable accuracy. Thus a knowledge of the effects which determine it's value is helpful. In dilute solution the viscosity and internal field effects are comparitively small, and the relationship between relaxation time and the location of the molecular dipole within the molecule may be examined for rigid molecules, of similar shape and size, such as quinoline, isoquinoline and phthalazine. Modification of the basic naphthalene nucleus presents the possibility of extending such a study to include the effect of molecular shape and size, by employing molecules such as 4-methylpyridine, acridine and 5,6-benzoquinoline.

The relaxation times of quinoline in the pure liquid state at 40°C.[26] and in naphthalene solution at 85°C.[27], have been found to be 29.7×10^{-12} and 9.5×10^{-12} sec. respectively. Isoquinoline, a molecule of identical shape and size, in the same circumstances was found to have relaxation times of 44.6×10^{-12} and 12.8×10^{-12} sec. respectively. The longer values obtained for isoquinoline being attributed to an amount of molecular orientation by rotation around the axis in the carbon-carbon bond held in common by the two rings, an orientation practically absent in quinoline, where the molecular dipole is almost parallel to this axis. However, measurements of these two molecules in cyclohexane [28] and nujol[29] solutions at 20°C. shows them to have almost identical relaxation times of $\backsim 10 \times 10^{-12}$ and $\backsim 46 \times 10^{-12}$ sec. respectively, indicating that molecular re-orientation occurs about the same axis in both cases, or that the differences in frictional resistance to rotation around the different molecular axes are small. Thus a new explanation of the behaviour in the pure liquid and naphthalene solution is required.

Discussion.

The mean relaxation times of quinoline, isoquinoline and phthalazine in p-xylene (Table 2.1) exibit a similar relationship to that shown by quinoline and isoquinoline both in the pure liquid[26] and in naphthalene[27] solution. Thus it appears that as the direction of the dipole vector moves from the short axis to the long axis, in the plane of the ring, there is an apparent increase in the molecular relaxation time. Which would be the result of an increased amount of orientation about the short axis, that being the one in the carbon-carbon bond held in common by the two rings. However, Hufnagel and Kilp[28] obtained a value of $\backsim 10 \times 10^{-12}$ sec. for the relaxation time of both quinoline and isoquinoline in cyclohexane solution at 20°C., offering

Table 2.1 Static Dielectric Constant, High Frequency Dielectric Constant, Relaxation Times, Weight Contributions, Distribution Coefficient, Dipole Moment and Weight Fraction of Six Heterocyclic Molecules in Cyclohexane and p-Xylene Solution.

Solute	Solvent	W_2	$T^\circ C$	ε_0	ε_∞	τ_0	τ_1	τ_2	C_1	α	μ_0
Quinoline	Cyclohexane	0.03866	50	2.0889	1.996	6.6	6.6	-	1.00	0.00	2.04
	p-Xylene	0.03780	25	2.4173	2.285	10.4	-	-	-	0.03	2.06
		0.03780	50	2.3487	2.230	6.7	-	-	-	0.02	2.08
Isoquinoline	Cyclohexane	0.03582	25	2.1797	2.035	10.5	-	-	-	0.03	2.48
		0.03328	50	2.1086	1.993	7.5	7.5	-	1.00	0.00	2.45
	p-Xylene	0.03647	25	2.4709	2.287	15.4	-	-	-	0.05	2.48
		0.03088	50	2.3706	2.244	10.3	-	-	-	0.01	2.38
Phthalazine	Cyclohexane	-	50	2.0438	1.982	6.7	6.7	-	1.00	0.00	-
	p-Xylene	0.01301	25	2.5391	2.286	19.9	-	-	-	0.06	4.88
		0.01301	50	2.4521	2.248	12.9	-	-	-	0.06	4.67
Acridine	Cyclohexane	0.02608	50	2.0327	1.991	15.1	-	-	-	0.02	1.97
	p-Xylene	0.05807	25	2.4560	2.309	21.9	21.9	-	1.00	0.00	2.06

Table 2.1 continued.

Solute	Solvent	W_2	$T^{\circ}C$	ε_0	ε_∞	τ_0	τ_1	τ_2	C_1	α	μ_0
Acridine	p-Xylene	0.04802	50	2.3514	2.251	14.7	14.7	-	1.00	0.00	2.00
5,6-Benzoquinoline	p-Xylene	0.05516	25	2.498	2.302	30.0	-	-	-	0.03	2.20
4-Methylpyridine	Cyclohexane	0.02380	50	2.1073	1.984	5.2	5.2	-	1.00	0.00	2.54
	p-Xylene	0.02310	25	2.4459	2.283	9.8	-	-	-	0.03	2.78

adequate support to the values listed in Table 2.1 for quinoline and isoquinoline, in cyclohexane and p-xylene solution respectively, at 25°C.. The relaxation times of these two molecules (46×10^{-12} sec.) in the viscous nujol solution and the relaxation times of 6.6×10^{-12} and 6.7×10^{-12} sec. for quinoline and phthalazine respectively in cyclohexane solution at 50°C., together with the data in cyclohexane at 20°C. when compared with the values in the pure liquid and naphthalene solution, suggest that the solvent plays an important role in determining the value of the relaxation times of such molecules, and that intermolecular forces increase along the series quinoline, isoquinoline, phthalazine.

Sharp and Walker[30] have shown that the difference in dipole moment of pyridine in cyclohexane and carbontetrachloride can be attributed to a weak form of donor acceptor interaction, confirmed by Morcom and Travers[31] using thermochemical measurements, whereas 2-phenyl- and 2,6--diphenylpyridine show no evidence of such interactions. Recent dielectric absorption studies[32] have shown the relaxation time of pyridine, in cyclohexane and p-xylene solutions at 25°C. to be 3.0×10^{-12} and 4.3×10^{-12} sec. respectively.

Rampolla and Smyth[33], in a study of several methylquinolines in the pure liquid state, observed somewhat shorter critical wavelengths for 2- and 8-methylquinoline, and attributed these anomalies to "the partial shielding of the heterocyclic nitrogen atom by the methyl group with it's attendant reduction of intermolecular attractions". Restriction of group rotation in substituted naphthalenes by the hydrogen in the 8- position is not unknown and dielectric studies have shown that for 1- and 2-acetonaphthone, group rotation is only possible in 2-acetonaphthone[34].

Thus the available evidence, and molecular models of quinoline, isoquinoline and phthalazine indicate that these molecules are capable of acting as donors in donor-acceptor interactions, and that the nitrogen atom in quinoline is shielded by the 8-hydrogen atom, from the approach of other molecules. Such shielding is diminished in the case of isoquinoline and phthalazine, the latter having two adjacent nitrogen atoms is expected to form stronger intermolecular bonds. The lengthening of relaxation times in p-xylene, and other solvents capable of acting as acceptors, of isoquinoline and phthalazine compared with their values in cyclohexane solution and the constancy of the quinoline value can be attributed to the degree of molecular interaction. Additional support for this theory is given by the results of acridine and 4-methylpyridine, the latter molecule, in which the nitrogen atom is unshielded, having relaxation times in p-xylene and cyclohexane[22] solutions at 25° C. of

9.8×10^{-12} and 7.2×10^{-12} sec. respectively. Whereas in acridine, the relaxation time of which is the same (15×10^{-12} sec.) in both solvents at 50°C., the nitrogen atom is effectively shielded by the two adjacent hydrogen atoms. Consequently in order to study the effect of the direction of the dipole moment vector within these molecules, the values in cyclohexane solution at 50°C., in which case intermolecular forces are at a minimum, provide the more realistic picture.

Attempts to correlate molecular relaxation times with the volume of the molecule have given rise to a number of equations notably that of Fischer[35]

$$\tau = \frac{4\pi abc\,\eta^{+} f}{kT} \qquad 2.1$$

where a,b and c are the lengths of the semi-axes of the molecular ellipsoid, η^{+} is an empirical viscosity, f a molecular structive factor and k the Boltzmann constant. The volume of the ellipsoid is given by

$$V = \frac{4\pi abc}{3} \qquad 2.2$$

In the derivation of Eq. 2.1 it was assumed that the molecule is surrounded by a continuous fluid, and it is not strictly applicable for a polar molecule in a non-polar solvent, where both solute and solvent molecules are of similar size. Meakins[36] concluded that when the solute

Fig 2.1 Rotational Axes – Quinoline, Isoquinoline and Acridine.

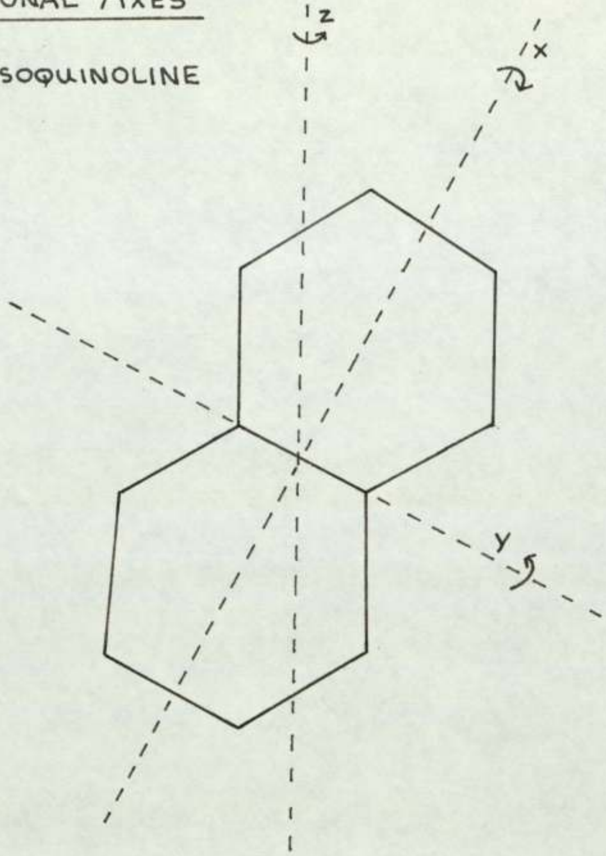


Fig 2.2 Rotational Axes – 4-Methylpyridine

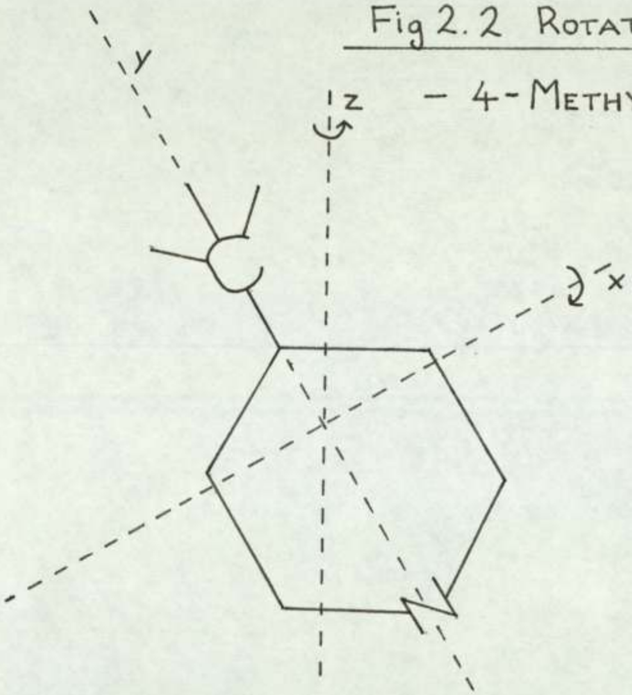


Fig 2.3 ROTATIONAL AXES

- 5,6-BENZOQUINOLINE

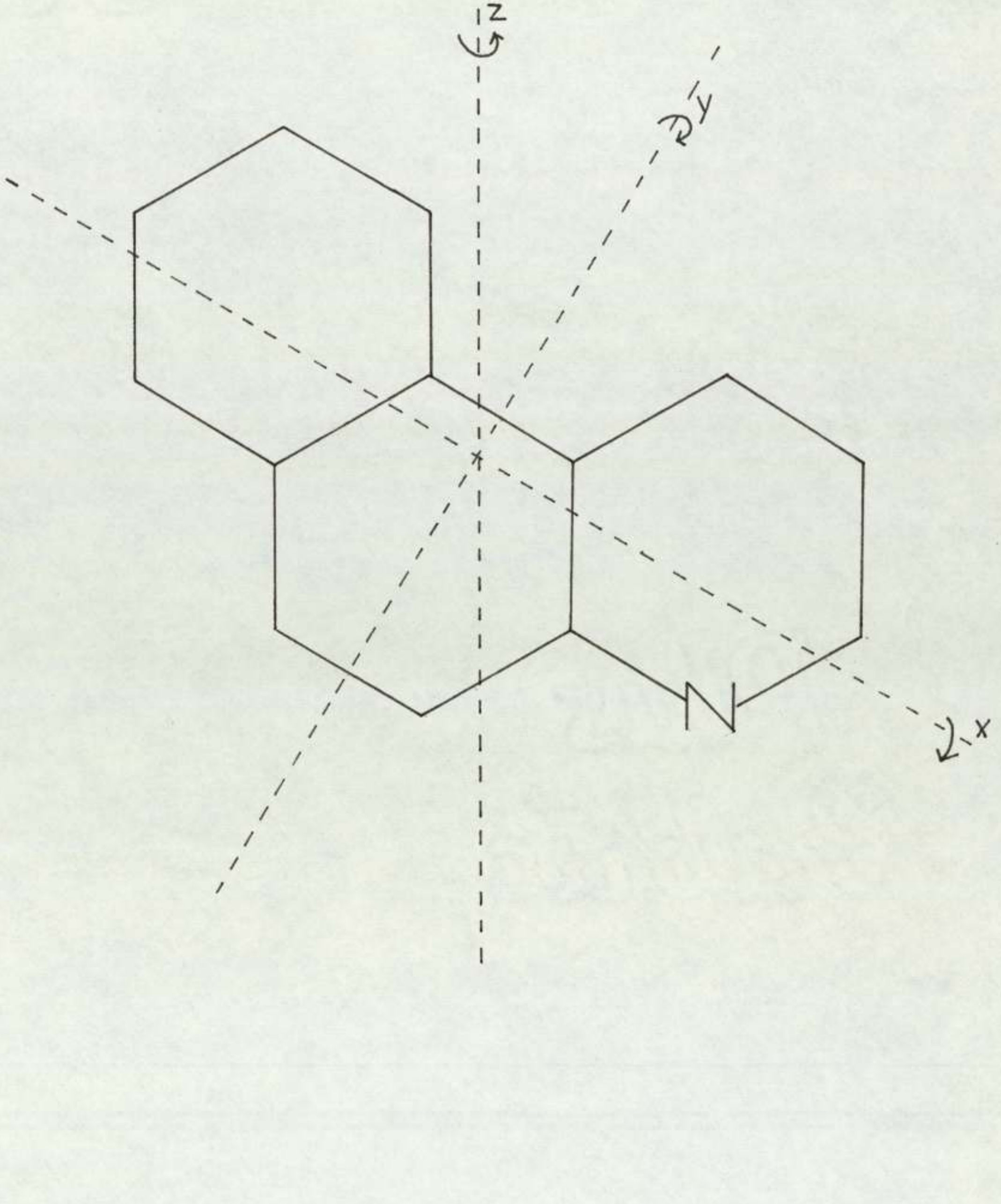
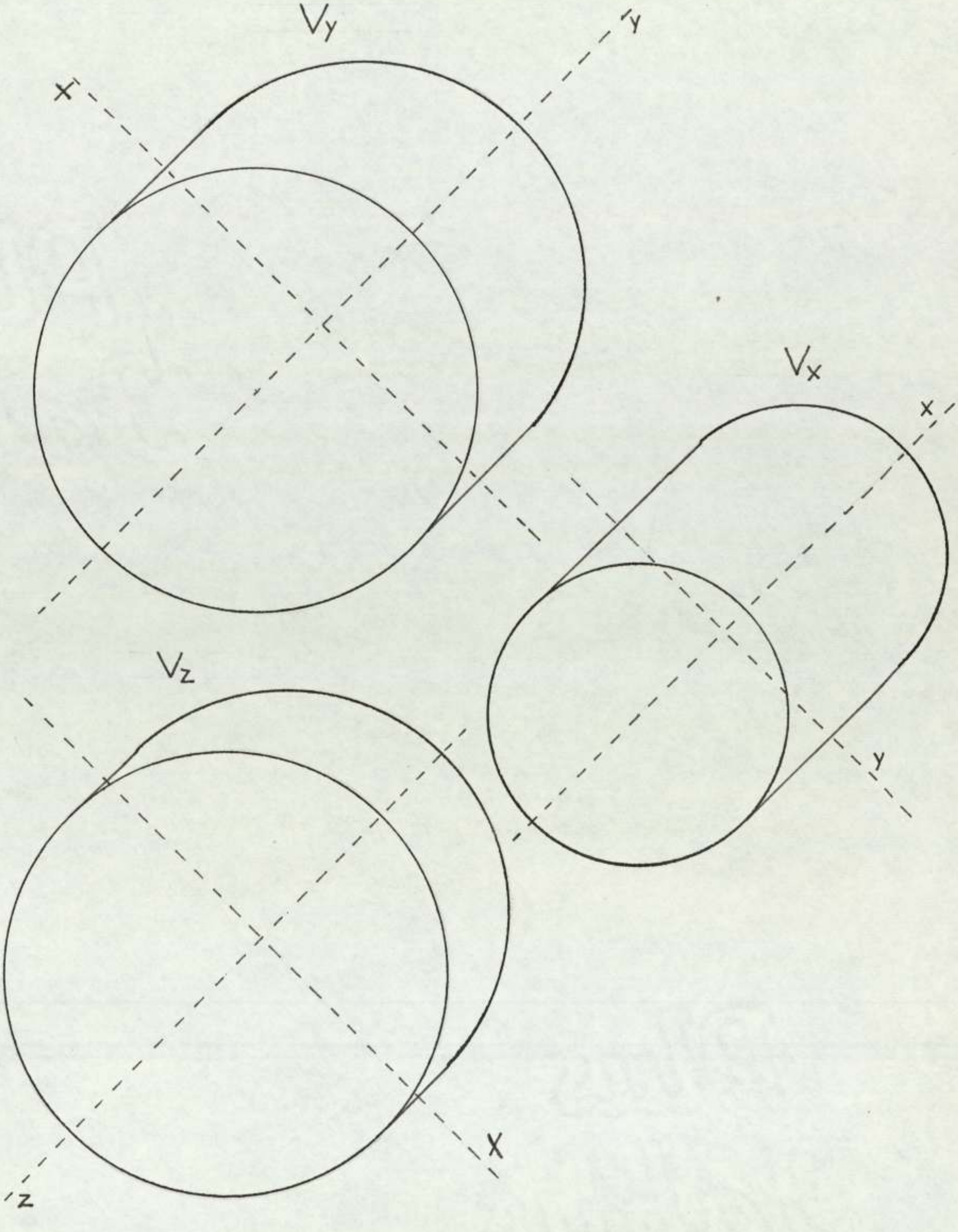


Fig 2.4 ROTATIONAL VOLUMES



molecule was three times as large as the solvent then Eq. 2.1 held true. These findings were confirmed by Nelson and Smyth[37], except for deviations caused by molecular shape and dipole orientation. In such cases, the differences in volume swept out in orientation about the different molecular axes must be taken into consideration. Fig. 2.1, 2.2 and 2.3 illustrate the direction of the major axes within these molecules. The method of calculating the volumes V_x, V_y and V_z, shown in Fig. 2.4, was to treat the volume swept out as being a cylinder of length equal to that of the axis of rotation and diameter equal to that of the axis perpendicular to it. Volumes listed in Table 2.2 were obtained by measurement of Courtaulds Models and are not considered to be better than ± 10%.

Quinoline and phthalazine have identical relaxation times in cyclohexane solution at 50°C. and only one common axis of rotation, thus it is probable that both orientate about this z-axis, which involves the smallest volume and presumably the least energy. Contributions from relaxation about the X- and Y-axes, in quinoline and phthalazine respectively cannot be discarded since V_y for phthalazine is only about 15% greater than V_x for quinoline. The slightly longer relaxation time observed for isoquinoline in cyclohexane at 50°C., compared with quinoline and phthalazine, is almost within the error for such values.

Table 2.2 Volumes Swept Out ($\mathring{A}^3$) by Orientation about the Short Axis (Vy), Long Axis (Vx) and the Axis Perpendicular to the Plane of the Ring (Vz), and Molecular Volumes (V), obtained from measurements using Courtaulds Models, and Relaxation Time/Volume Ratios. (τ/V values are multiplied by 10^{14}.)

Solute	Solvent	T°C.	Vx	Vy	Vz	V	τ/V_x	τ/V_y	τ/V_z	τ/V
Quinoline	Cyclohexane	50	355	-	217	116	1.9	-	3.0	5.7
Isoquinoline		50	355	447	217	116	2.1	1.7	3.5	6.5
Phthalazine		50	-	413	201	111	-	1.6	3.3	6.1
4-Methylpyridine		50	321	-	179	85	1.6	-	2.9	6.1
Acridine		50	482	-	359	152	3.1	-	4.2	9.9
Quinoline	p-Xylene	25	355	-	217	116	2.9	-	4.8	9.0
Acridine		25	482	-	359	152	4.5	-	6.1	14.4
5,6-Benzoquinoline		25	508	764	349	156	5.9	3.9	8.6	19.3

In view of the quinoline and isoquinoline results in p-xylene and cyclohexane at 25°C. respectively, and the previously mentioned behaviour in nujol solution, it is not unreasonable to consider their relaxation times as being equal. Isoquinoline is unique in that it's dipole vector within the molecule, is not coincident with a major axis but makes an angle of about 30° to the short- or Y-axis. Resolving the isoquinoline moment of 2.5D along the X- and Y-axes gives moments of 2.17D and 1.25D respectively. Examination of equations 2.3 (which at best only offers a rough estimate) and 2.4:

$$\tau = C_1\tau_1 + C_2\tau_2 \ldots\ldots \qquad 2.3$$

$$\frac{C_1}{C_2} = \frac{\mu_1^2}{\mu_2^2} \qquad 2.4$$

where τ is the mean relaxation time, τ_1 etc. are the relaxation times of the relaxation processes and C_1 etc. the respective contributions to the dielectric absorption. Shows that for isoquinoline rotation about the Y- or Z-axis would involve a contribution to the dielectric absorption about three times greater than rotation about the X-axis i.e. $2.17^2/1.25^2$, and it's relaxation time may be considered in terms of rotation about either the Y- or Z-axis. Thus the molecular relaxation time of these three molecules in cyclohexane at 50°C. is virtually independent of the molecular dipole direction, and in view of the τ/V_z ratios orientation is predominantly about the Z-axis. The constancy of the τ/V values for which V was obtained from Eq. 2.2, is only to be expected for molecules, of the same size in similar environment, which re-orientate about the same axis.

The relaxation time of acridine in p-xylene solution at 25°C., 21.9 x 10^{-12} sec., is in good agreement with values of 27.0 x 10^{-12} and 23.8 x 10^{-12} sec. for anthrone and fluorenone respectively in p-xylene at 25°C., recently measured by Hunt in this laboratory[38]. Pitt and Smyth[39] reported relaxation times of 24.8 x 10^{-12} and 19.9 x 10^{-12} sec. respectively for these two molecules, of similar shape and size to acridine, in benzene at 20°C.. Examination of the relaxation time-volume swept out ratios shows that the most favourable comparison with the quinoline family is given by the acridine τ/V_x value in both cyclohexane and p-xylene solutions. This is slightly unexpected since from the Vz and Vx values rotation about the Z-axis would, at first consideration, appear to be more likely. However, conclusions based on a single comparison may be misleading, especially in the absence of further information, regarding the differences in the frictional resistances experienced by rotation about the different axes, for such elongated molecules. The respective relaxation time-volume values of 4-methylpyridine and quinoline show a remarkable agreement.

However, the Vx and Vy values are of a similar magnitude which was not the case for acridine. Since the τ/V_x and τ/V_y values are in harmony with those of quinoline, the correct assesment given by Eq. 2.2 is not unexpected. Some information on the relationship between relaxation time and molecular shape may be expected from the results of 5,6-benzoquinoline. Because of it's low solubility in cyclohexane and the limited amounts available, this compound was only measured in p-xylene solution at 25°C.. However, the nitrogen atom in this molecule is "shielded" in a similar fashion to the nitrogen in quinoline, and comparison with the quinoline and acridine data, also in p-xylene solution at 25°C., is considered reasonable. Calculation shows the centre of mass and major axes of this molecule to be as depicted in Fig. 2.3. The dipole in this molecule makes a similar angle to the Y-axis as the dipole in isoquinoline. Thus orientation about either the Y- or Z-axes will make the major contribution to the dielectric absorption, the τ/V_y value giving the most favourable comparison with the quinoline τ/V_z value. For 5,6-benzoquinoline rotation about the Z-axis involves the smallest volume, the situation being analogous to that of acridine, and again more information on frictional resistances and the effect of shape is required before any inference can be made from these results.

Perrin[40] concluded that if the dipole moment of an ellipsoidal molecule lies along one axis of the ellipsoid, the dispersion is the same as if the molecule were spherical. Quinoline, phthalazine, acridine and 4-methylpyridine fall into this category and all show a negligible or zero distribution coefficient in cyclohexane solution at 50°C.. Isoquinoline may be expected to exhibit non-Debye behaviour since it's molecular dipole is at an angle of about 30° to the axis in the carbon-carbon bond held in common by the two rings, in fact the measurements showed it to have distribution coefficients of 0.0 and 0.03 in cyclohexane and p-xylene solution respectively. The non-zero distribution coefficients observed for all the molecules, except acridine, in p-xylene solution at 25°C. may well be related to local variations in intermolecular effects and not a contribution to the dielectric loss from a second relaxation process. Attempts to analyse the dielectric constant and loss data of these molecules yielded values with little or no physical significance.

The dipole moments of isoquinoline and acridine compare well with literature values of 2.56D[41] and 1.97D[42] respectively, indicating correct assignment of the high frequency dielectric constants. Previously reported dipole moment values for phthalazine and 5,6-benzoquinoline were unavailable. However such values for quinoline[43] are numerous and remarkably consistent at 2.20D in benzene solution, appreciably greater than the values shown in Table 2.1 which are also consistent at 2.06 ± 0.02D. The explanation of this discrepancy is not clear. Since the ε_∞ values are similar to those of isoquinoline and acridine, both of which have acceptable dipole moments. It would appear that the dipole moment of 4-methylquinoline is dependent on the solvent, the values may be compared with those of 2.59D and 2.74D in benzene and carbontetrachloride solutions respectively[43].

In conclusion molecular relaxation times of quinoline, isoquinoline and phthalazine seem to be independent of the direction of the dipole vector within the molecule. For these three molecules, acridine and 4-methylpyridine the relaxation time is apparently proportional to the volume swept out by the orientation of the molecular ellipsoid around the molecular axes. The importance of allowing for intermolecular forces, even in dilute solution, when predicting relaxation times is emphasized. In addition the sensitivity of the method in the detection of such forces is well illustrated.

CHAPTER 3

RELAXATION PROCESSES OF SOME SATURATED SIX MEMBERED RINGS CONTAINING OXYGEN AND SULPHUR ATOMS

Introduction

Numerous dipole moment determinations have been carried out on 1,4-dioxan and a few on 1,4-dithian. Calderbank and Le Fèvre[44] summarized the position in 1949 to be that, in the gaseous state 1,4-dioxan is nonpolar, and that in the liquid state both had either very small or zero moments. However, even the gaseous state value of zero is uncertain since values of 0 and 0.49D have been reported[43]. The nonmicrowave procedure in dipole moment (μ) evaluation of a solute in a solvent employs the equation:

$$\mu = 0.01281 \left[{}_2P_\infty - x R_D \right]^{\frac{1}{2}} \tag{3.1}$$

where R_D is the molar refraction of the sodium D line, ${}_2P_\infty$ is the polarization of the solute at infinite dilution, and the correction factor x is taken to be 1.0, 1.05 and 1.1 to allow for the fact that:

$$P_A + P_E \neq R_D \tag{3.2}$$

For substances with a very low moment the uncertain allowance to be made for the excess atomic polarization over the P_E contribution in R_D makes it impossible to decide whether the compound has a genuine moment, especially if a high value for the atomic polarization might be anticipated in connection with a particular bending mode. However, the microwave technique does not suffer from such approximations.

Cumper and Vogel[45] have examined 1,4-thioxan in benzene solution employing Eq. 3.2, and obtained a moment of 0.42D but pointed out that a large atomic polarization term could result in a significant error in the dipole moment.

It seemed worthwhile examining the dielectric absorption of these three compounds in order to ascertain their dipole moments. However, the major aim was to examine the energy barriers between conformational isomers in such ring systems and the extention of such a study to include tetrahydropyran, pentamethylene sulphide and s-trioxan. No such data appears to be available in the literature and, indeed, is quite sparse for any saturated ring systems. If the free energy barrier lies between about 1 to 3.5 kcal./mole, the microwave method would seem to be well suited to such studies for systems which may be analysed in terms of two relaxation times. In order to achieve such analyses on the weakly polar liquids or very dilute solutions, it is necessary to have a greater accuracy of measurement than most of the dielectric absorption methods employed in the past and it is desirable to measure at four or more microwave frequencies.

Discussion.

Since 1,4-dioxan, 1,4-dithian and 1,4-thioxan have measurable loss factors, this establishes that these systems contain contributions from polar species. From the data in Table 3.1 the apparent dipole moment of 1,4-thioxan was obtained from Eq. 1.39 and is 0.30 ± 0.01D in cyclohexane and 0.28 ± 0.01D in a mixture of 1,4-thioxan and nujol. For 1,4-dioxan and 1,4-dithian, largely as a result of the low loss factors and small dielectric constant variation at the different wavebands, the mean or the individual relaxation times cannot be deduced. Fortunately, the resulting dipole moments are fairly insensitive to the relaxation times assumed in the calculation (Table 3.2) and it would seem that the moments of 1,4-dioxan and 1,4-dithian are about 0.1D and 0.15D respectively.

Calderbank and Le Fèvre[44] considered the best value for the total molar polarization of 1,4-dioxan at 25°C. was 24.6 c.c.. From the atomic-electronic polarization data from dielectric constant sources[47], it then becomes possible to estimate the dipole moment to be 0.16D. If, however, the molar refraction of 21.7 c.c. for the sodium-D line is taken to equal the sum of the atomic and electronic polarization, then the corresponding moment is 0.38D. The microwave value thus bears out a high atomic polarization contribution in 1,4-dioxan. For both 1,4-dioxan and 1,4-dithian it would seem that in addition to the chair conformer, which has a zero moment, there is also some polar boat form present. An alternative explanation could be that the moment results from the dipole-dipole interaction, of the type visualized by Whiffen[48] involving a collision induced dipole.

Table 3.1 Static Dielectric Constant, High Frequency Dielectric Constant, Viscosity, Relaxation Times, Weight Contributions, Dipole Moment and Weight Fraction of Tetrahydropyran, Pentamethylene Sulphide, s-Trioxan and 1,4-Thioxan in Cyclohexane, and 1,4-Thioxan in Nujol, at 25°C..

Solute	Solvent	w_2	ε_0	ε_∞	$\eta_{c.p.}$	τ_0	$\tau_{1\,slope}$	τ_1	τ_2	C_1	α	μ_D
1,4-Thioxan		1.0000	2.5255	2.391	2.18	8.1	13.2	18.3	3.0	0.48	0.25	0.31
	Cyc.	0.9691	2.4975	2.390	2.03	8.3	11.0	11.8	3.0	0.69	0.18	0.28
		0.9363	2.4700	2.360	1.96	7.9	12.8	11.9	2.9	0.62	0.12	0.29
		0.8669	2.4275	2.332	1.75	7.5	12.1	11.6	3.0	0.64	0.19	0.29
		0.7107	2.3191	2.250	1.44	7.3	9.3	10.0	3.7	0.60	0.19	0.29
	Nujol	0.8740	2.4508	2.365	2.94	8.1	9.2	10.2	3.7	0.71	0.14	0.27
		0.7827	2.4186	2.337	3.73	8.2	10.8	13.9	3.0	0.59	0.21	0.28
		0.7109	2.3852	2.316	4.56	7.7	9.9	12.0	3.0	0.61	0.12	0.28
Tetrahydropyran	Cyc.	0.04823	2.1336	2.030	-	3.3	4.5	3.3	-	1.00	0.00	1.44
Pentamethylene-Sulphide	Cyc.	0.05255	2.1620	2.038	-	4.0	4.5	4.0	-	1.00	0.00	1.68
s-Trioxan	Cyc.	0.02031	2.1087	2.033	-	3.0	3.4	3.0	-	1.00	0.00	1.99
		0.02297	2.1225	2.032	-	3.1	3.2	3.1	-	1.00	0.00	2.04

Table 3.2 Dielectric Absorption Data for 1,4-Dithian in p-Xylene, 1,4-Dioxan and p-Xylene.

μ_a and μ_b are the apparent dipole moments corresponding to mean relaxation times of 3.0×10^{-12} and 7.0×10^{-12} sec. respectively as calculated from:

$$\mu = \left[\frac{27kT}{4\pi Nc} \cdot \frac{\varepsilon''}{(\varepsilon_1+2)^2} \cdot \frac{1+(\omega\tau)^2}{\omega\tau} \right]^{\frac{1}{2}} \tag{3.3}$$

where C is the concentration in moles/c.c. and ε_1 is the dielectric constant of the solution.

Solution	w_2	ε_0	Frequency (G.c./sec.)	ε'	ε''	μ_a	μ_b
1,4-Dithian	0.0635	2.2871	34.86	2.263	0.0056	0.13	0.13
			23.98	2.272	0.0043	0.17	0.14
			9.313	2.282	0.0025	0.17	0.13
p-Xylene	1.0000	2.2631	34.86	2.255	0.0052	-	-
			23.98	2.256	0.0037	-	-
			9.313	2.264	0.0022	-	-
1,4-Dioxan	1.0000	2.2173	34.86	2.213	0.0079	0.11	0.11
			23.98	2.214	0.0043	0.09	0.08
			9.313	2.219	0.0028	0.11	0.08

Table 3.3 Dielectric Constant and Refractive Index Data for 1,4-Thioxan in Cyclohexane Solution at 25°C..

w_2	ε	n^2_D
1.0000	2.5255	2.26846
0.9691	2.4975	2.25560
0.9363	2.4700	2.24400
0.8668	2.4264	2.22046
0.7939	2.3752	2.19873
0.7107	2.3191	2.17368

$\left(\frac{\varepsilon-\varepsilon_1}{w_2}\right)_{w_2\to 0} = 0.2321,$ $\left(\frac{n^2-n_1^2}{w_2}\right)_{w_2\to 0} = 0.1233,$

$R_D = 27.84\text{cm.}^3$ $P_o = 2.719\text{cm.}^3$

μ = 0.36D and using Smith's correction 0.35D[46,47].

For 1,4-dioxan the atomic polarization is about 15% of the electronic polarization[47] which is quite high relative to the majority of molecules. Such data are not available for 1,4-thioxan and 1,4-dithian. To gain an appreciation as to whether the former had a large atomic polarization term the moment in cyclohexane of 0.29D obtained by the microwave technique may be compared with that of 0.35D deduced from the Guggenheim approach. Thus, on comparison of these values with those of 1,4-dioxan, the atomic polarization contribution would appear significantly less for 1,4-thioxan.

Cumper and Vogel[45] obtained dipole moments of 1.55 and 1.71D for tetrahydropyran and pentamethylene sulphide respectively, Calderbank and Le Fèvre found the moment of s-trioxan to be 2.16D, both sets of workers using benzene as solvent at 25°C., comparison with the dipole moments listed in Table 3.1 shows, in each case, that the values obtained by the microwave technique are significantly smaller, with the possible exception of pentamethylene sulphide, the differences being too great to be accounted for in terms of any errors in the ε_∞ values. Thus it seems probable that there is a high atomic polarization term for these three molecules.

The dielectric loss of 1,4-thioxan was appreciably greater than that of 1,4-dioxan and 1,4-dithian and since it was the only molecule whose dielectric absorption showed an appreciable distribution coefficient it was chosen for a more detailed study. In Table 3.1 the apparent dipole moment in cyclohexane and also in the nujol - 1,4-thioxan mixture is virtually constant. Such consistency is not to be expected for the individual relaxation times, for a most favourable case the accuracy would not be expected to be better than ± 10%. The mean relaxation time of $\sim 7.9 \times 10^{-12}$ sec., when compared with those of 3.3×10^{-12}, 4.0×10^{-12} and 3.0×10^{-12} sec. for tetrahydropyran, pentamethylene sulphide and s-trioxan respectively, indicates a contribution to the dielectric absorption from a process having a longer relaxation time than that required for molecular orientation. Confirmation of this is exhibited by the τ_1 slope values which also afford an approximation of the magnitude of the long relaxation process. The shorter relaxation time of 1,4-thioxan $\sim 3.0 \times 10^{-12}$ sec. may be compared with the mean relaxation times of the other three molecules and all four with that of tetrahydrofuran in cyclohexane[28] and in the pure liquid state[26] at 20°C. of 1.82×10^{-12}sec. and 2.9×10^{-12}sec. respectively. Further comparison may be made with pyridine whose relaxation time in cyclohexane at 20°C. has been found to be 2.7×10^{-12} sec.[28]. Miller and Smyth[27] have measured s-trioxan, which is known to exist predominantly in the chair form, and found it to have a relaxation time of 2.9×10^{-12} sec. and a distribution coefficient of zero in benzene solution at 20°C., in excellent agreement with the results in Table 3.1. Thus the τ_2 value of 1,4-thioxan can be identified with the relaxation of the chair form, which, from the dipole moment value must be the form predominantly present. Even bigger molecules, such as chlorocyclohexane[28] and camphor[49], which are roughly of a similar shape to 1,4-thioxan, have relaxation times of only 7.4×10^{-12} sec. and 7.1×10^{-12} sec. respectively in cyclohexane at 20°C.. One candidate for the longer relaxation time of $\sim 12 \times 10^{-12}$ sec. is the overall rotation of another conformational isomer. However, the difference in volume and shape amongst the possible forms would seem insufficient to account for this. In the case of the chair form the re-orientation of the dipole could be analysed in terms of rotation about two axes. Whereas with a skew boat the resultant dipole would be almost perpendicular to the long axis, as in the chair form of s-trioxan, of this roughly ellipsoidal molecule. Thus in terms of volume swept out by such a species the relaxation time may be expected to be of similar magnitude to that of the chair form and consistent with the conclusions in Chapter 2.

It's being related to the existence of an associated species of the type $(OC_4H_8S)_n$ would seem improbable since both dipole moment and relaxation time values remain sensibly constant both in cyclohexane and nujol solutions of different concentration and in the pure liquid. In addition, the dipole-dipole relaxation mechanism visualized by Whiffen[48] would hardly account for the value, since that type of interaction leads to relaxation times $\sim 1 \times 10^{-12}$ sec.. The results reported in a later chapter suggest that this value is dependent on the size and molecular weight of the molecule, However, it is also indicated that the mechanism is not detectable for spherical saturated molecules. Estimates of the dipolar contribution to the cohesive energy may be obtained[2] from the equations 3.3 and 3.4:

$$W_1 = -\frac{4}{3}\pi\frac{d}{M}N^2 \frac{(\varepsilon_0-1)(n_D^2+2)}{(2\varepsilon_0+n_D^2)3}\mu^2 \qquad 3.3$$

$$W_2 = -RT\frac{(\varepsilon_0-1)(\varepsilon_0-n_D^2)}{(n_D^2+2)} \qquad 3.4$$

where d is the density, M the molecular weight and n_D the refractive index for the Na D line.

For 1,4-thioxan in the pure liquid state the dipolar contribution is the energy W required to cause infinite separation of the molecules if dipolar forces alone were present. An estimate of the cohesive energies may be obtained from Hidebrand's equations[50]:

$$\begin{aligned} \Delta H_T^v &= -2950 + 23\cdot 7T_b + 0\cdot 02T_b^2 \\ \Delta E_T^v &= \Delta H_T^v - RT \end{aligned} \qquad 3.5$$

where ΔE_T^v is the energy of vapourization (approximately equal to the cohesive energy), ΔH_T^V the heat of vapourization at temperature T°K and Tb the boiling point. Values of W and ΔE_T^V for 1,4-thioxan are found to be $\sim$ 0.05 and 9.94 kcal/mole. respectively, neither of which are of requisite magnitude to suggest they be responsible for the τ_1 process. However, in a study of some alkyl benzenes, Hassell and Walker[51] concluded that London dispersion forces were the predominating factor in intermolecular interactions in these molecules, but the absence of any strong absorption for p-xylene ruled out the possibility of such forces being associated with a relaxation process. By analogy the very weak absorption of 1,4-dioxan indicates that the τ_1 process of 1,4-thioxan is not the result of such intermolecular forces. Another interpretation is that τ_1 corresponds with a relaxation process involving the inter-conversion of two conformational isomers, that is an intramolecular re-orientation between two positions of equilibrium.

If only the chair and skew boat forms are present, then from the bond angles and bond moment data summarized by Cumper and Vogel[45] and the measured moment the proportions of chair and boat may be estimated as approximately 99 to 1 respectively. This may be compared with the IR and Raman results of 1,4-dioxan which have shown that those molecules in the boat form are present in almost a negligible amount[52]. Calculation shows that an asymmetrical boat form of 1,4-thioxan with a moment of about 0.5D would correspond to an appreciable contribution from that form - sufficient to be readily detected by other spectroscopic methods.

It is interesting to note that each process is giving similar contributions (i.e.$C_1 \backsim C_2$) to the dielectric loss. Two of the factors which determine these values are the: (a) relative magnitude of the dipole moments involved in the relaxation processes, that is μ_1 and μ_2 corresponding respectively to τ_1 and τ_2, since the dielectric loss is directly proportional to the square of the relevant dipole moment, (b) relative populations of the re-orienting species.

Since $C_1 \backsim C_2$, it follows that if only two forms are present and C_2 corresponds to the relaxation contribution from the chair forms with the low dipole moment, which is present to the extent of about 99%, then $\mu_1^2 \gg \mu_2^2$. This large C_1 contribution could result from the re-orientation of the appreciable COC or the CSC dipoles where the μ_{C-O} and μ_{C-S} bond moments are about 1.7 and 1.6D respectively and the COC and CSC angles of inclination to the mean plane of the carbon atoms in the chair forms are about 60° and 55° respectively. The normal boat form which involves eclipsed hydrogen atoms would seem unlikely whereas the transformation:

$$\text{skew boat} \rightleftharpoons \text{chair}$$

may be achieved by "rotation" about the C-S or C-O bonds without introducing interactions due to eclipsed hydrogen atoms, and such a transformation would be consistent with the C_1/C_2 ratio. Little is known of potential or free energy barriers relating to conformational changes in such heterocyclic six-membered ring compounds and no appropriate comparison can be made with the experimental free energy value of 2.6 kcal/mole. Such a comparison is desirable for a more definite identification that the τ_1 relaxation process is to be associated with a conformational change and that the transformation is of this type.

In conclusion, both dipole moment and the relaxation time data indicate the presence of more than one conformational isomer for 1,4-thioxan in the liquid state, in cyclohexane and nujol solutions. The dielectric data may be analysed in terms of two relaxation times - one corresponding with the re-orientation of the chair form (τ_2) while a strong candidate for the τ_1 value is an interconversion between two conformational isomers in equilibrium. The τ_2 value of 3×10^{-12} sec. and the τ_1 of 12×10^{-12} sec. by means of transition state theory lead to free energies of activation for these relaxation processes of 1.7 and 2.6 kcal/mole. respectively. Even if the relaxation time errors were of the order of ± 20%, the corresponding errors in the energy barriers would be only about ± 0.1 kcal/mole. This compares most favourably with the values quoted by other methods. The potential of this procedure in the study of suitable energy barriers between conformational isomers would seem considerable.

CHAPTER 4

RELAXATION PROCESSES OF SOME CYCLIC KETONES

Introduction

Introduction of trigonal atoms into alicyclic systems alters the torsional energies in their neighbourhood and reduces the number of non-bonded atom interactions, although many of the free energies of activation for conformational change in simple heterocycles are not very different from the corresponding values obtained with analogous carbocycles. However, measurements reported in Chapter 3 indicated the presence of a small amount of a polar species, namely a boat conformer, for 1,4-dioxan, 1,4-dithian and 1,4-thioxan.

Fairly large dipole moments (1.2 - 1.5D) have been reported for cyclohexane - 1,4-dione[53-56]. Higasi and co-workers[57] measured the dielectric absorption of this substance at microwave frequencies and calculated a moment of 0.43D. In view of these results it seemed worthwhile examining a series of cyclic ketones: cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone, by the microwave method.

Discussion

The apparent dipole moment evaluated by the microwave procedure at 25°C. when compared with that obtained by the Guggenheim approach, yields a discrepancy with cyclopentanone, the values being 2.78D and 2.87D respectively. Evaluation of the latter involved measurements on eight solutions and the dielectric constant determined by a heterodyne apparatus working at 1 Mc/sec., were then remeasured on another such apparatus working at 2 Mc/sec.. Similar measurements, using thiacyclohexane and tetrahydrofuran in cyclohexane solution at 25°C., have given values of 1.83D and 1.58D respectively by the microwave procedure, compared with 1.93 and 1.71D obtained using the Guggenheim method[58]. The moment of cyclopentanone obtained by the non-microwave method is in good agreement with the literature value of 2.84D in cyclohexane[43], as are those of thiacyclohexane and tetrahydrofuran for which literature values are 1.90 and 1.75D respectively in benzene solution. Inspection of the dipole moment values of cyclopentanone (Table 4.1) in cyclohexane at both 40 and 60°C. shows them to be the same as that obtained using Guggenheim method at 25°C.. Calderwood and Smyth[59] found the dipole moment of cyclohexanone to show a consistent increase from 2.86D at 1°C. to 2.97D at 60°C., however, these workers measured the pure liquid and the situation is not directly comparable with values obtained in dilute solution. Even so an increase in dipole moment with increasing temperature is not uncommon[47], and the constancy of the microwave value at 25°C., together with the non-zero distribution coefficient observed at 40 and 60°C., indicates that the discrepancy between the results of the two methods for cyclopentanone is valid.

Moments from the Halverstadt-Kumler[60] and Guggenheim[61] procedures are usually in good agreement and both involve an inadequate allowance for the atomic polarization. For the former the final equation is 3.1 where:

$$xR_D = P_A + P_E \qquad 4.1$$

Normally x is now arbitrarily taken to be one. If, however, an abnormally high atomic polarization was present and this procedure was followed, then if ${}_2P_\infty$ was not appreciably greater than R_D, the evaluated moment would be too large.

From the dipole moment values of cyclopentanone obtained by the Guggenheim and microwave methods and the calculated molar refraction, x is estimated to be about 1.5. This is exceptionally high and the maximum allowance made for x has usually been 1.15, and this has been only for systems which have been considered to have a large atomic polarization, such as alkylethers. Gent[62] from gas measurements reported an exceptionally high P_A for tetrahydrofuran and this was confirmed by Garg and Smyth[63] at a wavelength of 2.2mm.. The abnormally high atomic polarization contributions for five membered ring systems could be accounted for by a flexible ring, and as Smith[47] pointed out such systems lead to this kind of behaviour. Kilpatrick, Pitzer and Spitzer[64] have indicated the lack of rigidity in such molecules and have advanced the concept of restricted pseudo-rotation.

For cyclohexanone the moment of 2.94D is the same as that obtained by the non-microwave method in benzene solution at

Table 4.1 Static and High Frequency Dielectric Constant, Relaxation Times, Weight Contribution, Distribution Coefficient, Dipole Moment and Weight Fraction in Cyclohexane Solution for Four Cyclic Ketones.

Solute	$T^{o}C.$	W_2	ε_0	ε_∞	τ_1 slope	τ_0	τ_1	τ_2	C_1	α	μ_0
Cyclopentanone	25	0.00944	2.0964	2.023	5.4	4.4	7.0	2.6	0.50	0.06	2.77
		0.01149	2.1140	2.025	5.0	3.9	7.0	2.4	0.50	0.05	2.78
		0.01438	2.1403	2.028	6.1	3.9	6.7	2.4	0.40	0.04	2.78
	40	0.01437	2.1120	2.000	4.2	3.2	5.8	1.8	0.40	0.05	2.89
	60	0.01432	2.0655	1.965	4.3	2.9	4.9	1.5	0.44	0.05	2.88
Cyclohexanone	25	0.01241	2.1200	2.027	5.2	5.0	5.0	-	1.00	0.00	2.94
Cycloheptanone		0.01554	2.1265	2.034	5.7	5.1	5.1	-	1.00	0.00	2.80
Cyclooctanone		0.01919	2.1278	2.025	8.6	7.6	-	-	-	0.02	2.82

Table 4.2 Dielectric constant and Refractive Index.

Data for Cyclopentanone in Cyclohexane Solution at 25°C..

W_2 $\times 10^3$	ε 2Mc/s	ε 1Mc/s	n_D^2
0.0000	2.0163	2.0163	2.02658
0.991	2.0254	2.0275	2.02652
2.234	2.0385	2.0393	2.02691
3.427	2.0488	2.0483	2.02672
4.711	2.0570	2.0584	2.02672
5.954	2.0675	2.0693	2.02647
7.122	2.0777	2.0812	2.02677
9.585	2.0977	2.1013	2.02677
12.220	2.1229	2.1231	2.02672

μ = 2.87D (using the Smith correction[47]).

$20^oC.^{43}$. Cyclooctanone and cycloheptanone values of 2.82D and 2.80D are low in comparison with literature values[43] of 2.96 (benzene) and 3.07D (cyclohexane), indicating a high atomic polarization. Information regarding the flexibility of such ring systems will be discussed later in this chapter.

For molecules having relaxation times less than $\sim 4 \times 10^{-12}$ sec., the distribution of points on the Cole-Cole arc is such that they all lie on the low frequency side, and the τ_0, ϵ_∞ and α values obtained by computer analysis are less accurate than for molecules having two or more points on the high frequency side of the plot. Consequently the mean relaxation times for the cyclopentanone systems were evaluated from Eq. 1.37. These values are shorter than the corresponding $\tau_{1\,slope}$ values (Table 4.1) obtained from the initial slope of the ϵ' against $\epsilon''\omega$ plot suggesting a contribution to the dielectric absorption from a second relaxation process. Comparison of the relaxation time values in Table 4.1 suggests the cyclohexanone τ_0 is anomalously high, being of equal magnitude to that of cycloheptanone and suspiciously longer than the cyclopentanone τ_2 value. Gaumann and co-workers[65] have measured the dielectric absorption of all these ketones in the pure liquid state, and their results show cyclohexanone to have a longer relaxation time than cycloheptanone, they also reported zero distribution coefficients for all four cyclic ketones but since they measured pure liquids at radio-frequencies, this does not conflict with the small α values observed for cyclopentanone at more suitable frequencies.

Calderwood and Smyth measured cyclohexanone in the pure liquid state in the microwave region, and obtained a relaxation time of $\sim 12 \times 10^{-12}$ sec. at 20°C., and distribution coefficients of 0.1 at four temperatures. Corfield and Davies[66], at radio-frequencies, obtained the same relaxation time value and a zero distribution coefficient. However, a more realistic comparison is possible with the value of 6.5×10^{-12} sec. obtained by Whiffen and Thompson[67] for cyclohexanone in benzene at 20°C., in view of the difference in solvent and temperature, the agreement with the value of 5.0×10^{-12} sec. in cyclohexane at 25°C. (Table 4.1) is quite reasonable.

For cyclopentanone the dielectric data may be analysed into two relaxation times. The data of Holland and Smyth[26] at K and X bands, together with that of Garg and Smyth[63] at 2.2 mm. wavelength, in liquid tetrahydrofuran has also been analysed and the results are displayed in Table 4.3. Possible interpretations of the two relaxation times are (i) puckering of the ring with an associated re-orientation of the main dipole; (ii) re-orientation about a principal axis; (iii) rotation about all axes; (iv) some form of relaxation motion relating to the presence of aggregates of polar solute

Table 4.3 Comparison of Measured and Calculated Dielectric Constants and Losses for Liquid Tetrahydrofuran. Static Dielectric Constant, High Frequency Dielectric Constant, Relaxation Times and Weight Contributions are also listed.

T°C.	Frequency (Gc/sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}	ε_0	ε_∞	τ_1	τ_2	C_1
1	24.39	6.92	2.95	6.90	2.77	8.9	2.39	6.2	2.7	0.50
	9.313	8.32	1.44	8.43	1.54					
20	136.3	3.17	1.89	3.19	2.00	8.20	2.20	5.0	1.7	0.48
	24.39	6.91	2.14	6.85	2.24					
	9.313	7.87	1.13	7.92	1.14					
40	136.3	3.07	1.90	3.54	2.10					
	24.39	6.67	1.66	6.71	1.74	7.60	2.12	4.5	1.3	0.44
	9.313	7.30	0.81	7.43	0.84					

Table 4.4 Volumes (V) of Ellipsoidal Molecules and Ratio (Relaxation Time/V).

Solute	Solvent	$T°C$	$V Å^3$	τ/V	τ_1/V	τ_2/V
Pyrrole[74]	Cyclohexane	25	39	2.6	-	-
Furan[28]	-	20	39	3.5	-	-
Tetrahydrofuran	-	20	47	-	10.6	3.6
Thiophen[28]	Cyclohexane	20	50	4.1	-	-
Tetrahydrothiophen[58]	"	25	54	-	11.2	3.3
Cyclopentanone	"	25	57	-	12.0	4.2
Cyclohexanone	"	25	90	5.6	-	-
Cycloheptanone	"	25	106	4.8	-	-
Cyclooctanone	"	25	120	6.3	-	-
1,4-Thioxan	"	25	63	4.8	-	-
Piperidine[75]	"	25	63	4.3	-	-

(The τ/V values have been multiplied by 10^{14}.)

molecules.

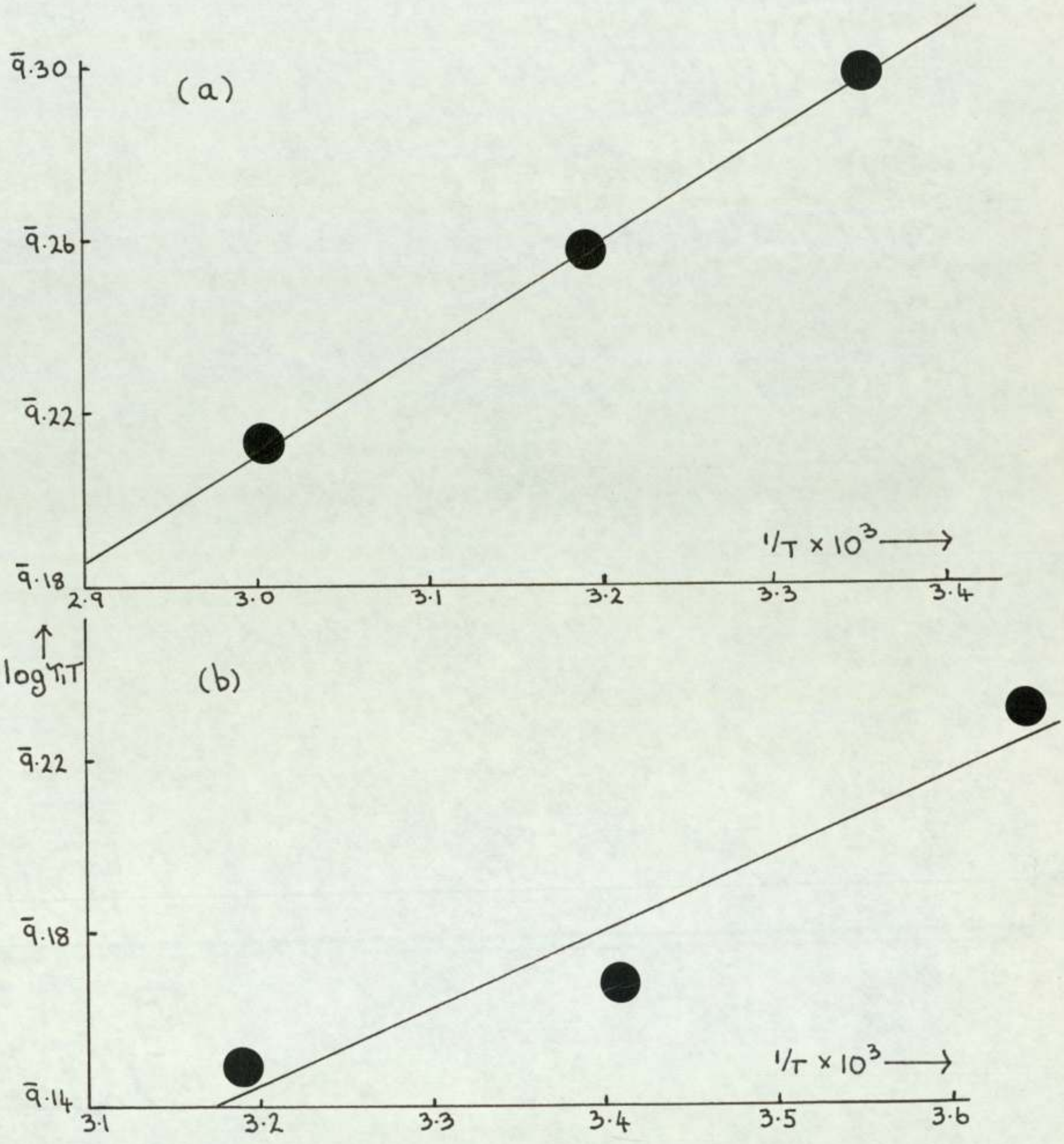
To identify the relaxation time which characterized (ii) or (iii) the relationship between the relaxation time and the volume of the molecule is considered. The Fischer equation (Eq. 2.1) may be expected to apply to molecules of similar shape and not differing substantially in size. The molecules in Table 4.4 fulfil this condition, and in dilute solutions of cyclohexane at constant temperature, η^{+} and f should be roughly constant. It, therefore, follows that the ratio (relaxation time/V) should be constant for motions of the types (ii) and (iii) and values of τ_2/v and τ_1/v have been tabulated. Klages and co-workers[68] have evaluated the lengths of the semiaxes and the values of V in Table 4.4 result from their estimations.

A feature of Table 4.4 is that the τ_2/v and τ/v are 3.9 ± 25% for all the molecules except cyclohexanone and cyclooctanone, whereas the τ_1/v relative to the τ/v values exhibit no consistent pattern. It would, therefore, seem that the relaxation time τ_2 is to be identified with (ii) or (iii). However, since pyrrole, furan and thiophen have the main dipole lying along a rotational axis, then according to the Perrin theory[40] only one relaxation time is expected. Thus, for nine of the solute molecules it would seem that τ and τ_2 are to be identified with (ii). The anomalous behaviour of cyclohexanone and cyclooctanone has been discussed and the latter having a non-zero distribution coefficient

Fig 4.1 PLOTS OF LOG T_1T AGAINST $1/T$

(a) CYCLOPENTANONE IN CYCLOHEXANE

(b) TETRAHYDROFURAN – PURE LIQUID



merits comment later in this chapter.

The possibility of (i) accounting for the relaxation time τ_1 is now examined. Pitzer and Donath[69] in pseudo-rotation studies calculated the energy barrier ΔV_{calc} to surmount on passing from the symmetrical Cs (envelope) form to the C_2 (half chair) and their values are compared with the $\Delta G_1^{\ddagger}$ and $\Delta H_1^{\ddagger}$ values, evaluated from equations 1.21 and 1.24 respectively, for cyclopentanone, tetrahydrofuran and thiacyclopentanone in Table 4.5.

Table 4.5

	$-\Delta V_{calc}$	$\Delta H_1^{\ddagger}$	$\Delta G_1^{\ddagger}$
Tetrahydrofuran	2.5	0.8	2.1
Thiacyclopentanone[58]	3.0	1.1	2.1
Cyclopentanone	2.4	1.2	2.2

The plots of log τ_1 T against $^1/T$ for tetrahydrofuran and cyclopentanone are shown in Fig. 4.1.

Unlike ΔV_{calc} the $\Delta H_1^{\ddagger}$ values are for thiacyclopentanone and cyclopentanone in cyclohexane solution and for tetrahydrofuran as the pure liquid. From the limited evidence available, such values appear to be less than those deduced from measurements in the gaseous state. In addition, a number of assumptions were made in the evaluation of ΔV_{calc}, and the approximation of taking the cyclopentane bond torsional angles for cyclopentanone and heterocyclic substances will tend to make the ΔV_{calc} values too large. The probable errors in this term were not quoted. For the $\Delta G_1^{\ddagger}$ values the accuracy should be ± 0.1 Kcal/mole., while the $\Delta H_1^{\ddagger}$ values would not be better than ± 0.5 Kcal/mole..

It would seem that the dipole moment evidence is in favour of a flexible ring system, for cyclopentanone and tetrahydrofuran, which would be in harmony with the presence of pseudo-rotation. However, the enthalpy of activation data in relation to the ΔV_{calc} values, are indecisive with regard to some form of restricted pseudo- rotation.

Case (iv) is now considered. The dipole moments of cyclopentanone, cyclohexanone and cycloheptanone are of the same order. Thus, it might be expected for a dissociative process the $\Delta H_1^{\ddagger}$ values for these molecules, of similar shape and size, would be similar. Since the latter two compounds have zero-distribution coefficients it is improbable that the τ_1 process of cyclopentanone is due to some form of dipole--dipole interaction. However, a τ_1 process for cyclohexanone and cycloheptanone, of similar magnitude to that for cyclopentanone, would not be sufficiently different from the molecular relaxation time, and a small or zero distribution coefficient would be observed.

Gaumann[65] in a radiofrequency study using pure liquids found the relaxation time of cyclooctanone to be high in comparison with other five-, six-, seven- and ten membered cyclic ketones, Table 4.1 and 4.4 show this to be true for these molecules in cyclohexane solution and the τ_1 slope is slightly greater than the τ_0 value, and like cyclopentanone the dipole moment obtained by the microwave method is lower than the literature value. However, attempts to analyse the data in terms of contributions from two relaxation processes failed to give values with any physical significance, although a small distribution coefficient of 0.02 was observed.

For a fairly wide range of pseudo-rotational arrangements of the cyclohexanone boat the potential energy does not vary much[70], however, the molecules are predominantly in the rigid chair conformation. The prefered conformations of cycloheptanone are twisted forms of the regular chair and the regular boat[70], both chair and boat are quite flexible and may undergo pseudo-rotation[71]. For cyclooctanone the situation is more complex, having nine possible forms, however, the existence of two interconvertible forms of about equal energy has been proposed[72,73].

Thus the moment of cyclohexanone, which is in agreement with the literature values, and those of cyclopentanone, cycloheptanone and cyclooctanone which show evidence of abnormal atomic polarization contributions, are in accordance with current theories regarding the conformation of such cyclic systems.

CHAPTER 5

RELAXATION PROCESSES OF SOME HALOETHANES IN CYCLOHEXANE SOLUTION

Introduction

Numerous techniques[52,76] have been employed in conformational studies of haloethanes with respect to the potential-energy barrier hindering rotation about the carbon--carbon axis. Reported barrier heights for 1,1-dichloroethane and lower barrier heights for 1,2-dichloroethane and 1,1,2-trichloroethane are 2.95, 3.41 and 2.87 kcal/mole. respectively[77]. If internal rotation i.e. a dipole switching from one equilibrium position to another, is considered as an intramolecular relaxation process, dielectric absorption studies in the microwave region would be suited, in principle at least, to detecting such a process for the low energy barriers. It seemed worthwhile making a dielectric investigation on haloethanes with this end in view and also a basic dielectric study of a number of small molecules of similar size and shape.

Discussion

The inaccuracy of computer analyses, for τ_0, α and ε_∞ when the mean relaxation time is less than $\sim 4 \times 10^{-12}$ sec., was mentioned in Chapter 4. For the results in this chapter the τ_0 and α values (Table 5.1) were determined by the $\frac{v}{u}$ method (Eq. 1.37) in the case of relaxation times less than 4×10^{-12} sec., and the remainder by computer analysis.

For molecules of similar shape and not differing substantially in size the Fischer equation (Eq. 2.1) may be

Table 5.1 Static Dielectric Constant, High Frequency Dielectric Constant, Relaxation Times, Distribution Coefficient, Dipole Moment and Weight Fraction of some Haloethanes in Cyclohexane Solution.

Solute	$T\,^\circ C$	W_2	ε_0	ε_∞	τ_0	$\tau_{1\,slope}$	α	μ_D
1,1-Dichloro-	25	0.01482	2.0661	2.016	3.6	5.7	0.18	1.98
		0.02151	2.0879	2.016	3.6	5.9	0.12	1.97
		0.03050	2.1174	2.016	3.6	5.8	0.18	1.98
1,1-Dibromo-	25	0.03169	2.0697	2.017	4.4	7.6	0.12	1.92
		0.04079	2.0854	2.017	4.2	7.5	0.14	1.93
		0.06909	2.1350	2.019	3.9	6.7	0.11	1.93
1,2-Dichloro-	25	0.05157	2.1120	2.030	2.5	4.2	0.10	1.36
		0.1014	2.1901	2.032	2.5	2.9	0.07	1.35
1,1,1-Trichloro-	25	0.03969	2.1010	2.016	3.2	6.4	0.12	1.83
		0.04241	2.1065	2.016	3.2	4.8	0.12	1.84
		0.05281	2.1303	2.017	3.2	4.8	0.10	1.83

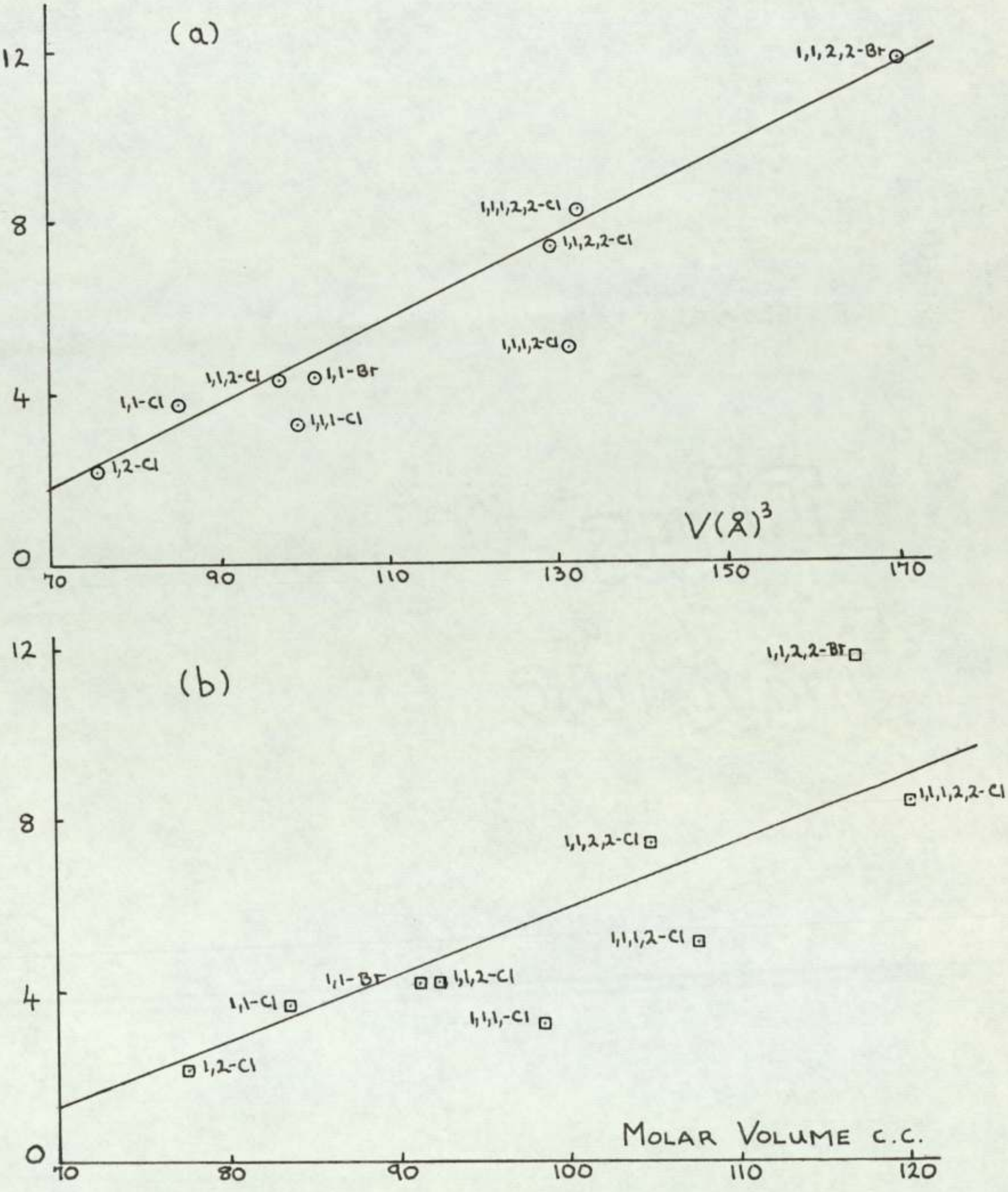
continued

Table 5.1 continued

Solute	T°C	W_2	ε_0	ε_∞	τ_0	τ_1 slope	α	μ_0
1,1,2-Trichloro-	25	0.06323	2.1090	2.026	4.2	4.9	0.06	1.44
		0.08175	2.1384	2.026	4.1	4.9	0.07	1.47
1,1,1,2-Tetrachloro-	25	0.1035	2.1464	2.036	5.0	5.6	0.00	1.45
1,1,2,2-Tetrachloro-	15	0.1089	2.2077	2.046	8.3	9.2	0.08	1.65
	25	0.1107	2.1842	2.034	7.3	8.1	0.05	1.64
	40	0.06416	2.0789	2.000	6.1	6.6	0.08	1.62
	40	0.1089	2.1418	2.009	6.2	6.5	0.04	1.62
	50	0.06416	2.0547	1.986	5.3	4.9	0.00	1.55
	50	0.1089	2.1180	1.994	5.4	5.7	0.02	1.60
Pentachloro-	25	0.1004	2.0734	2.028	9.0	8.5	0.00	1.04
		0.1918	2.1345	2.048	8.2	9.0	0.00	1.04
		0.2081	2.1489	2.054	8.4	8.7	0.00	1.04
1,1,2,2-Tetrabromo-	25	0.1778	2.1384	2.057	11.7	11.2	0.00	1.37

Fig 5.1 RELAXATION TIME – VOLUME PLOTS

FOR SOME HALOETHANES IN CYCLOHEXANE SOLUTION AT 25°C USING (a) MEASURED VOLUME (b) MOLAR VOLUME



expected to hold true. The molecules under discussion fulfil these conditions and in dilute cyclohexane at a constant temperature, η^{+} and f should be roughly constant, and a plot of relaxation time against volume estimated from Courtaulds models (Fig. 5.1a) should be at least approximately linear if molecular orientation is the sole process. By way of comparison, a similar plot (Fig. 5.1b) is made of relaxation time against molar volume and a slightly worse correlation results. However, both are reasonably linear though they are at variance with the Fischer equation in that the line does not pass through the origin. The deviations from the straight line observed for 1,1,1-trichloro- and 1,1,1,2-tetrachloroethane suggested that their relaxation times are short in comparison with the others.

Methylchloroform molecules are almost spherical in shape and such have been shown[78] to rotate with little displacement of the solvent molecules since the relaxation times tend to be independent of the macroscopic viscosity. Thus a shorter relaxation time than that predicted by comparison with other less spherical molecules is to be expected. However, the deviation of 1,1,1,2-tetrachloroethane from this plot is less readily explained since the dielectric data can be characterised solely by the molecular relaxation time. It may well be that since pentachloro-, 1,1,2,2-tetrachloro- and 1,1,2,2-tetrabromoethane exhibit the strongest hydrogen bonding interaction of the molecules examined, the slope of the straight line in Fig. 5.1a is too great, and since the volume of 1,1,1,2-tetrachloroethane, a relatively weak interactor[79], is similar to that of pentachloro- and 1,1,2,2-tetrachloroethane the relaxation time may appear too short.

Even when the Cole-Cole distribution parameter is not zero this does not necessarily indicate contributions from more than one relaxation process. An indication of a second process may sometimes be gained if the value of τ_1 slope is significantly greater than the mean relaxation time (τ_0) . The experimental results show that τ_0 and τ_1 slope are of a similar magnitude (Table 5.1), and apart from 1,1,1,2-tetrachloro- and 1,1,1-trichloroethane the relaxation time against volume plot reveals no significant deviation amongst those molecules. The non-zero distribution coefficients could be accounted for by:

(a) variation in local environment experienced by the solute molecules giving rise to a distribution of relaxation times for the single process of molecular reorientation.

(b) one process, for example molecular relaxation, is dominant and only a small contribution to the dielectric absorption is given by a second.

(c) a contribution from two relaxation times, of fairly similar magnitude.

Since pentachloro-, 1,1,2,2-tetrabromo- and 1,1,1,2-tetrachloroethane have distribution coefficients of zero then (a) is not generally acceptable. Case (c) is unlikely since the molecular relaxation times vary significantly over this series and it is improbable that the second relaxation process would exhibit parallel behaviour. It seems likely that a second relaxation time would be the result of some intra- or intermolecular process. From N.M.R. work it follows that of the molecules examined pentachloroethane would form the strongest intermolecular hydrogen bond but, as with chloroform[80] which forms slightly stronger intermolecular hydrogen bonds, the distribution coefficient is zero. Thus the most probable explanation for the non-zero distribution coefficients is an intramolecular process.

The molecules may be divided into two categories when considering internal rotation, namely those in which such a mechanism leads to energy barriers (V) brought about either by (i) eclipsed halogen atoms or (ii) by eclipsed halogen-hydrogen atoms. The molecules which fall into group (i) the 1,1,2,2-tetrabromo-, pentachloro- ($V = 9.01$ kcal/mole.) 1,1,1,2-tetrachloro- ($V = 6.02$ kcal/mole.) and 1,1,2,2-tetrachloroethane ($V = 6.21$ kcal/mole.) have potential energy barriers[77] too great for such a relaxation process to be detectable in the microwave region and all but the 1,1,2,2-tetrachloroethane have distribution coefficients of zero. Those in group (ii) have lower potential energy barriers and, providing the weight factor contribution is favourable, a detectable intramolecular process is to be expected for 1,1-dichloro-, 1,2-dichloro- and 1,1,2-trichloroethane, Table 5.1, shows that, for these molecules as opposed to those in group (i) the $\tau_{1\,\mathrm{slope}}$ is proportionately greater than τ_0. Analysis of their dielectric data into contributions from two relaxation times is not considered feasible since the values correspond to a wavelength absorption maximum around 8 mm., and as the 4 mm. band is by far the least accurate then estimation of ε_∞ is not sufficiently accurate for any subsequent type of Bergmann analysis Furthermore, another factor against resolution into two relaxation times is the likelihood that the weight factor for molecular relaxation is much greater than that for the intramolecular process since the $\tau_{1\,\mathrm{slope}}$ values are not appreciably longer than the mean relaxation time.

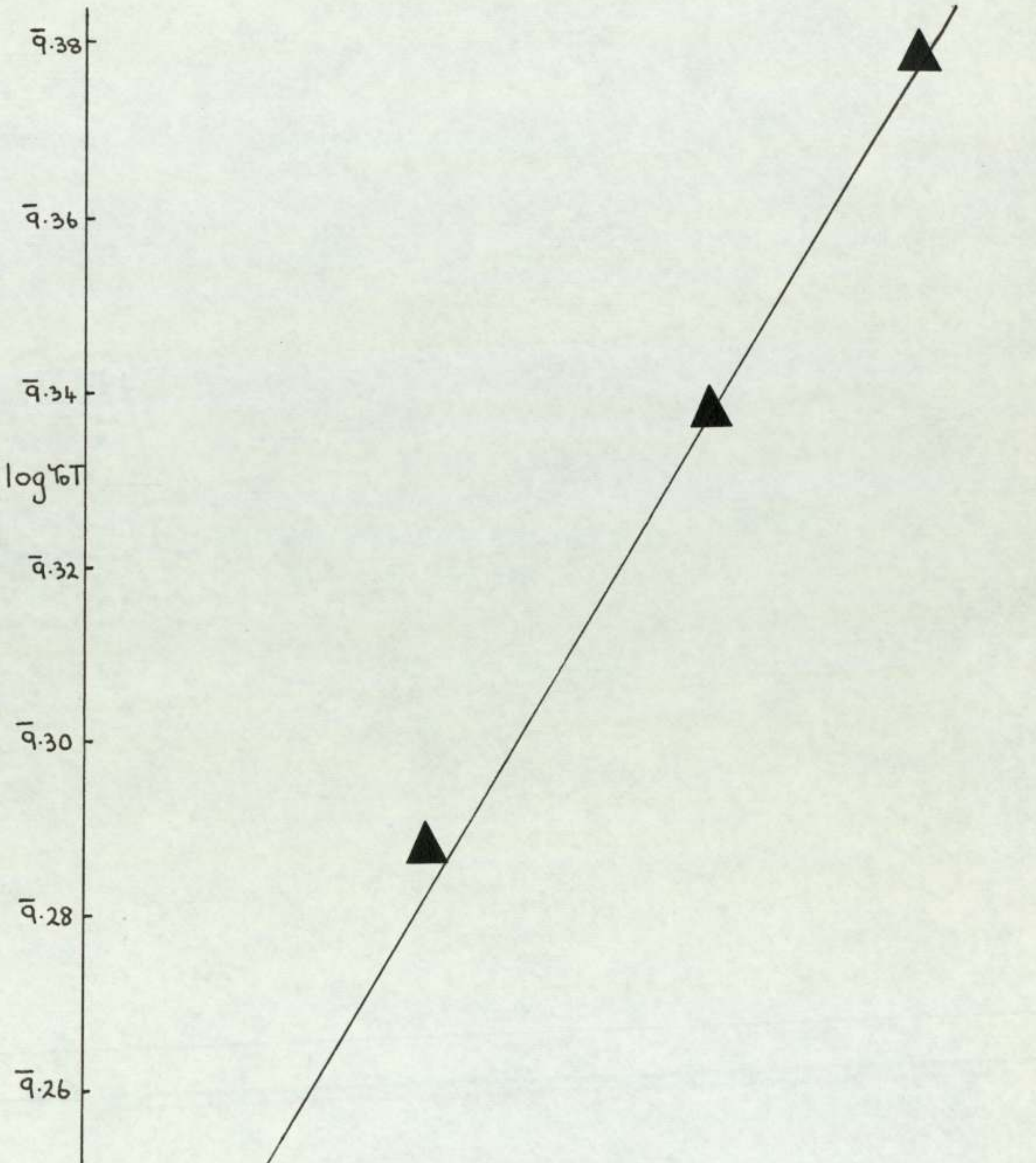
Methylchloroform differs from the other solute molecules in that it's dipole acts along the carbon-carbon axis, hence there can be no component of the moment normal to the axis about which the groups rotate. Thus an intramolecular relaxation process would not be anticipated unless some exceptional mechanism, such as oscillation of electric charge along the carbon-carbon bond occurred during intramolecular rotation. A more detailed investigation of this molecule by Smyth et al[78,81] has shown it to have distribution coefficients over a temperature range in n-heptane solution. With carbontetrachloride as solvent, however, the distribution coefficients of 0.10 and 0.07 observed at 2°C. and 20°C. respectively disappear at 40°C.. This type of behaviour would seem unlikely for an intramolecular process though not impossible.

The relaxation times, observed by these workers for methylchloroform, in n-heptane and carbontetrachloride solutions, and in the pure liquid of 2.4, 3.6 and 5.5 x 10^{-12}sec. respectively at 20°C., may be compared with the value in cyclohexane solution at 25°C. (Table 5.1) of 3.2 x 10^{-12}sec..

Though the mean relaxation time of 1,1,2,2-tetrachloroethane, which is 7.3 x 10^{-12} sec. at 25°C., is longer than that of 5.0 x 10^{-12}sec. for 1,1,1,2-tetrachloroethane - a molecule of similar size - a second relaxation process for the symmetrical molecule does not follow since in this case molecular interaction would be greater. In addition the distribution coefficient α is almost zero at 50°C. which indicates either τ_1 and τ_2 are of similar magnitude, or the contribution from one process approaches unity, at the higher temperature. However, the decrease in α with increase in temperature is often observed for molecules whose relaxation time is affected by weak intermolecular forces. The distribution of such molecules within the solvent may

Fig 5.2 PLOT OF LOG τ₀T AGAINST 1/T

– 1,1,2,2-TETRACHLOROETHANE IN CYCLOHEXANE



not average out sufficiently during the orientation process to give uniform environment to the solute molecules. A plot of log τ_0 T against 1/T for this molecule, at the greater concentration in cyclohexane solution, yields a good straight line (Fig 5.2) from which $\Delta H_0^{\ddagger}$ is found to be 1.6 kcal/mole.. Similar plots for toluene[51] (log τ_1 T) and chlorobenzene[82] have given $\Delta H_1^{\ddagger}$ values of 1.1 and 1.3 kcal/mole. respectively. However, these molecules are of a different shape to 1,1,2,2-tetrachloroethane, and the latter may be expected to exhibit stronger intermolecular bonds than the benzene derivatives. Thus, considering the errors on such $\Delta H^{\ddagger}$ values may be as great as ± 0.5 kcal/mole., the agreement is favourable and furnishes evidence for the 1,1,2,2-tetrachloroethane τ_0 value being the molecular relaxation time. Though the possibility of a second process of similar magnitude or one having a small value cannot be discounted.

The likelihood of detecting some intermolecular process involving the two equally protonic hydrogen atoms is not feasible since the corresponding bromo- compound which exhibits slightly stronger molecular interactions, is characterised by a single relaxation time.

Comparison of the dipole moment values with those given in the literature[43] is limited. Since only the value of 1.37D for 1,2-dichloroethane is given for cyclohexane as solvent. This compares favourably with our value of 1.35D.

In general, the apparent moment of the haloethanes seem to be highly solvent dependent. A comparison of values for three haloethanes whose dipole moment has been determined in several solvents is interesting (see Table 5.2).

Table 5.2 Dipole moments (in D) obtained by other workers in benzene(μ_B), carbontetrachloride (μ_{CCl_4}), n-hexane (μ_{Hx}) and in the gas phase (μ gas).

Solute	μ_{gas}	μ_{Hx}	μ_{CCl_4}	μ_B
1,2-dichloro-	1.28	1.37	1.56	1.77
1,1,2,2-tetrachloro-	1.37	1.45	1.85	1.95
1,1,1-trichloroethane	2.03	1.75	1.69	1.58

The moments of 1,2-dichloro- and 1,1,2,2-tetrachloroethane are greater in the more polarizable solvents carbontetrachloride and benzene and smaller in less polarizable solvents, such as n-hexane, and in the gas phase, whereas the reverse is true for 1,1,1-trichloroethane. With the 1,2-dichloro- and 1,1,2,2-tetrachloroethane both polar and non-polar conformations exist and it is well known that for 1,2-dichloroethane increases in temperature result in a larger proportion of the higher energy polar conformation thus increasing the dipole moment[83]. On the other hand the moment of 1,1,2,2-tetrachloroethane is almost temperature independent[84], and there is only one (stable) possible polar conformation of 1,1,1-trichloroethane. Thus for the latter two solute molecules at least it would appear that the solvent dependency of their dipole moments is not to be sought in a lowering of the potential energy barriers, but more in molecular interaction.

In conclusion the evidence indicates that pentachloro-, 1,1,2,2-tetrabromo-, 1,1,1,2-tetrachloro- and 1,1,2,2-tetrachloroethane provide no detectable contribution to the dielectric absorption from intramolecular relaxation and are to be contrasted with 1,1-dichloro-, 1,1-dibromo-, 1,2-dichloro- and 1,1,2-trichloroethane which appear to do so.

CHAPTER 6

RELAXATION PROCESSES OF SOME HALOETHANES IN p-XYLENE SOLUTION

Introduction

The results reported in the previous chapter, for the haloethanes in cyclohexane solution, indicated that for 1,1-dichloro-, 1,1-dibromo-, 1,2-dichloro- and 1,1,2-trichloroethane an intramolecular relaxation process contributed to their dielectric absorption. In addition there appears to be some evidence to suggest that the dipole moments of the haloethanes are dependent upon their environment, i.e. the state or solvent.

Proton magnetic resonance studies have shown that molecules of this type form weak intermolecular bonds with benzene, Schneider[85] considered, for molecules such as chloroform, that there is no specific interaction with the solvent, other than weak van der Waals and dipole interaction, if cyclohexane is employed. For his studies cyclohexane was regarded as an inert medium, and the linearity of the τ_0 against volume plot for the haloethanes in cyclohexane (Fig. 5.1) offers support to this supposition since the degree of interaction with the solvent would not be constant for these compounds. Alternatively, the π-electron clouds of molecules such as benzene and p-xylene offer a relatively exposed area of negative charge and molecules which may be regarded as electron acceptors are known to interact with benzene.

Antony and Smyth[80] have studied the dielectric absorption of chloroform in a variety of solvents. The mean relaxation times for chloroform in cyclohexane, carbon tetrachloride and benzene at 20°C. were reported to be 3.2, 5.0 and 7.1×10^{-12} sec., and it is apparent that the relaxation time is influenced by the electron donating capacity of the solvent. These workers pointed out the similarity between this behaviour and the shift in the -OH stretching frequencies of alcohols in these solvents. The association constant for chloroform - benzene and chloroform - dioxan complexes have been shown[86,87] to be about 1-2 mole fraction^{-1}, and thus the extreme sensitivity of relaxation times to molecular interaction is again illustrated (compare chapter 2).

Methlychloroform is the only one of the compounds studied in chapter 5 that has been measured by Smyth and his students[81], in dilute solution. For this spherical molecule and t-butylchloride, a molecule of similar shape and size, the mean relaxation times are almost independent of the macroscopic viscosity. However, the relaxation times of these molecules in carbontetrachloride solution are unexpectedly long and they have been explained in terms of local dipole-dipole interactions.

The haloethanes, especially 1,1,2,2-tetrachloro-, 1,1,2,2-tetrabromo- and pentachloroethane, might be expected to interact with benzene or p-xylene in a similar manner as chloroform. The microwave method gives rise to relaxation times and dipole moments, both of which are known to be sensitive to molecular interaction. Thus it was proposed to measure solutions of the haloethanes in p-xylene, and by comparison with the results using cyclohexane solution some insight into the intermolecular effects was anticipated. Furthermore, a lengthening of the molecular relaxation times for the haloethanes in p-xylene solution may yield additional information regarding an intramolecular relaxation process.

In their work with chloroform Antony and Smyth[80] detected a complex formed between chloroform and 1,4-diazobicyclo (2,2,2) octane, $N(CH_2CH_2)_3N$, and equimolar mixtures of the latter and the haloethanes have been measured in p-xylene solution.

Discussion

The results of the measurements using p-xylene solution are given in Table 6.1, and comparison with those obtained in cyclohexane solution (Table 5.1) reveal that 1,1,1,2-tetrachloroethane and pentachloroethane show zero distribution coefficients, and 1,1-dichloro-, 1,1-dibromo-, 1,2-dichloro-, 1,1,1-trichloro-, 1,1,2-trichloro and 1,1,2,2-tetrachloroethane show non-zero distribution coefficients, in both solvents. The results for 1,1,2,2-tetrabromoethane reveal non-zero distribution coefficients in p-xylene solution at 15, 25 and 37.5°C. and zero distribution coefficients at 50 and 25°C. in p-xylene and cyclohexane solutions respectively. For 1,1,2,2-tetrabromoethane in p-xylene solution

Table 6.1 Static Dielectric Constant, High Frequency Dielectric Constant, Relaxation Times, Distribution Coefficient Dipole Moment and Weight Fraction for some Haloethanes in p-Xylene Solution.

Solute	T°C.	W_2	ε_0	ε_∞	τ_0	τ_1 slope	α	μ_D
1,1-Dichloro-	25	0.03005	2.3871	2.281	4.9	6.6	0.04	1.82
+ D.B.O.		0.02912	2.3870	2.284	5.1	5.7	0.05	1.82
1,1-Dibromo-	25	0.05628	2.3782	2.273	6.8	8.6	0.06	1.82
1,2-Dichloro-	25	0.06529	2.4657	2.295	5.6	7.0	0.08	1.56
+ D.B.O.		0.03447	2.3780	2.290	5.2	5.8	0.06	1.54
1,1,1-Trichloro-	25	0.04265	2.3600	2.268	4.2	5.0	0.05	1.65
+ D.B.O.		0.04725	2.3833	2.274	4.5	6.3	0.10	1.71
1,1,2-Trichloro-	25	0.06869	2.4040	2.277	8.5	9.7	0.07	1.53
+ D.B.O.		0.05220	2.3814	2.283	9.7	9.0	0.03	1.45
1,1,1,2-Tetrachloro-	25	0.1379	2.4814	2.300	10.7	11.4	0.00	1.44
+ D.B.O.		0.07332	2.3910	2.276	10.7	8.9	0.13	1.56
1,1,2,2-Tetrachloro-	25	0.1133	2.5182	2.273	16.7	19.0	0.11	1.85
+ D.B.O.		0.06164	2.4071	2.276	17.6	18.6	0.16	1.84
Pentachloro-	25	0.2726	2.4948	2.298	18.2	19.4	0.00	1.17
+ D.B.O.		0.1191	2.3887	2.300	25.1	25.0	0.00	1.19
1,1,2,2-Tetrabromo-	15	0.1614	2.4411	2.305	29.7	28.1	0.06	1.62
	25	0.1643	2.4178	2.287	27.5	25.2	0.08	1.63
	37.5	0.1633	2.3825	2.272	19.4	19.5	0.03	1.50
	50	0.1619	2.3489	2.250	17.2	17.1	0.00	1.66

at 15, 25 and 37.5°C. analyses yielded results with little or no physical significance, and it is concluded that the non-zero distribution coefficients are probably brought about by variations of local environment experienced by the re-orientating solute molecules.

The relaxation time for pentachloroethane in p-xylene is considerably longer than in cyclohexane solution and the later discussion will confirm that this compound is much more likely to be involved in an intermolecular process than 1,1-dichloro-, 1,1-dibromo- and 1,1,2-trichloroethane. Both pentachloroethane in p-xylene and chloroform in benzene show zero distribution coefficients and relaxation times which may be attributed to molecular re-orientation. Thus it would seem unlikely that the di- and trisubstituted compounds would exhibit an intermolecular relaxation process. Furthermore, because of the relatively small dipole moment and long relaxation time for pentachloroethane, a process other than molecular re-orientation would be more readily detected.

It appears that the non-zero distribution coefficients for the symmetrical tetrahaloethanes are not related to contributions from more than one relaxation process i.e. molecular re-orientation. Thus the zero distribution coefficients for 1,1,1,2-tetra- and pentachloro- ethane, together with the absence of any reasonable analyses for the symmetrical tetrahaloethanes, all of which have potential energy barriers[77] to internal rotation too great to be detected in this region, suggests that the distribution coefficients observed for the remaining compounds might be related to an intramolecular relaxation process.

Higasi, Bergmann and Smyth[88] have analysed the dielectric constant and loss data for sixteen n-alkylbromides, in the pure liquid state at three microwave frequencies, in terms of a distribution of relaxation times between two limiting values. The lower short relaxation times were relatively independent of molecular size and were accordingly attributed to an intramolecular relaxation process i.e. rotation of the $-CH_2Br$ group about the carbon-carbon bond. For pure liquid ethylbromide at 25°C. they obtained a short relaxation time of 1.8×10^{-12} sec.. For the di- and trisubstituted ethanes a short relaxation time (τ_2) of this magnitude would lead to smaller τ_1/τ_2 ratios, where τ_1 is the molecular relaxation time, in cyclohexane compared with p-xylene solution, and small or zero distribution coefficients would be anticipated for the cyclohexane solutions. However, the α values in cyclohexane are greater than in p-xylene solution and consequently cast some doubt on an intramolecular relaxation process as the sole explanation of the distribution coefficients.

The molecular dipole in methylchloroform acts along the carbon-carbon axis and there can be no component of this moment normal to the axis about which the groups rotate. Consequently, as it was pointed out in chapter 5, an intramolecular relaxation process for this molecule could only be envisaged if a mechanism such as a mesomeric shift of charge along the carbon-carbon bond were involved. The dipole moments of chloroform and methylchloroform in the gaseous state are about 1.0 and 1.8D respectively[43], which suggest that the $-CH_3$ group moment supports the $-CCl_3$ group moment. Similarly, the dipole moments of 1,1-dichloroethane and dichloromethane, in the gas phase, are 2.07 and 1.60D respectively[43]. Smyth[1] has indicated that the above discrepancies are due to an increased shift of electronic charge in the direction of the negative ends of the molecular dipoles for the ethane derivatives. Hurdis and Smyth[89] have described this behaviour in terms of resonance or hyperconjugation, though Smyth[1] has pointed out that these assumptions based on the above dipole moments are extremely arbitary. The magnitude of the distribution coefficients for 1,1,1-trichloroethane suggest that a contribution from a second process (C_2) would be in the region of 0.6 to 0.8. For an oscillation of charge mechanism then from $C_1/C_2 = \mu_1^2/\mu_2^2$, where μ_1 is the molecular dipole moment, μ_2, which would relate the order of magnitude of a mesomeric moment, would be about 1-1.3D. Such a value is considerably larger than anticipated for a mesomeric moment in a molecule of this kind, and values for aromatic compounds rarely exceed 1D.

In conclusion, at this stage, it would appear that the distribution coefficients reported for the haloethanes probably arise from variations in local environment experienced by these molecules during molecular re-orientation. This is supported by the zero distribution coefficients for 1,1,1-trichloro-, 1,1,2,2-tetrachloro- and 1,1,2,2-tetrabromoethane at higher temperatures. However, by analogy with the n-alkylbromides, a contribution from an intramolecular process to the dielectric absorption for 1,1-dichloro-, 1,1-dibromo-, 1,2-dichloro- and 1,1,2-trichloroethane would not be unreasonable.

The mean relaxation times and apparent dipole moments of the haloethanes in cyclohexane and p-xylene are given in Table 6.2, from which, and by comparison with the results in Table 6.1, several interesting points are readily apparent.

(i) The mean relaxation times for all the haloethanes in p-xylene solution are not appreciably lengthened by the addition of 1,4-diazobicyclo (2,2,2) octane - D.B.O.-, whereas chloroform has been shown to complex with D.B.O.[80]. The results for the haloethane - D.B.O. mixtures indicate that the former are more readily attracted to the solvent, which is present in a large excess. It would have been desirable to measure the pure liquids with D.B.O. and mixtures of these in cyclohexane solution. Unfortunately the apparatus is not

Table 6.2 Mean Relaxation Times and Dipole Moments for some Haloethanes in Cyclohexane and p-Xylene Solution at 25°C..

Solute	τ_0		$\frac{\tau_{0\,p\text{-}xyl}}{\tau_{0\,cyc}}$	μ		$\Delta\mu$
	Cyc	p-Xyl		Cyc	p-Xyl	p-Xyl-Cyc
1,1-Dichloro-	3.6	4.9	1.36	1.98	1.82	-0.16
1,1-Dibromo-	4.2	6.8	1.62	1.93	1.82	-0.11
1,2-Dichloro-	2.5	5.6	2.24	1.36	1.56	0.20
1,1,1-Trichloro-	3.2	4.2	1.30	1.83	1.65	-0.18
1,1,2-Trichloro-	4.2	8.5	2.03	1.46	1.53	0.07
1,1,1,2-Tetrachloro-	5.0	10.7	2.14	1.45	1.56†	0.11
1,1,2,2-Tetrachloro-	7.3	16.7	2.29	1.62	1.85	0.23
1,1,2,2-Tetrabromo-	11.7	27.5	2.35	1.37	1.63	0.26
Pentachloro-	8.3	18.2	2.20	1.04	1.17	0.13

† p-xylene - D.B.O. value.

Table 6.3 Dipole Moments (in D) for the Haloethanes obtained by Other Workers in Benzene (μ_B), Carbontetrachloride (μ_{CCl_4}), n-Hexane (μ_{Hx}), n-Heptane (μ_{Hp}) and in the Gas Phase (μ_{gas}).

Solute	μ_{gas}	μ_{Hx}	μ_{Hp}	μ_{CCl_4}	μ_B
1,1-Dichloro-	2.07-2.63	-	-	1.80	1.80-2.00
1,1-Dibromo-	-	-	-	-	2.14
1,2-Dichloro-	1.28	1.37	1.42	1.50	1.78
1,1,1-Trichloro-	1.79 2.03	1.75	-	-	1.58
1,1,2-Trichloro-	1.42	-	-	1.15	1.55
1,1,1,2-Tetrachloro-	-	-	-	1.20	1.20
1,1,2,2-Tetrachloro-	1.29-1.37	1.45	-	1.85	1.70-1.95
1,1,2,2-Tetrabromo-	-	1.30	-	-	-
Pentachloroethane	0.92	-	-	-	1.00

applicable to measurements of pure polar liquids, and D.B.O. is only sparingly soluble in cyclohexane.

(ii) From the τ_o p-xyl/τ_o cyc ratio's it is evident that all the haloethanes are weakly bonded to p-xylene, and thus the energy required for the molecular re-orientation process is increased, compared with cyclohexane. In addition the interaction varies throughout the series, the compounds which are α -substituted only having the smallest ratio's.

(iii) The dipole moment differences ($\Delta\mu = \mu_{p\text{-}xyl} - \mu_{cyc}$) are not consistent in sign. However, all the α -substituted compounds show a negative $\Delta\mu$ compared with a positive value for all the α,β-substituted compounds.

Thus the interaction between the haloethanes and p-xylene is manifested by their dipole moments and relaxation times.

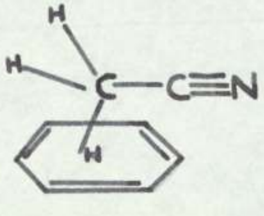
In order that the dipole moments may be compared with values obtained by other workers, a list of literature values[43], for a variety of solvents, are given in Table 6.3. From Tables 6.2 and 6.3 it would appear that the dipole moments of the haloethanes are related to the electron donating power or dielectric constant of the medium. For 1,1-dichloro-, 1,1-dibromo- and 1,1,1-trichloroethane the moments decrease with increased electron donor capacity, or dielectric constant, of the solvent, whilst the reverse is true for the remaining compounds.

The energy of a dipole is known to decrease with increased dielectric constant of the medium containing it. Thus for the symmetrical molecules, which may exist in non-polar and polar conformations, (trans and gauche), the energy of the gauche form will be decreased in p-xylene compared with it's value in cyclohexane, whereas the energy of the trans form will be the same. By this argument the energy difference between the two forms will be decreased and a larger proportion of the polar form might be anticipated in p-xylene solution. However, increasing temperature will have a similar effect but the dipole moment of 1,1,2,2-tetrachloroethane, in the gas phase, is almost independent of temperature[84], and the $\Delta\mu$ value for this compound is not likely to be related to an increased proportion of the gauche form. Alternatively, the potential energy barrier to internal rotation is much smaller for 1,2-dichloroethane and it's dipole moment increases with increasing temperature, and the positive value for this compound may be partially due to an increased amount of the gauche form. Pentachloro- and 1,1,1,2-tetrachloroethane have only one stable (polar) conformation and they show positive $\Delta\mu$ values, whereas 1,1-dichloro-, 1,1-dibromo- and 1,1,1-trichloroethane, molecules which also have only one stable conformation, show negative $\Delta\mu$ values. It would appear therefore that the $\Delta\mu$ values are related to inter- rather than intramolecular effects.

Numerous attempts[47] have been made to account for the variation of molecular dipole moments with the nature of the solvent, and deviations of these from their values in the gas phase, even when molecular association is known to be absent. Several equations have been derived to relate the above behaviour purely in terms of the dielectric constant. However, these equations fail to predict a positive solvent effect. More rigorous treatments have related these effects to the shape of the solute and solvent molecules and the location of the molecular dipole within the former.

Hruska, Bock and Schaefer[90] measured the proton resonance shifts for cis and trans dichloroethylene in a variety of solvents, and explained anomalous results in terms of the variations in molecular shape. For the haloethanes molecular models show no correlation between the shape and the $\Delta\mu$ values, or the former and the degree of interaction.

For the chloroform it is generally accepted that the molecule approaches a phenyl ring, along the sixfold axis and above the ring plane of the latter, with the chlorine atoms directed away from the aromatic ring[91]. Schneider[85] has proposed that for acetonitrile interaction with benzene leads to the following configuration.



Models have been constructed for the haloethanes and p-xylene involving both the above types of configuration, although the situation is complicated by the rotating dipoles, and the direction of the molecular dipoles with respect to the phenyl ring, have been estimated. From which it is evident that the angles for 1,1,1-trichloro- and 1,1-dichloroethane are smallest and largest respectively and again there is no obvious relationship with either the $\Delta\mu$ or the τ_0 p-xyl/τ_0 cyc values.

In an attempt to relate the $\Delta\mu$ values to the degree of interaction, which is given by the τ_0 p-xyl/τ_0 cyc ratio, a plot of $\Delta\mu/\mu$ cyc against τ_0 p-xyl/τ_0 cyc is enlightening. The plot (Fig. 6.1) reveals a relationship, between these two values, for all the haloethanes which have been measured. In view of the errors in both parameters the excellence of this curve, which embraces all nine points, is remarkable, and indicates that the $\Delta\mu$ values are related to the degree of interaction.

The plot shows that the bromoethanes interact more strongly than the corresponding chloro compounds. This is not unexpected and is in agreement with N.M.R.[92] measurements of the haloforms, which have shown the spectral shifts for $CHCl_3$ to be less than for $CHBr_3$ although this is contrary to enthalpy of association data[93]. N.M.R. spectrum of 1,1-dichloro-, 1,1-dibromo- and 1,1,2-trichloroethane in

FIG 6.1 PLOT OF $\Delta\mu/\mu_{cyc}$ AGAINST $\tau_{op\text{-}xyl}/\tau_{ocyc}$. FOR SOME HALOETHANES

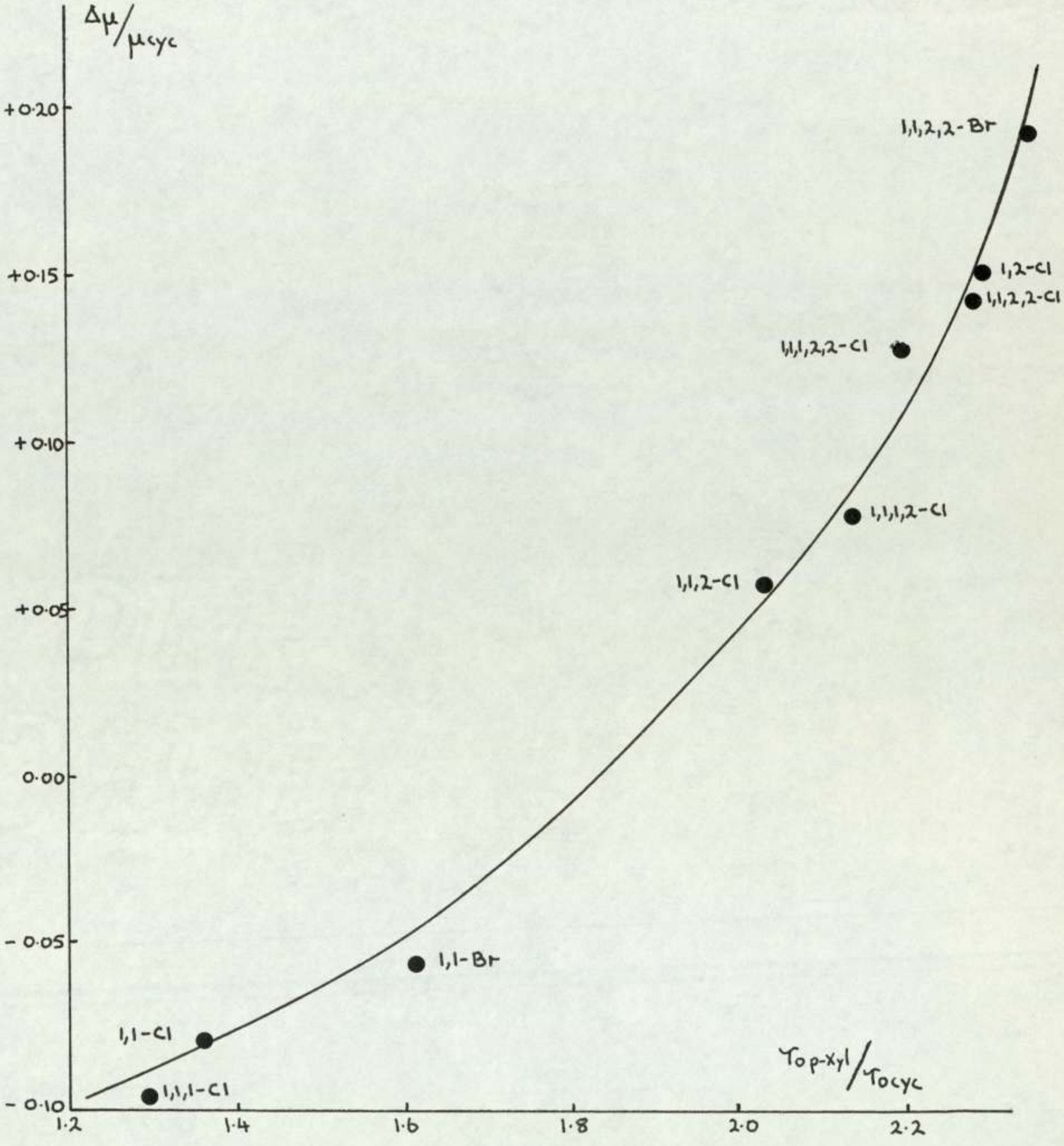
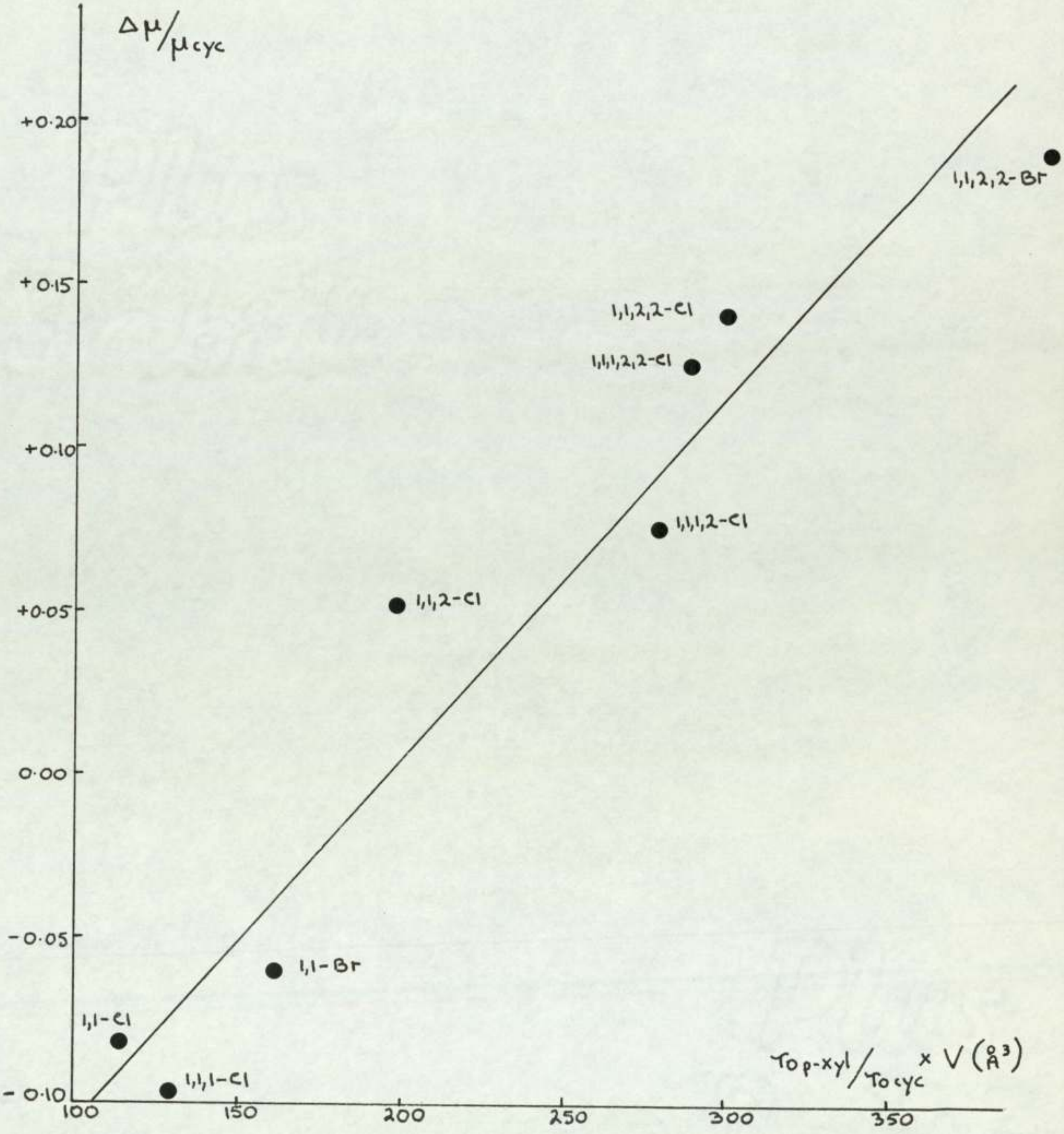


FIG 6.2 PLOT OF $\Delta\mu/\mu_{cyc}$ AGAINST $\tau_{o\,pxyl}/\tau_{o\,cyc} \times V$

FOR SOME HALOETHANES



cyclohexane and p-xylene solutions have been obtained and the difference between the chemical shifts in the two solvents ($\Delta\delta$) were obtained. The $\Delta\delta$ values for the hydrogen atoms attached to the carbon bonded to the halogen atoms were greater than those for the other hydrogens. This would indicate that the group containing the single hydrogen atom is bonded to the phenyl ring, and suggests that the degree of interaction is related to the inductive effect of the chlorine atoms and the protonic character of the hydrogen atoms. Such an explanation is supported by the weak interaction of 1,1,1-trichloroethane. The two equally protonic hydrogen atoms of the symmetrical tetrahaloethanes would account for the slightly stronger interaction for these two compared with pentachloroethane, which has a greater halogen: hydrogen ratio. The relatively weak interaction for 1,1-dichloroethane compared with pentachloroethane, and the larger $\tau_{\text{p-xyl}}/\tau_{\text{cyc}}$ ratio for 1,1,1,2-tetrachloroethane compared with 1,1,2-trichloroethane suggest that the inductive effects within these molecules are not confined to each group.

The position of 1,2-dichloroethane on the curve (Fig. 6.1) is anomalous, since it would be anticipated that the degree of interaction for this molecule with p-xylene would be similar to that for the other dihaloethanes. In addition N.M.R. measurements showed that the association of

1,2-dichloroethane with p-xylene was less than for 1,1,2-trichloroethane.

From a study employing proton magnetic resonance techniques, Schneider[85] considered that, for polar alkyl-X and vinyl-X molecules, the magnitude of the interactions with benzene were dependent upon the molecular volumes, which determine the mean distance of approach, and that the molecular shape had very little influence. In view of this a plot of $\Delta\mu/\mu_{\text{cyc}}$ against $\tau_0\,\text{p-xyl}/\tau_0\,\text{cyc} \times V$, where V is the measured volume (Fig. 5.1), was made and is shown in Fig. 6.2. The plot reveals an approximately linear relationship and the deviations from the curve are not unreasonable in view of the additional errors brought about by the measured volumes. The $\tau_0\,\text{p-xyl}/\tau_0\,\text{cyc} \times V$ value for 1,2-dichloroethane ($175\ \text{Å}^3$) compares favourably with the others on the basis of the inductive effects within the molecules. However, the $\Delta\mu$ value for this compound remains anomalously large. Mizushima and co-workers[94,95] have found that the energy difference between the polar gauche and the non-polar trans forms of 1,2-dichloroethane is less in solution than in the gas phase. Furthermore the dipole moment of this molecule in the liquid phase is less dependent upon temperature than is the value in the gas phase, which would indicate a lower barrier height and greater proportion of the higher energy polar form in solution[96]. This behaviour has been attributed to electrostatic forces in solution and the effect is most pronounced with solvents such as benzene and toluene[97]. Thus, as it was indicated earlier in the discussion, the anomalous $\Delta\mu$ value for 1,2-dichloroethane may be due to a lowering of the barrier height, and the apparently large τ_0 p-xyl/$\tau_0$cyc ratio can be attributed to it's relatively small volume.

The dipole moments of benzotrichloride and the monohalobenzenes in the gas phase are about 0.3D greater than in solutions, and inspection of the literature values in various solvents reveals that they decrease with increasing dielectric constant. For the haloethanes under discussion it would seem reasonable to suggest that the molecular dipole moments are smaller in p-xylene than in cyclohexane solution at 25°C., by about 0.2D (Fig. 6.1). The measured moments in the former might then show an increase in the former solvent due to an induced-dipole, the magnitude of which is determined by the degree of interaction with p-xylene, which is itself determined by the molecular volume and the protonic character of the hydrogen atoms within the molecule.

CHAPTER 7

DIPOLE MOMENTS AND RELAXATION PROCESSES OF SOME SYMMETRICAL ALKYLBENZENES

Introduction

It was mentioned in chapter 1 that when p-xylene has been employed as a solvent the dielectric loss of the solution required a correction for the absorption of the solvent. The magnitude of this absorption was shown in Table 3.2, from which it is apparent that the maximum loss for p-xylene at 25°C. would be observed at frequencies greater than that of Q-band. Thus a relaxation time, much shorter than would be anticipated for molecular re-orientation, of a similar magnitude to that reported by Whiffen[48] for a number of other non-polar compounds, is indicated.

Whiffen found that the loss of benzene-carbontetrachloride mixtures increased linearly with frequency between 10 and 0.8 cm. wavelength, and estimated dipole moments to be 0.04 - 0.10D, and relaxation times about 10^{-12} sec.. It was suggested that the absorption results from the dipole moments induced in collisions between molecules, giving rise to an out-of-phase component of the polarization or a dielectric loss, and that the induced dipole will change direction not by rotation of the molecule containing it, but because of a new distortion produced at another instant by another neighbour. The plots of loss tangent against frequency suggested Debye behaviour and a relaxation time of the order of the time between collisions in a liquid.

Similar behaviour has been reported for other non-polar compounds such as carbontetrachloride, n-heptane, carbon disulphide and carbon dioxide in both liquid[98] and gaseous[99] states. The gaseous measurements show that the absorption is proportional to the square of the gas density, and may result from the temporary dipole moments induced in collisions between molecules. Alternatively, the absorption may be regarded as a transition between states of different translational energies of the colliding molecules[100], and such translational spectra have been observed in the far infrared down to the region of 20 cm.$^{-1}$. [101]

In view of this information it is interesting to compare the static dielectric constant (ε_0) with the square of the refractive index (n_D^2) for a number of non-polar compounds[102].

Table 7.1 Static Dielectric Constant and Refractive Index for some Non-Polar Compounds at 20°C..

Hydrocarbon	ε_0	n_D^2	$\varepsilon_0 - n_D^2$
Benzene	2.284	2.253	0.031
p-Xylene	2.270	2.237	0.033
Mesitylene	2.283	2.240	0.043
p-Cymene	2.243	2.223	0.020
Cyclohexane	2.023	2.034	-0.011
n-Heptane	1.924	1.926	-0.002
n-Hexane	1.890	1.890	0.000

For the aromatic compounds the difference ($\varepsilon_0 - n_D^2$) is too great to be attributed to experimental error, and in view of the agreement between ε_0 and n_D^2 for the aliphatic compounds these results suggest that the aromatic molecules might absorb in the microwave region.

DiCarlo and Smyth[103] have measured the dielectric constant and loss at 1.25 and 3.22 cm., the static dielectric constant and the refractive index of several symmetrical molecules. For benzene the dielectric loss at 1.25 cm. was about 0.003 at 25°C. and the results for hexamethylbenzene indicated that this molecule may have a small dipole moment.

The microwave method is well suited to the detection and estimation of small permanent dipole moments. In this frequency region, the dielectric constant ε' of a polar liquid decreases with increasing frequency, and the dielectric loss changes from a small value through a maximum to a small value again. Converseley, if the molecule is non-polar the dielectric constant is essentially independent of frequency, and the dielectric loss is very nearly zero. An added advantage of measurement at microwave frequencies is that, unlike classical methods of determining dipole moments, no approximation for the atomic polarization is involved.

It was proposed to use the microwave method to measure possible dipole moments and relaxation times of some symmetrical molecules, and since the absorption reported for benzene might cast some doubt on the intramolecular relaxation process, suggested to explain the short relaxation time which contributes to the dielectric absorption, for some monoalkylbenzenes[51], the emphasis was placed on symmetrically substituted alkylbenzenes.

Discussion

The errors involved in the dielectric constant for low-loss solutions are such that Cole-Cole plots are difficult to formulate, and it is more realistic to discuss the absorption in terms of the dielectric loss. However, the data obtained for the pure liquids at 25°C. were analysed by the computer method, for τ_0 , α and ϵ_∞ , the results are shown in Table 7.2 together with the dipole moments calculated from Eq. 1.40. The close agreement between the ϵ_∞ values and n_D^2 for these liquids bears out the analyses, and the non-zero distribution coefficients are reassuring.

At this juncture it is pertinent to mention the purification of the compounds used, in order to eliminate the possibility of the absorption being attributed to small amounts of polar impurities. Special attention was paid to ensuring that the compounds were absolutely dry. The liquids were treated with sulphuric acid to remove sulphur compounds, and after preliminary drying with magnesium sulphate, the liquids were stood over phosphorous pentoxide for 24 hours before refluxing and distilling from sodium, the distillates were stored over sodium wire in amber bottles. In the course of their projects several other workers found it necessary to measure p-xylene, and in all cases the absorption, using different samples, was found to be similar to that reported in this thesis. Furthermore, the relaxation times of benzene and p-xylene are too short to be attributed to impurity, and the absorptions are of such a magnitude that relatively large proportions of polar hydrocarbons would be required.

The Debye equation as used by Jackson and Powles[104], Heston and Smyth[105] and DiCarlo and Smyth[103] and given in Eq. 7.1 was used in the interpretation of theloss measurements in terms of dipole moments, Table 7.3.

$$\mu^2 = \frac{27kT\varepsilon''\left[1+(\omega\tau)^2\right]}{4\pi Nc(\varepsilon_1+2)^2\omega\tau} \qquad 7.1$$

where μ is the permanent dipole moment ε_1 is the dielectric constant, T is the absolute temperature, k is the Boltzmann constant, ω is the angular frequency, τ is the relaxation time, N is the Avogadro number, c is the number of moles of solute per c.c. of solution and ε'' is the dielectric loss. For durene and hexamethybenzene the loss of the solvent, mesitylene, has been subtracted from the loss for the solution.

In calculating dipole moments using Eq. 7.1 it has been

Table 7.2 Static Dielectric Constant, High Frequency Dielectric Constant, Mean Relaxation Time, Distribution Coefficient and Weight Fraction for some Symmetrically Substituted Alkylbenzenes.

(Hexamethylbenzene and Durene were measured in Mesitylene solution.)

Solute	$T^{\circ}C$	W_2	ε_0	ε_∞	τ_0	α	μ_D
Benzene	25	1.0000	2.2776	2.256	0.7	0.00	0.13
p-Xylene	25	1.0000	2.2627	2.250	2.1	0.00	0.11
Mesitylene	25	1.0000	2.2746	2.234	6.3	0.00	0.21
p-Cymene	25	1.0000	2.2444	2.224	2.7	0.02	0.16
Hexamethylbenzene	60	0.1260	2.2367	-	-	-	-
Durene	60	0.4300	2.2385	-	-	-	-

Table 7.3 Dielectric Loss and Dipole Moment for some Symmetrically Substituted Alkylbenzenes. The Pure Liquids were Measured at 25°C., Durene and Hexamethylbenzene were Dissolved in Mesitylene and Measured at 60°C..
(μ_a and μ_b were calculated from Eq. 7.1 using relaxation times of 2.0 and 5.0 x 10^{-12} sec. respectively.)

				Frequency (G.c./sec.)			
Solute	ε_0	W_2		70.00	35.09	23.98	9.313
Benzene	2.2776	1.000	ε''	0.00594	0.00350	0.00250	0.00028
			μ_a	0.10	0.08	0.08	0.05
			μ_b	0.11	0.07	0.06	0.03
p-Xylene	2.2627	1.000	ε''	0.00629	0.00540	0.00368	0.00218
			μ_a	0.12	0.12	0.11	0.11
			μ_b	0.13	0.10	0.09	0.09
p-Cymene	2.2444	1.000	ε''	0.00711	0.00760	0.00595	0.00467
			μ_a	0.15	0.16	0.15	0.17
			μ_b	0.16	0.14	0.13	0.15

Table 7.3 continued

Solute	ε_0	w_2		Frequency (G.c./sec.)			
				70.00	35.09	23.98	9.313
Mesitylene	2.2746	1.000	ε''	0.00741	0.00744	0.00644	0.00337
			μ_a	0.14	0.15	0.14	0.14
			μ_b	0.15	0.13	0.12	0.12
Durene	2.2385	0.430	ε''	0.00394	0.00303	0.00420	0.00343
			μ_a	0.17	0.16	0.18	0.22
			μ_b	0.18	0.14	0.16	0.20
Hexamethylbenzene	2.2367	0.126	ε''	0.00039	0.00000	0.00152	0.00105
			μ_a	0.11	0.00	0.23	0.25
			μ_b	0.12	0.00	0.21	0.23

found that the values are relatively insensitive to the choice of relaxation time, and for the results in Table 7.3 values of 2.0 and 5.0^{-12} sec. were used in each case. The agreement between the dipole moments listed in Tables 7.2 and 7.3 is reasonably good, and for benzene the values in Table 7.3 compare favourably with those of 0.06 and 0.02D calculated from the results of DiCarlo and Smyth at 1.25 and 3.22 cm. respectively, using a relaxation time of 5.0×10^{-12} sec..

A more critical appraisal of the results, and an indication of the respective relaxation times, may be obtained by inspection of the ϵ'' against log ω plots, Fig. 7.1. These plots exemplify the errors especially for the very low-loss durene and hexamethylbenzene solutions, and indicate that the relaxation times increase with increased size of molecule and polarizability. The plots of ϵ'' against log ω for p-xylene and mesitylene at different temperatures suggest that the relaxation times are not detectably dependent on temperature. For benzene the results may be compared with those obtained by Whiffen, DiCarlo and Smyth at 20 and 25°C. respectively, the ϵ'' against log ω plot shows the agreement between the three sets of results to be remarkably good, and indicates the validity of the values. The broken line curves on these plots were obtained from calculated ϵ'' values evaluated from Eq. 7.1 by substitution of dipole

Fig 7.1 Plots of ε'' against Log ω

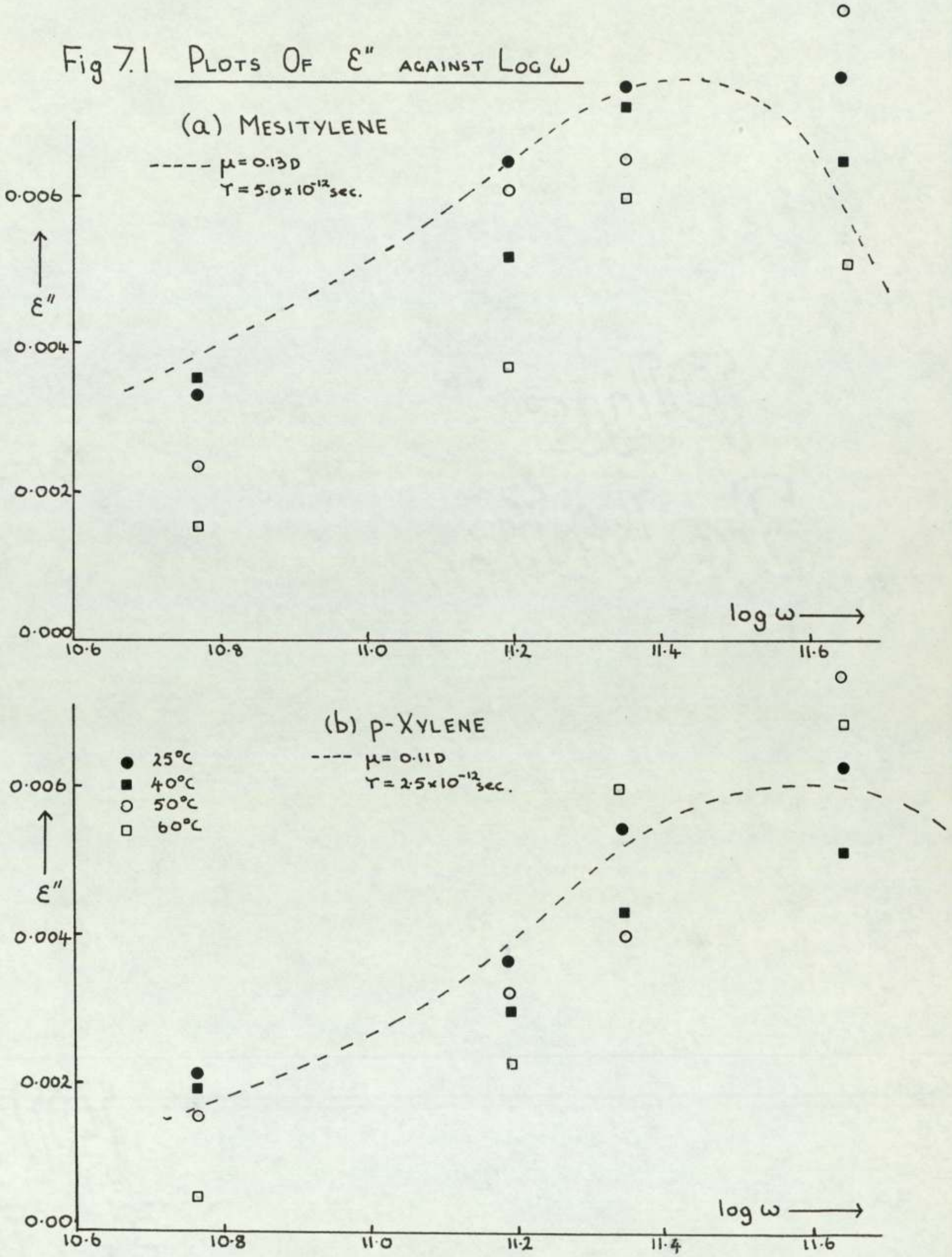
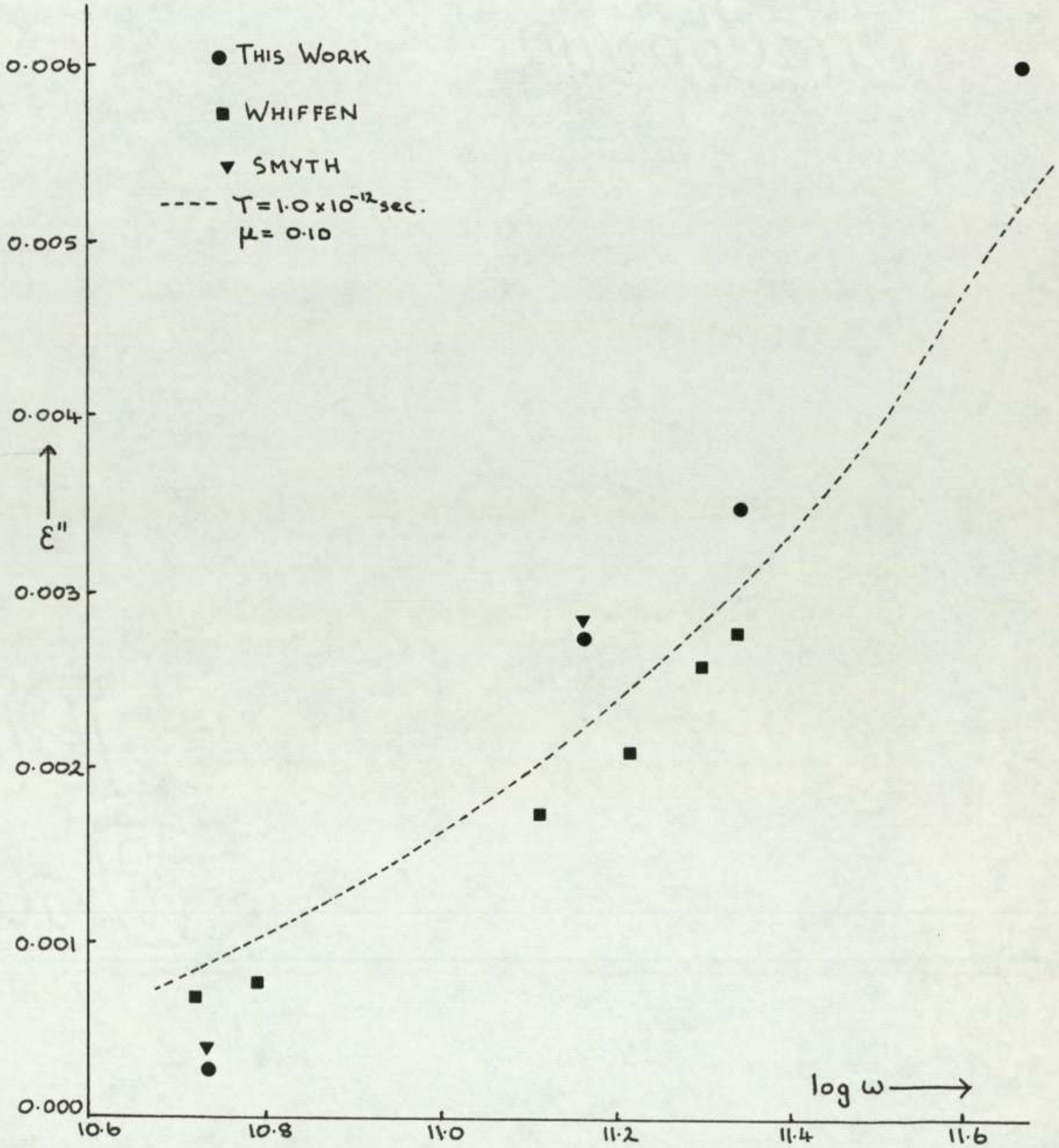
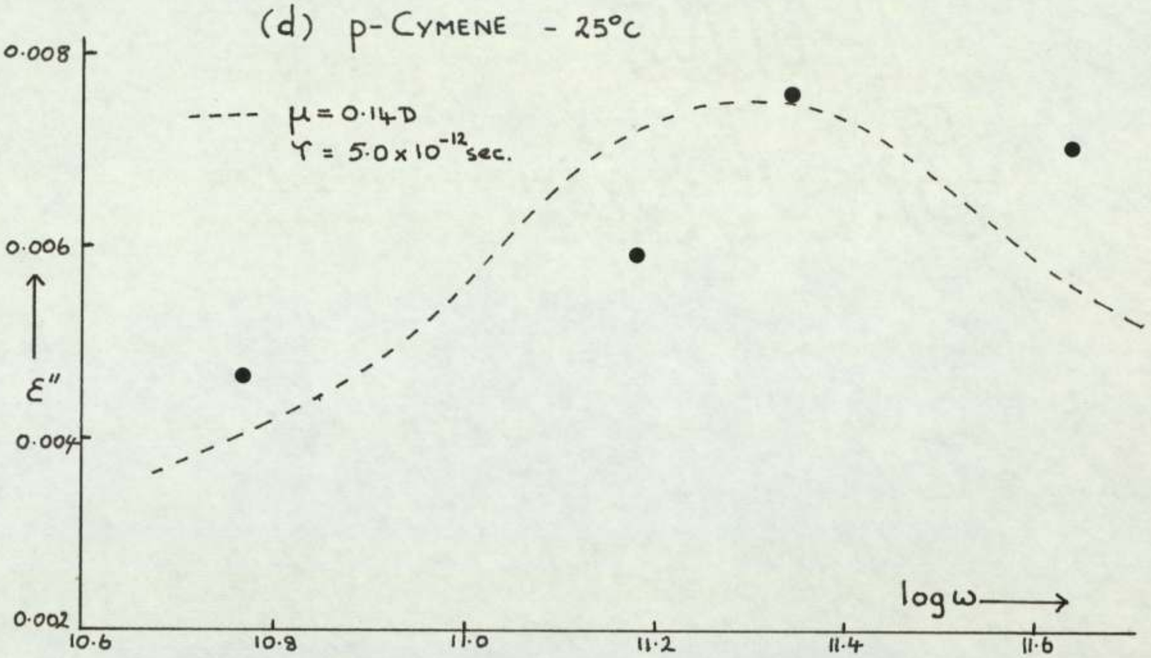
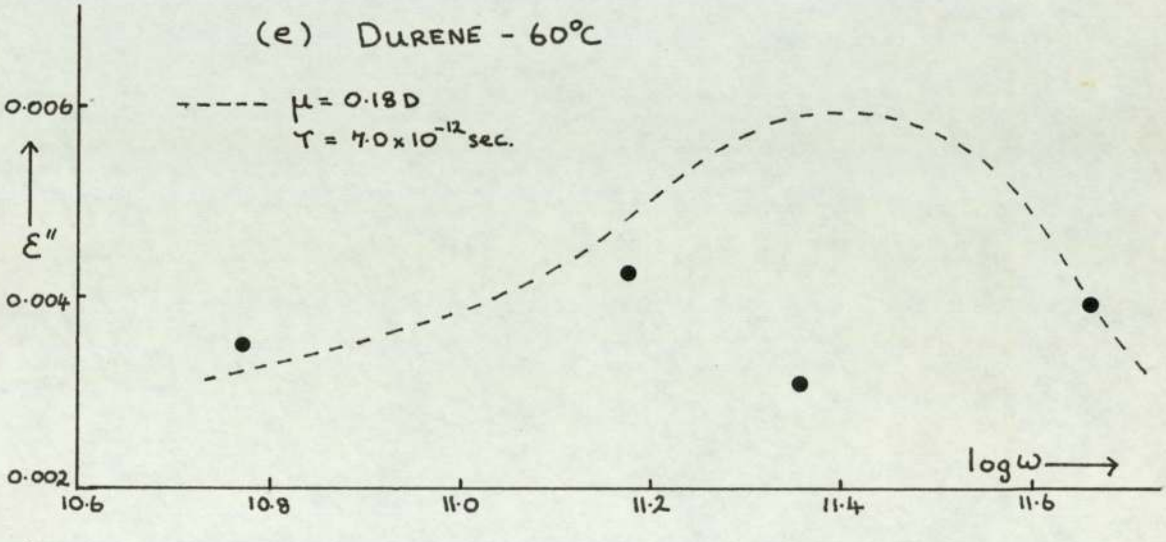
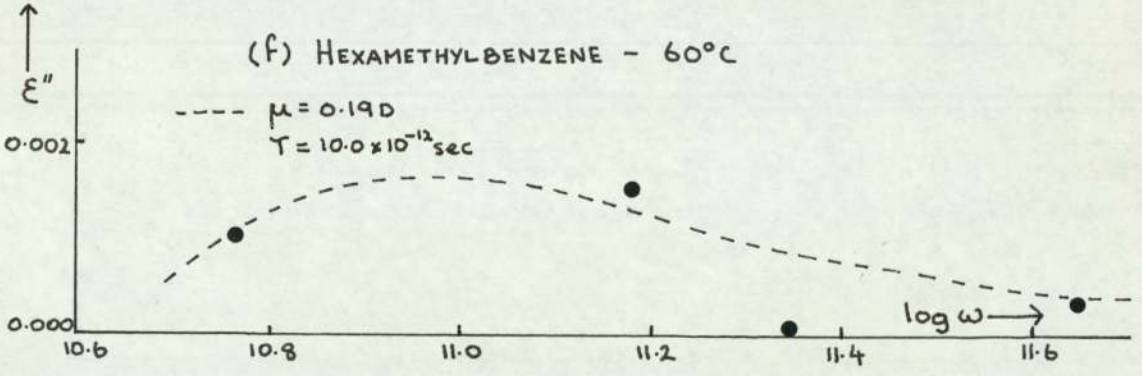


Fig 7.1(G) BENZENE




(d) p-Cymene - 25°C


(e) Durene - 60°C


(f) Hexamethylbenzene - 60°C

moments and relaxation times giving ε'' values comparable with the experimental points for the frequencies employed. These curves show reasonable agreement with the experimental points and suggest relaxation times of about 1.0, 2.5, 5.0, 5.0, 7.0 and 10.0 x 10^{-12} sec. for benzene, p-xylene, p-cymene, mesitylene, durene and hexamethylbenzene respectively at 25°C., which is consistent with the previously suggested trend for the relaxation times of these molecules.

The molecular relaxation times of toluene[51] and bromobenzene[22], in cyclohexane solution, at 25°C. are known to be $\sim$ 9.0 x 10^{-12}sec.. Such molecules are of the same shape but of smaller volume than all of the symmetrical alkylbenzenes. However, the relaxation times of p-xylene, p-cymene, mesitylene and durene are shorter than 10.0 x 10^{-12} sec.. In addition, the mean relaxation times of t-butylbenzene, in the pure liquid, and benzotrichloride, in cyclohexane solution, are $\sim$ 20 and 23.5 x 10^{-12} sec. respectively and are much longer that that obtained for p-cymene (5.0 x 10^{-12} sec.) a molecule of similar size as these monosubstituted molecules.

Whiffen and Thompson[67] have measured the dielectric absorption for p-cymene over a range of temperatures and calculated, using a dipole moment of 0.19D, relaxation times of 11.0 and 8.0 x 10^{-12} sec. at 10 and 30°C. respectively. These values were obtained from measurements at one microwave frequency, and though they are somewhat longer than the relaxation time obtained in this thesis, $\sim 5 \times 10^{-12}$ sec., the values are again much shorter than would be anticipated for molecular re-orientation.

The dielectric data for several monoalkylbenzenes have been analysed in terms of contribution from two relaxation processes, one attributed to molecular re-orientation and a short relaxation time process[51]. One possible explanation appeared to be intramolecular rotation about the alkyl-aryl bond due to rapid movement of charge to and fro between the alkyl group and the π-electron cloud of the phenyl group with an associated change in mesomeric moment. However, the absorption for benzene and hexamethylbenzene suggests that such a process is not responsible for the relaxation times obtained for the symmetrical molecules, since benzene is not substituted and the energy barrier to methyl group rotation for hexamethylbenzene (3 - 7 kcal/mole.)[106] is appreciably greater than the 0.5 kcal/mole. for toluene[107].

Whiffen considered the possibility that the loss tangents are the long wavelength tails of vibrational absorption bands. However, the absorption for these symmetrical molecules seem to be too strong to be accounted for by such tails. Furthermore the ε'' against $\log\omega$ plots, Fig. 7.1, show maximum in the loss well before the infrared frequencies, and since the line breadths of the infrared bands increase with temperature, the results for p-xylene and mesitylene are also inconsistent with such a picture.

It is interesting to consider the absorption for the symmetrical molecules in terms of intermolecular forces, such as a rate process connected with the dissociation of one molecule from an aggregate. Dipole-dipole and dipole-induced dipole forces would not normally be expected to contribute to the total attractive forces between non-polar molecules, since the calculation of such forces requires a dipole moment term. However, if individual group moments, such as a C-H dipole of 0.4D, are considered then these forces may be estimated. For the monoalkylbenzenes, all having moments $\sim$0.4D, such values are of the order of 0.1 kcal/mole[51]. The relaxation times for the symmetrical molecules correspond to free energies of activation in the region of 1.5 - 2.5 kcal/mole.. Thus it seems unlikely that dipolar forces alone could be responsible for the absorption.

In order to explain the fact that non-polar molecules readily condense from gas to liquid, and that they can be solidified, processes which require attractive forces between molecules, it is necessary to describe the electron cloud of a non-polar molecule as not being spherically symmetrical at any one instant. Thus a non-polar molecule will have an instantaneous dipole which results in attractive dipole-induced dipole interactions with surrounding molecules.

Such forces are known as London dispersion energies. The instantaneous dissymmetry is related to the ease of ionization, and they are independent of temperature[3].

London dispersion energies can be estimated from the equation:

$$E_L = -\frac{3}{4} \cdot \frac{\alpha^2}{r^6} \cdot I \qquad 7.2$$

where α is the polarizability, I the ionization potential and r the distance between a pair of isotropic molecules. Substitution of reasonable values of r, an ionization energy of 10 ev., and values of α (Table 7.4) taken from a list of the principal polarizabilities evaluated by Le Fèvre and LeFèvre[108], for some non-polar compounds gives the E_L values listed in Table 7.4. Also listed are estimates of the cohesive energies (ΔE^{v}_{298}) obtained from Hildebrand's equations, Eq. 3.5, and the intermolecular distance (r') at which the London dispersion energy equals the cohesive energy.

The van der Waals radii of the methyl and phenyl groups are 2.0 and 1.8°A respectively, i.e. about $r'/2$ in Table 7.4. Thus the London dispersion forces are the predominating factor in the attractive forces between the symmetrically substituted alkylbenzenes. However, if London dispersion forces were responsible for the observed relaxation times, then cyclohexane might be expected to show an absorption of

Table 7.4 Comparison of Estimated Cohesive Energies and Values of Dispersion Energies (in kcal/mole.) for Three Intermolecular Distances. The Value of r' is the Value of the Intermolecular Distance at which the London Dispersion Energy Equals the Cohesive Energy.

			E_L			
	$10^{23}\alpha$ cm^3	ΔE^{v}_{298}	3Å	4Å	5Å	r'Å
Benzene	0.947	7.3	23.1	4.1	1.1	3.6
p-Xylene	1.363	9.6	44.1	7.8	2.1	3.8
Mesitylene	1.546	10.7	56.8	10.1	2.6	3.9
Hexamethylbenzene	2.069	15.0	101.6	18.0	4.8	4.1
Cyclohexane	1.070	7.3	24.8	5.1	1.3	3.7

a similar magnitude to that observed for benzene. Cyclohexane has been measured, using the bridge method, and was found to have a negligible loss factor (< 0.0001) at all the frequencies available. Whiffen[48] and Penrose[109] have reported tanδ values equivalent to loss factors of about 0.0002 at 1.4 cm. wavelength compared with their respective values of 0.0018 and 0.0009 for benzene at the same frequency.

The possibility that the observed dipole moments arise from transient dipoles brought about by collisions between molecules provides a more favourable interpretation of the results.

For a non-polar molecule containing highly polar bonds, such as C-Cl in carbontetrachloride, a relatively small distortion could produce small temporary dipole moments, and for carbontetrachloride if one C-Cl bond were at an angle of only 6° from it's equilibrium position a moment of 0.1D would result, which is the order of magnitude observed for this molecule[48]. However, the aromatic C-H and C-CH_3 bond moments are only 0.4 and $\sim$ 0.8D respectively, and thus a relatively large distortion of such bonds from their planar configuration, with respect to the nucleus, would be required to account for the moments reported in Table 7.3. Le Fèvre and Le Fèvre[110] suggested that a dipole moment is able to induce a moment in liquid benzene 0.4 times it's own value, and Whiffen[48] considered that a suitable arrangement of C-H bonds, each having a moment of 0.4D, might induce a moment of 0.1D. However the $C-CH_3$ bond moment in aromatic compounds is $\sim$ 0.8D and yet the moment of p-xylene is similar to that for benzene (Table 7.2 and 7.3) which is inconsistent with the above explanation.

In a more recent paper Whiffen suggested that if suitably orientated in collision a pair of non-polar molecules may possess a dipole moment as a result of their mutual interactions, such as that between the quadrupole moment of one molecule and the polarizability of the other[111].

Thus on the basis of such a mechanism it might be expected that the observed moments for the symmetrical molecules would increase with increased polarizability. This is consistent with the observed values (in Table 7.3) increasing along the series benzene, p-xylene, mesitylene, and hexamethylbenzene for which Le Fevre and Le Fevre have given polarizability values of 0.947, 1.363, 1.546 and 2.069×10^{-23} cm.^{3} respectively. However, as previously mentioned, the polarizability of cyclohexane is slightly greater than benzene and might be expected to show an absorption of similar magnitude. It may be possible to explain the negligible absorption for cyclohexane, and the relative orders of the dipole moments for the symmetrical benzene molecules, if the molecular anisotropies of the colliding molecules are considered. The principle polarizabilities, b_1, b_2 and b_3, of the molecules are listed in Table 7.5 and refer to the polarizability axes illustrated in Fig. 7.2.

Table 7.5 Specification of Molecular Polarizability Ellipsoids (cm.^{3}) - Le Fevre and Le Fevre[108].

Molecule	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{23}\left[\frac{b_1+b_2}{2}-b_3\right]$
Cyclohexane	1.117	1.117	0.975	0.142
Benzene	1.114	1.114	0.733	0.381
p-xylene	1.613	1.402	1.075	0.433
Mesitylene	1.696	1.696	1.247	0.439
Hexamethylbenzene	2.263	2.263	1.681	0.582

These polarizabilities (b_1, b_2 and b_3) will be the net moments induced in their respective directions by local electric fields. For a pair of, non-polar, colliding molecules the latter will contain a contribution from the electric quadrupole fields.

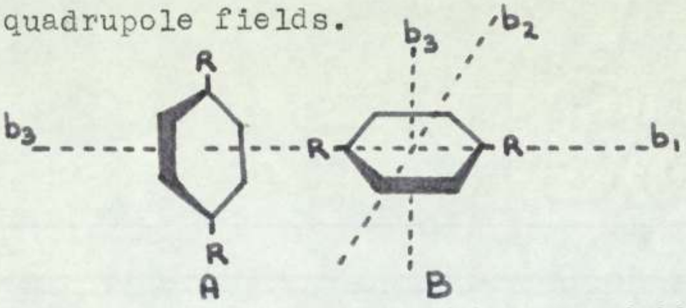
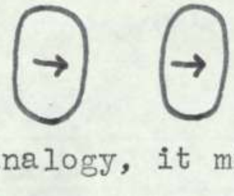


Fig 7.2

Consider a molecule approaching a neighbour, as illustrated in Fig. 7.2 which is the most favourable configuration for a quadrupole-quadrupole interaction[112], involving interaction between b_3 for molecule A and b_1 or b_2, for molecule B. Then, if the induced moment is related to the difference between b_1 or b_2, and b_3 i.e. the anisotropy of polarizability, the last column in Table 7.5 might give some indication of the order of the moments for the different molecules. The b values show cyclohexane to be almost symmetrical with respect to the polarizability, and the values of $\left[b_1+b_2/2 - b_3\right]$ show the same trend as the dipole moment values in Table 7.3 and Fig.7.1. This type of hypothesis is not without precedence, and similar treatments have been employed in equations constructed to account for the effect of solvent on dipole moments. Sugden[113] derrived an equation relating the orientation polarization of a solute in various media, and included a small constant which varies with solvent and solute. For benzene this constant proves to be large, which infers an induced moment, and this has been attributed to the difference between b_1 (and b_2) and b_3, similar conclusions result from a different approach to the subject given by Weigle[114]. Such a description would explain the absorption reported for n-heptane[48,98], which is of similar magnitude as that for benzene, since the straight chain will have a greater polarizability along its length than across its section. However, on this basis carbontetrachloride would be expected to have a zero moment since for this molecule $b_1 = b_2 = b_3$. There is some suggestion that carbontetrachloride may have a small anisotropy due to distortion of the tetrahedral structure[3], and it has already been suggested that only small distortions of the C-Cl bonds are required to account for the observed absorption.

Satisfactory quantitative interpretations of the pure rotational spectrum of hydrogen have been obtained, based on the assumption that the transition moments are induced by the quadrupole fields of the hydrogen molecules[115,116]. Far infrared spectrum of compressed nitrogen[117] and carbon dioxide[118] have been explained in terms of electric dipole moments induced in collisions. Thus the absorption of non-polar liquids at microwave frequencies might be similarly explained, and Buckingham and Pople[119] have suggested that such molecules may possess a dipole moment induced by the quadrupole moments of adjacent molecules. These authors pointed out that the non-spherical shape of a "polar" molecule should influence the absorption, and an increase would be expected for "plate like" molecules[120]:



Thus, by analogy, it might be reasonable to assume a greater absorption, from this type of alignment, for the planar benzenes than for the almost spherical cyclohexane. In addition, planar and linear molecules having a centre of symmetry, such as benzene and acetylene, have a quadrupole moment, whereas tetrahedral molecules such as methane do not have a quadrupole moment. Therefore, it is anticipated that the planar benzene molecule would have a greater quadrupole moment than cyclohexane.

Theoretical estimates of quadrupole moments are not readily obtained because of the various factors which must be considered. However, experimentally determined quadrupole moments have been reported for some di- and triatomic molecules[121,122]. Maryott and Birnbaum[121] have measured the dielectric loss, by a resonant cavity technique, for several compressed gases, and they attributed the loss to transient dipoles induced by the molecular quadrupole fields during molecular collisions. These workers have reported polarizabilities (α) of 4.27 and 4.44 x 10^{-24}cm^3, and quadrupole moments (Q) of 2.6 and $< 0.3 \times 10^{-26}$e.s.u. for ethylene and ethane respectively, and by comparison it would not be unreasonable to suggest that the quadrupole moment of benzene would be greater than for cyclohexane, and that the value for the latter would be small. The quantitative expression of the quadrupole moment is given by[3]:

$$Q = \sum e_i r_i^2 \qquad 7.3$$

where e_i represents an individual charge at a distance from the centre of mass of the molecule, the summations are taken over all the charges present. Thus, it is expected that for the symmetrical benzene molecules, Q will increase with increasing number of methyl groups since the summation will contain more terms. Furthermore, Buckingham and Pople[119,120] have shown that the induced dipole moment of a molecular pair averaged over all orientation of the quadrupole fields, is proportional to the square of the quadrupole moment and the polarizability. However it follows from Eq. 7.3 that quadrupole moments will be smaller than dipole moments, by a factor of 10^8, and consequently the magnitude of the former would seem to be insufficient to account for the loss factors and dipole moments given in Table 7.3.

A further point of interest arises from measurements of the Kerr constant for benzene at high pressures[123]. Such results have been interpreted to suggest an anisotropic deformation of the π-electrons resulting in an increased polarizability in the plane of the ring and a decrease perpendicular to it.

The short relaxation times for all the symmetrical molecules, with the possible exception of benzene, can be explained if the moment arises only as a result of an exact configuration of the neighbouring molecules, and these are changing at such a rate as to have disappeared before molecular re-orientation can take place. Thus as Whiffen[48] pointed out: "The new direction of the dipole moment may be random in any direction with respect to the earlier one, except that in the presence of an electric field (F) each dipole moment (μ) will have a probability, $e^{-\mu F \cos\theta / kT}$, of being aligned at an angle θ to the applied field. - At a measuring field frequency comparable to the time required to establish the induced moment, the field will change direction before the full polarization is set up and so dispersion and absorption will be present at these frequencies."

Such a collision picture may also be used to explain the indication the the relaxation times, for the symmetrical benzenes, increase with increased size of molecule (see Fig. 7.1) and are apparently independent of temperature.

The number of collisions between molecules of the same kind is given by[124]:

$$\frac{N^2}{V^2} \cdot d^2 \cdot \left[\frac{4\pi kT}{m}\right]^{\frac{1}{2}} \qquad 7.5$$

where N is the number of molecules in volume V, d is the collision diameter, m is the mass of a molecule, k is the Boltzmann constant and T the absolute temperature.

For a temperature increase 25-60°C. the collision frequency will be increased by a factor $\left(333/298\right)^{1/2}$ which is only slightly greater than unity. Similarly the number of molecules per c.c. will not be appreciably effected, since the p-xylene densities at 25 and 60°C. are $\sim$ 0.86 and $\sim$ 0.83 respectively. Thus it may be expected that the frequency between collisions or relaxation time, which using the microwave bridge method, and in view of the small absorption, are not accurate to better than ± 20%, would be insensitive to such a change of temperature.

From Eq. 7.3 it is apparent that the collision frequency will be dependent upon the values N and d. In the case of the alkylbenzene under consideration, the diameters, either the thickness or longest axis, are approximately constant. Thus their collision frequencies should be proportional to N, the number of molecules per unit volume, which is a function of density and reciprocal of the molecular weight. The densities of benzene, p-xylene, p-cymene and mesitylene are 0.8737, 0.8567, 0.8533 and 0.8602 respectively at 25°C. and thus the relaxation time might be expected to lengthen, with increasing molecular weight. This is not inconsistent with the observed results, and the short relaxation time for benzene is also predicted from the smaller collision diameter i.e. in the plane of the ring, for this molecule. Durene and hexamethylbenzene were measured in mesitylene solution, and hence the number of molecules per c.c. for these two compounds were much less than for the pure liquids.

However, a shorter relaxation time for these two molecules is not expected since collisions between solute and solvent are likely to be fruitful, and the relaxation times for durene and hexamethylbenzene, though less accurate than the others, due to their small loss, are considered to be reasonable.

Thus the relaxation times reported in this chapter offer support to the theory that the dipole moments for the symmetrical benzenes are brought about by collisions between molecules. Furthermore the respective dipole moments for these molecules suggest that the absorption may be related to the polarizabilities of the colliding molecules. However, the origin of the absorption is not readily apparent and it is evident that a correct interpretation must await further experimental work on a wide range of non-polar liquids. In a recent paper[125] Birnbaum, Levine and McQuarrie have interpreted the collision induced absorption in a gas containing quadrupolar non-dipolar molecules in terms of two and three body collisions. These workers analysed the loss measurements to yield relaxation times, of the order of 10^{-12} sec., for such interactions. A similar theoretical treatment for non-polar liquids should give valuable information about collision processes in liquids.

CHAPTER 8

RELAXATION PROCESSES OF SOME ALKYLBENZENES AND RELATED COMPOUNDS

Introduction

The results reported in the previous chapter may offer a possible interpretation for the shorter relaxation time process observed for a number of monoalkylbenzenes[51]. In view of this, and the non-zero distribution coefficients observed for the spherical methylchloroform, in both cyclohexane and p-xylene solution, which is somewhat analogous to the non-zero distribution coefficient reported for toluene in the pure liquid and a variety of solvents, it was decided to investigate the dielectric behaviour of a number of alkylbenzenes in order to test the intramolecular relaxation hypothesis.

For the monoalkylbenzenes and methylchloroform the molecular dipole vector acts along a major axis of the molecule. Thus an intramolecular relaxation process, involving rotation about this axis, would not be expected since there is no component of this moment perpendicular to the carbon--carbon and alkyl-aryl bond, in methylchloroform and toluene respectively. An extensive study of this subject has already been carried out in this laboratory[22], and a summary of the results and their implications is relevant at this juncture.

Hassell observed that the mean relaxation times for toluene, ethyl-, isopropyl- and t-butylbenzene were short in comparison with other molecules of similar shape and size such as the monohalobenzenes, all of which exhibit Debye absorption in the microwave region. The dielectric data for these monoalkylbenzenes were analysed in terms of contributions from two relaxation processes, one identified with molecular re-orientation and a shorter relaxation time. Comparable short relaxation times were obtained from analyses of the dielectric data for solutions of p-chloro- and p-bromotoluene below 40°C., 1-methyl- and 2-methylnaphthalene at 50°C., and ortho- and meta-xylene at 25°C.. Rigid molecules of similar shape and size were characterised by a single relaxation time identified with molecular re-orientation. A short relaxation time process of possible dipolar origin contributed to the dielectric absorption of 4-methyl and 4-t-butylpyridine in cyclohexane at 25°C. (no evidence for such a process was observed for the former in cyclohexane at 50°C. - chapter 2). Calculation of dipole-dipole interaction energy, dipolar contribution to the cohesive energy, cohesive energy and London dispersion energy for each of the monoalkylbenzenes, indicated that only the latter could be responsible for the short relaxation time. From the available evidence Hassell concluded that the most plausible explanation of the short relaxation time process, appeared to be intramolecular rotation about the alkyl-aryl bond, although an intermolecular process was not ruled out.

Such an intramolecular process could only be envisaged if the alkyl-aryl bond was not a pure single bond, but had some multiple bond character due to π -electron resonance involving charge migration from the alkylgroup to the ring, then during rotation about this bond the overlap of the alkyl group orbitals with the π-electrons of the ring might vary. This would cause a rapid movement of charge to and fro between the π -electron cloud of the phenyl group, and the alkyl group, and implies oscillation of negative charge with an associated mesomeric moment. Thus if this moment were comparable with that of the molecule, and the free energy of activation for such a process was of a suitable magnitude, it would be detectable in the microwave region. The dipole moment of toluene is 0.3 – 0.4D and the enthalpy of activation for the τ_2 process was found to be 1.3 ± 1 k.cal/mole., which is of similar magnitude to that reported for methyl group rotation in the gaseous state[107].

The τ_2 values for toluene were longer in the pure liquid and in the more polarizable solvents, than in cyclohexane solution and showed an increase from toluene to t-butylbenzene. Such behaviour may be explained if the energy barrier to group rotation were increased by local interaction between adjacent molecules and steric factors within the molecule respectively. In addition the value of μ_2 calculated from the relationship $c_1/c_2 = \mu_1^2/\mu_2^2$, where μ_1 is the molecular dipole moment, revealed a decrease from toluene through ethyl- and isopropyl- to t-butylbenzene. If μ_2 were related to movement of charge due to an intramolecular process it should reflect the magnitude of the mesomeric moment, and the observed trend is in harmony with one concept of hyperconjugation in the monoalkylbenzenes[126].

Finally the mean relaxation times of some phenyl substituted compounds were investigated and found to be significantly short, indicating a large contribution to the dielectric absorption from a short relaxation time process.

Benzotrichloride provides a link between toluene and methylchloroform, thus the dielectric absorption of this molecule might prove useful in correlating and interpreting the non-Debye absorption for both molecules. Furthermore, benzotrichloride is of similar shape and size as t-butylbenzene. Thus a study of these two compounds together with phenyltrimethylsilane, ethyl- and isopropylbenzene, at a range of temperatures, was proposed in order to provide further means of studying the second relaxation process for the monoalkylbenzenes.

In order to test the intramolecular relaxation hypothesis conjugated molecules such as styrene, allylbenzene and phenylacetylene together with the non-conjugated 4-methylcyclohexene and the rigid benzocyclobutene, indane and tetralin, all of which have small dipole moments, have been measured.

In addition it was proposed to examine the data in the light of the results reported in chapter 7.

Discussion

The non-zero distribution coefficient and mean relaxation time of 23.5×10^{-12} sec. for benzotrichloride in cyclohexane at 25°C. (Table 8.1) is in good agreement with the non-zero distribution coefficient and identical relaxation time reported by Hufnagel and Kilp[28] for this compound in cyclohexane at 20°C.. The dipole moments of 2.16 and 2.06D in cyclohexane and p-xylene solutions respectively, are comparable with literature values[43] of 2.14 and 2.09D in heptane and benzene respectively and offer support to the validity of the extrapolated ε_∞ values. The non-zero α for benzotrichloride in cyclohexane at 25°C. might suggest that a τ_2 process of similar origin to that detected for the alkylbenzenes contributes to the dielectric absorption for benzotrichloride. However, the dipole moment of this molecule is large compared with those for the alkylbenzenes, and for an intramolecular process to be detectable an increased mesomeric moment is necessary.

The mean relaxation time of benzotrichloride in p-xylene solution at 25°C. is a little shorter than in cyclohexane solution at the same temperature, and the non-zero distribution coefficient observed for the measurements

Table 8.1 Static Dielectric Constant, High Frequency Dielectric Constant, Relaxation Time, Weight Contribution, Distribution Coefficient, Dipole Moment and Weight Fraction for some Substituted Benzene Compounds.

Solute	Solvent	T°C	W_2	ε_0	ε_∞	τ_0	$\tau_1$slope	τ_1	τ_2	C_1	α	μ_D
Toluene	p-Xyl.	25	0.7863	2.3571	2.262	6.3	7.2	8.7	4.2	0.54	0.04	0.32
	Mesit.	25	0.5055	2.3268	2.266	6.4	8.0	7.1	2.6	0.88	0.02	0.32
+ Acridine	p-Xyl.	25	-	2.4365	2.294	19.2	23.5	22.0	6.5	0.85	0.09	-
+ T.H.P.	Cyc.	25	-	2.1842	2.066	3.9	5.4	6.5	3.3	0.16	0.04	-
Benzotrichloride	Cyc.	15	0.07387	2.2077	2.052	25.8	26.0	-	-	-	0.05	2.18
		25	0.06200	2.1559	2.030	22.3	23.5	-	-	-	0.05	2.16
		37.5	0.07315	2.1533	2.018	17.8	19.1	-	-	-	0.03	2.18
		45	0.07244	2.1352	2.006	16.6	16.6	-	-	-	0.01	2.15
		50	0.07381	2.1247	1.998	15.0	15.9	-	-	-	0.00	2.15
	p-Xyl.	25	0.07167	2.4503	2.282	20.5	23.1	28.0	15.0	0.54	0.00	2.06
Ethylbenzene		15	1.0000	2.4236	2.273	13.7	20.0	17.7	5.3	0.75	0.06	0.37
		37.5	1.0000	2.3675	2.232	10.0	11.3	14.4	5.7	0.59	0.06	0.37

Table 8.1 continued

Solute	Solvent	$T^{\circ}C$	W_2	ε_0	ε_∞	τ_0	τ_1 slope	τ_1	τ_2	C_1	α	μ_0
		50	1.0000	2.3365	2.214	8.8	8.3	11.6	6.7	0.50	0.02	0.37
Isopropylbenzene		15	1.0000	2.4012	2.249	19.8	23.2	24.6	5.2	0.81	0.08	0.40
		37.5	1.0000	2.3473	2.217	14.0	15.5	15.1	4.0	0.90	0.03	0.39
		50	1.0000	2.3180	2.195	11.8	13.2	13.9	7.8	0.71	0.02	0.40
t-Butylbenzene	Cyc.	15	0.6757	2.2547	2.169	24.0	24.1	31.7	8.1	0.77	0.12	0.40
		37.5	0.6840	2.2148	2.142	16.6	16.0	20.9	8.1	0.75	0.05	0.39
		45	0.6800	2.2009	2.131	14.7	15.8	16.6	7.5	0.83	0.02	0.39
		50	0.6757	2.1839	2.116	12.3	13.3	17.1	7.0	0.68	0.04	0.38
Benzocyclobutene		25	1.0000	2.6210	2.424	12.6	12.6	12.6	-	1.00	0.00	0.40
Indane	Cyc.	25	0.5718	2.3766	2.224	12.6	12.8	12.6	-	1.00	0.00	0.55
Tetralin	Cyc.	15	0.5293	2.3904	2.204	19.0	23.8	22.3	3.0	0.91	0.07	0.61
		25	0.5412	2.3673	2.194	16.7	20.1	19.0	4.2	0.66	0.08	0.62
		50	0.5293	2.3004	2.146	12.6	12.7	13.8	3.0	0.91	0.00	0.61

Table 8.1 continued

Solute	Solvent	$T^{\circ}C$	W_2	ε_0	ε_∞	τ_0	$\tau_{1\,slope}$	τ_1	τ_2	C_1	α	μ_D
4-Methyl-cyclohexene		25	1.0000	2.1771	2.093	5.6	5.1	5.6	-	1.00	0.00	0.29
Phenyl-acetylene	Cyc.	25	0.2001	2.1514	2.088	13.6	13.5	13.6	-	1.00	0.00	0.59
		25	0.5668	2.4680	2.248	15.7	17.7	-	-	-	0.04	0.62
Styrene		25	1.0000	2.4290	2.406	6.5	8.1	16.0	3.3	0.52	0.41	0.14
Allylbenzene	Cyc.	25	0.4008	2.2180	2.132	8.5	18.4	-	-	-	0.28	0.52
Phenyltri-methylsilane		15	1.0000	2.3726	2.324	17.0	19.2	38.7	4.0	0.63	0.31	0.25
		37.5	1.0000	2.3314	2.294	10.3	14.7	27.1	3.0	0.54	0.30	0.23
		50	1.0000	2.3020	2.274	7.3	8.9	17.4	5.0	0.44	0.19	0.21

using p-xylene and cyclohexane solvents, at 25 and 50°C. respectively, cast further doubt upon the validity of analysing the benzotrichloride data in terms of two relaxation times.

The monoalkylbenzenes have been measured over a range of temperatures in order to determine the reality of a τ_2 process, and to obtain enthalpies of activation $\Delta H_0^{\ddagger}$ and $\Delta H_1^{\ddagger}$ for the τ_0 and τ_1 processes repectively.

For phenyltrimethylsilane, ethyl-, isopropyl- and t-butylbenzene non-zero distribution coefficients were observed at 15, 37.5 and 50°C., and their dielectric data were analysed in terms of contributions from a molecular relaxation process (τ_1) and a short relaxation time process (τ_2), the results are shown in Table 8.1. The values obtained for isopropyl- and t-butylbenzene are subject to large errors since C_2 is small. However, no apparent decrease of the τ_2 values, and that for the silicon compound, with increasing temperature are apparent, and thus the enthalpy of activation for the τ_2 process is indistinguishable from zero. Such behaviour is not entirely in harmony with intramolecular rotation about the alkyl-aryl bond, since as models show, the steric hinderence to rotation for t-butylbenzene is considerably greater than for ethylbenzene and toluene. For the latter $\Delta H_2^{\ddagger}$ was found to be 1.3 ± 1 kcal/mole. compared with a potential energy barrier of 0.5 kcal/mole. from gas measurement[107]. Unfortunately values of the barrier heights for such a process in molecules of this type are not available for comparison.

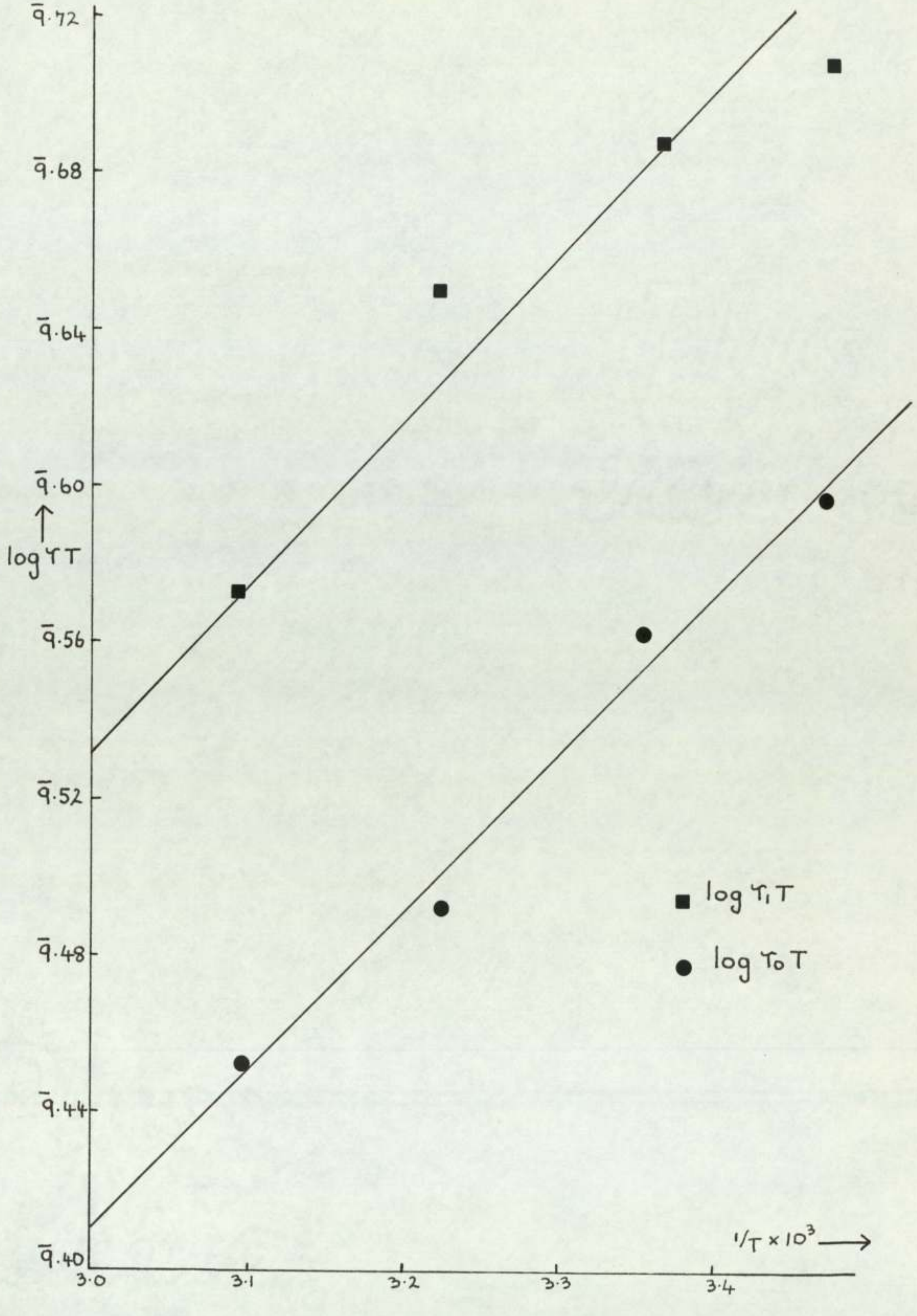
The enthalpies of activation obtained from the plots of $\log \tau T$ against $1/T$ for benzotrichloride, tetralin, phenyltrimethylsilane, ethyl-, isopropyl- and t-butylbenzene are shown in Table 8.2.

Table 8.2 Enthalpies of Activation (kcal/mole.) Evaluated from the Results Given in Table 8.1 for some Substituted Benzenes.

Compound	$\Delta H_0^{\ddagger}$	$\Delta H_1^{\ddagger}$	Fig.
Ethylbenzene	1.8_6	1.9_3	8.1
Isopropylbenzene	2.4_7	2.3_5	8.2
t-Butylbenzene	2.5_9	2.8_0	8.3
Benzotrichloride	2.3_9	-	8.4
Phenyltrimethylsilane	3.1_7	3.5_6	8.5
Tetralin	1.6_0	1.9_0	8.6

For ethyl-, isopropyl- and t-butylbenzene the τ_0 and τ_1 values at 25°C. were those obtained by Hassell and the plots of $\log \tau_0 T$ and $\log \tau_1 T$ against $1/T$ show good agreement with the results obtained in this study. The τ_0 value, at 25°C., for phenyltrimethylsilane was that obtained by Hassell, and the τ_1 value was obtained from computer analysis of the dielectric data at 25°C. reported by Hassell. It is evident from the plots that the τ_0 values may be determined

Fig 8.1 PLOT OF LOG τT AGAINST 1/T - ETHYLBENZENE



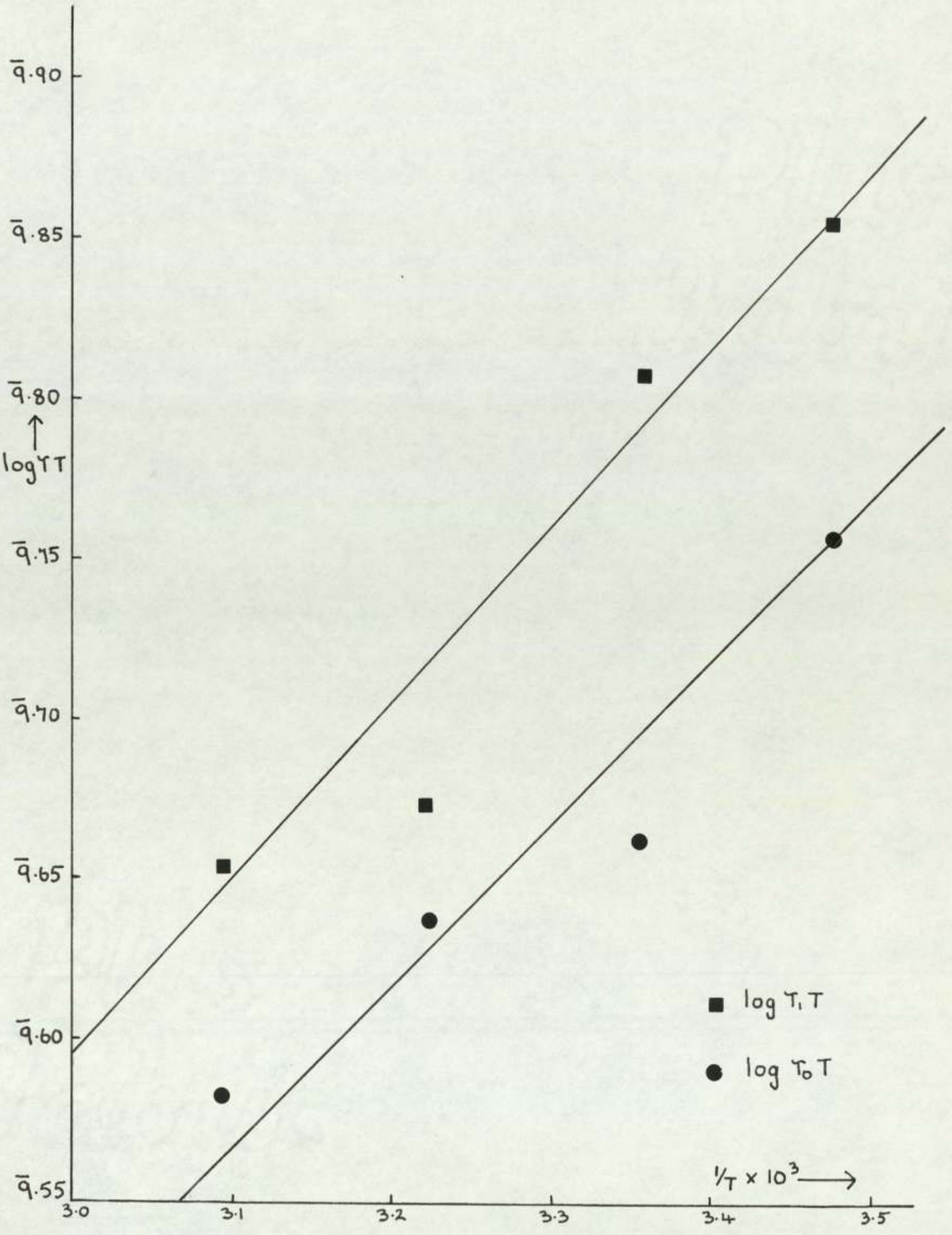


Fig 8.2 PLOT OF LOG τT AGAINST $^1/_T$ – ISOPROPYLBENZENE

Fig 8.3 Plot Of Log τT against $1/T$ – t-Butylbenzene

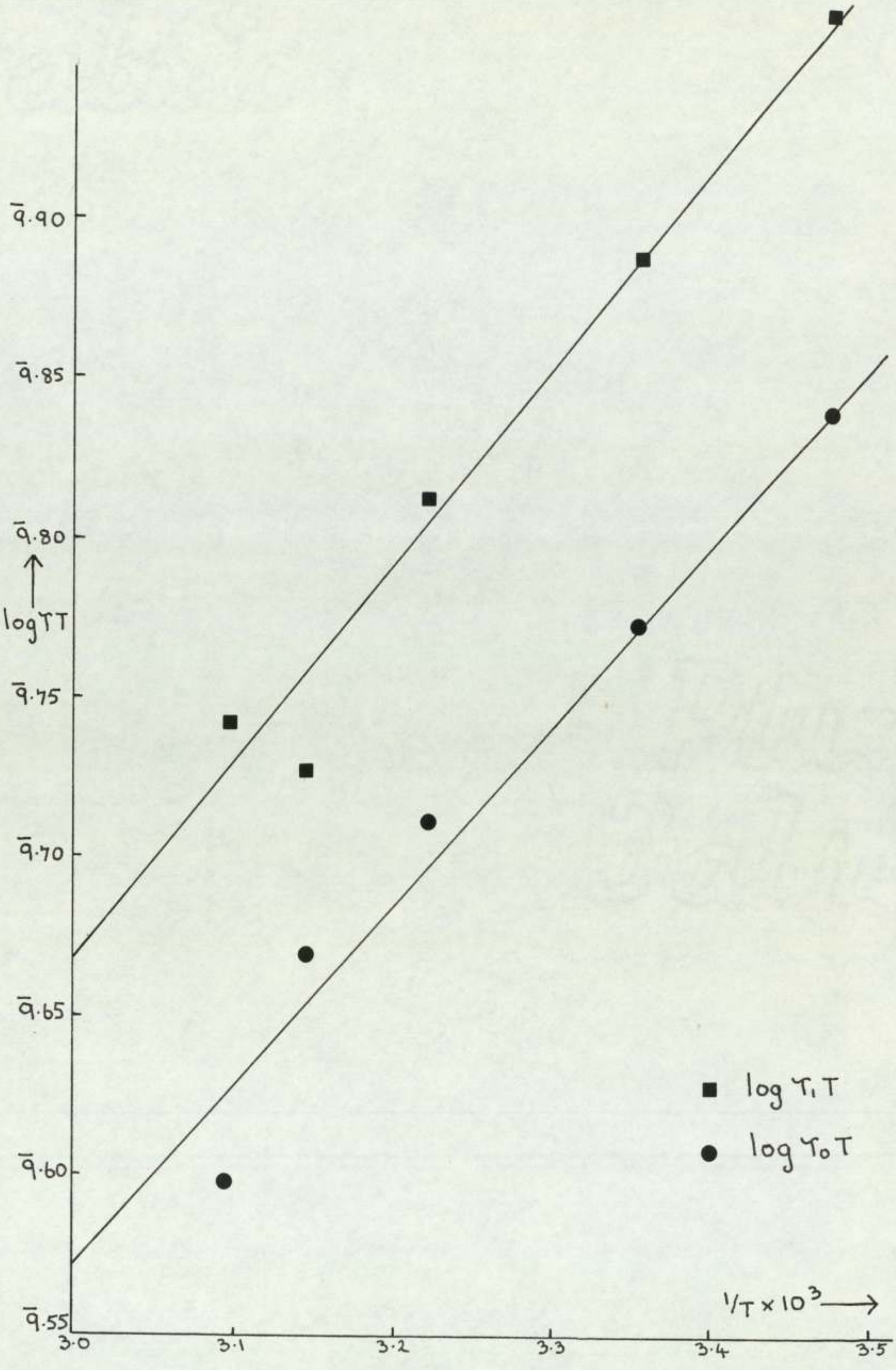


Fig 8.4 PLOT OF LOG $\tau_0 T$ AGAINST $1/T$ - BENZOTRICHLORIDE

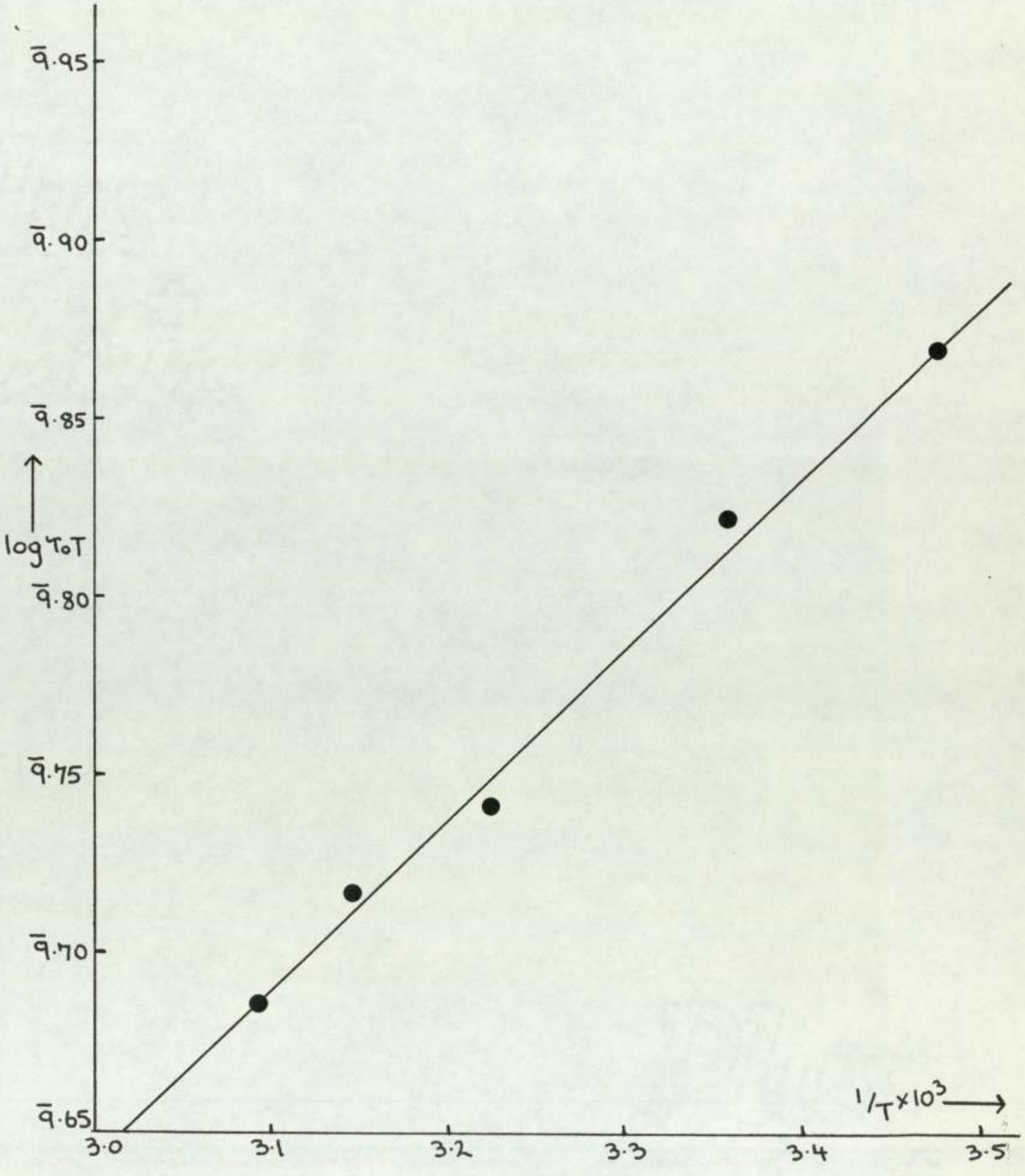


Fig 8.5 a PLOT OF LOG $\tau_0 T$ AGAINST 1/T - PHENYLTRIMETHYLSILANE

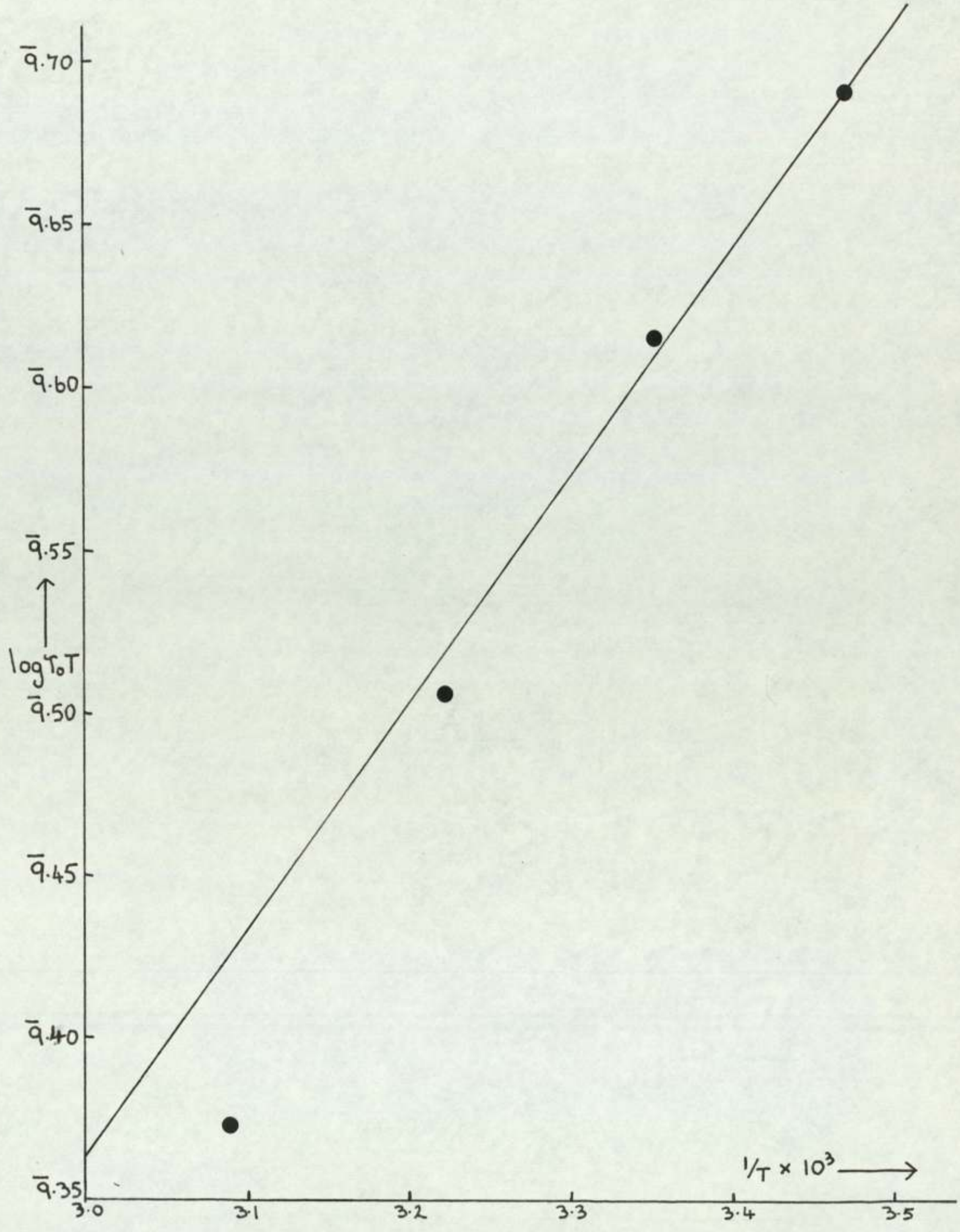


Fig 8.5 (b) PLOT OF LOG T_1T AGAINST $^1/_T$

- PHENYLTRIMETHYLSILANE

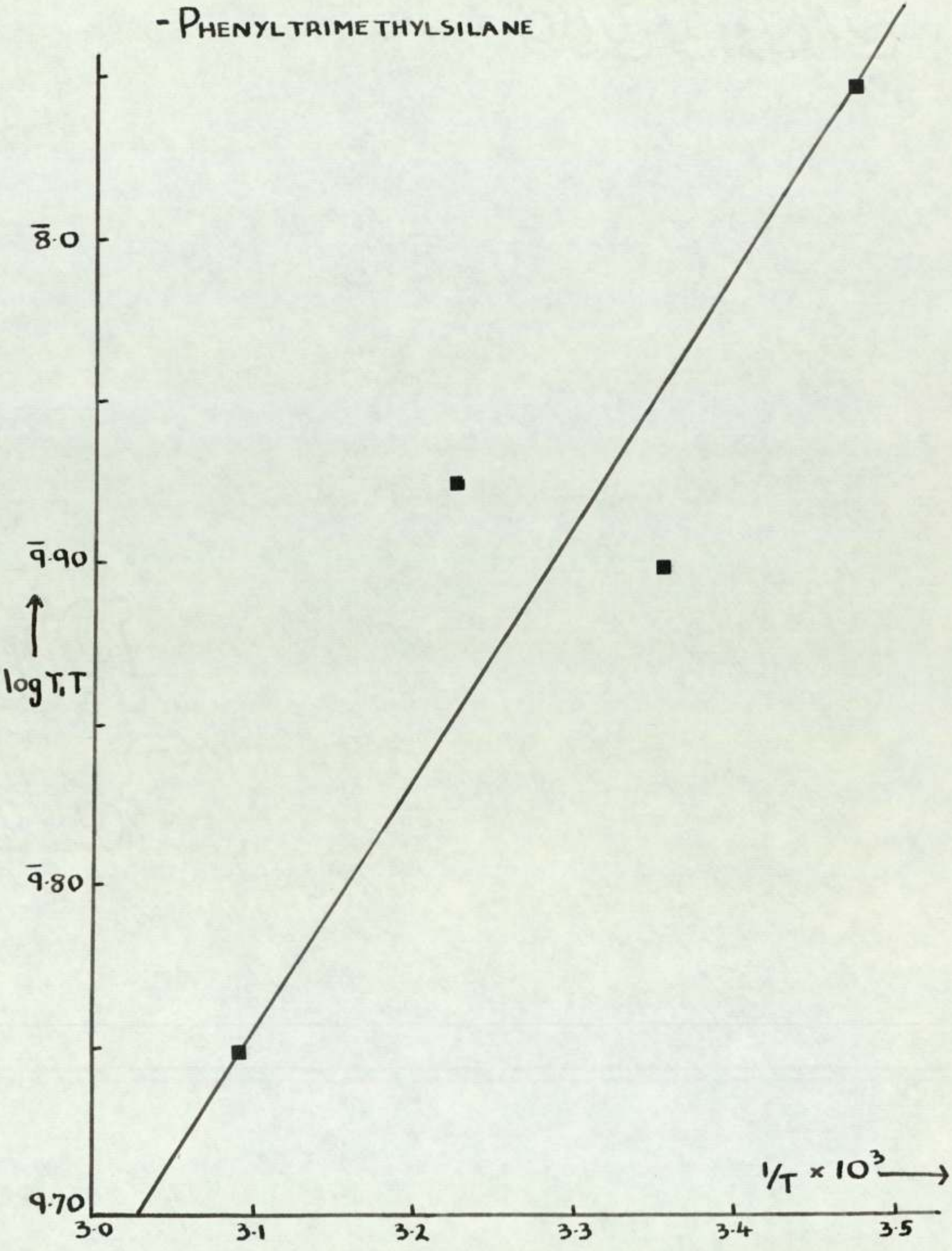
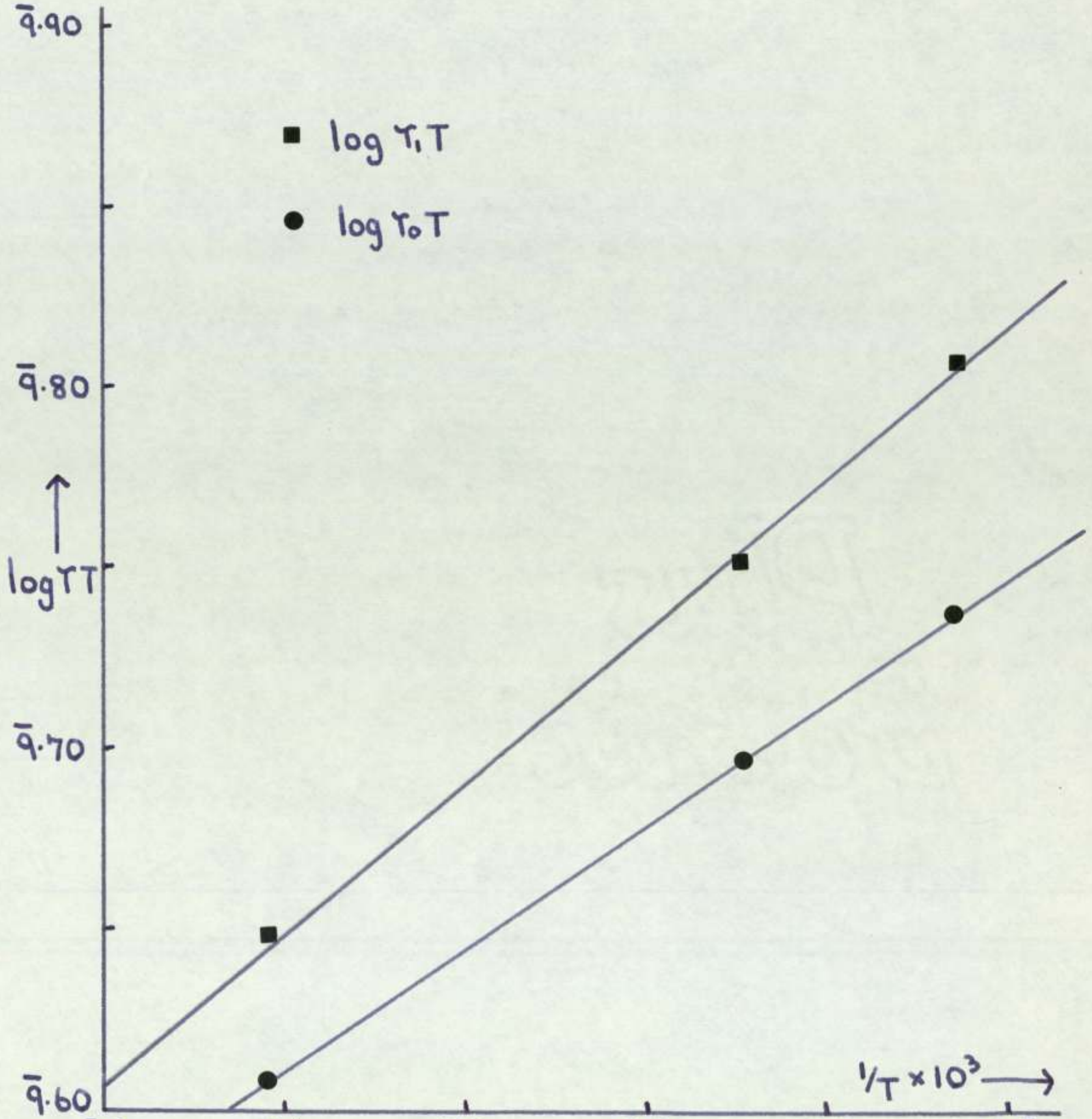


Fig 8.6 Plot Of Log τT against $1/T$ - Tetralin



much more accurately than the τ_1 values.

The close similarity between $\Delta H_0^{\ddagger}$ and $\Delta H_1^{\ddagger}$ for these compounds is only to be expected since the C_1 values are large and hence $\Delta H_0^{\ddagger}$ contains a large contribution from the $\Delta H_1^{\ddagger}$ process and it is consistent with the indications that $\Delta H_2^{\ddagger}$ is small. The increase of $\Delta H_1^{\ddagger}$ with increased size of molecule (for toluene $\Delta H_1^{\ddagger}$ is 1.1 kcal/mole.) is to be expected, and suggests the values are of the right order, tetralin is anomalous in this respect and this compound will be discussed later in the chapter. Petro and Smyth[127] have measured pure liquid toluene, ethyl- and isopropylbenzene at three temperatures, and reported significant distribution coefficients for all three, and $\Delta H_0^{\ddagger}$ values of 1.6, 1.9 and 2.5 kcal/mole. respectively, considering the errors involved in such values may be ± 0.5 kcal/mole. the agreement with the values in Table 8.2 is remarkably good.

The τ_2 values for toluene in cyclohexane at 25°C. decrease with increasing dilution to a constant value of 1.6×10^{-12} sec., and the apparent dipole moment increases to a constant value at a weight fraction of 0.6. In carbontetrachloride the τ_2 value is 3.5×10^{-12} sec., and the apparent dipole moment is similar to that for the pure liquid.

For toluene in p-xylene at 25°C. the τ_2 value is 4.2×10^{-12} sec. and the apparent dipole moment is the same as that obtained for the pure liquid at 25°C.. Since interaction between toluene and p-xylene should be fairly similar to that for toluene alone, it would appear that the magnitude of τ_2 is related to the nature of the surrounding molecules. However, the results for toluene in mesitylene, a solvent of increased polarizability, and having a greater electron density in the phenyl ring than toluene and p-xylene, at 25°C., show no indication of a longer τ_2 value. The constancy of the τ_0 value in a variety of solvents, and the τ_2 value in mesitylene, indicate that the τ_2 process might not be dependent on the basicity of the surrounding molecules.

If the τ_2 value for toluene were the result of a mechanism involving dipolar aggregates or some form of intermolecular forces, then the effect might be diminished in dilute solution. Unfortunately the low dipole moment of toluene prohibits any accurate measurement for weight fractions less than 0.4. However, the addition of a compound having a relatively large dipole moment will increase the total loss and thus facilitate more accurate measurement. By suitable choice of additive, compounds which display Debye absorption and have relaxation times sufficiently different from toluene, the dielectric data for the mixture may be analysed in terms of two relaxation times; that for the added compound and that for toluene in dilute solution. Kilp, Garg and Smyth[128] have measured binary mixtures of several compounds and analysed their data in terms of two superimposed Debye regions. Similar work has been carried out by Magee and Walker[25] for mixtures of chlorobenzene and bromobenzene, and chloroform and bromobenzene, in cyclohexane solution at 25°C., the resulting analyses were in excellent agreement with the predicted values. Other measurements at several microwave frequencies have indicated that the dielectric behaviour of rigid non-associated molecules in binary mixtures can be described by two relaxation times[129,130]. If both components retain their individuality in the mixture two relaxation times are expected, provided they are sufficiently distinct in magnitude.

The dielectric absorption of acridine in p-xylene and tetrahydropyran in cyclohexane are characterised by a single relaxation time, the values being 22.0 and 3.3×10^{-12} sec. respectively at 25°C.. Neither molecule would be expected to interact with toluene and their relaxation times are sufficiently different from that for toluene. Since the mole fractions and dipole moments of toluene and the added compounds can be determined the weight contribution (C_1) may be calculated from :

$$\frac{C_1}{C_2} = \frac{\mu_1^2 f_1}{\mu_2^2 f_2} \qquad 8.1$$

where f_1 and f_2 are the mole fractions of the components having dipole moments μ_1 and μ_2 respectively. Thus the relaxation time of toluene is the only unknown. The analyses of the dielectric data for toluene-acridine in p-xylene, and toluene-tetrahydropyran in cyclohexane, for which the calculated C_1 values are 0.84 and 0.20 respectively, are listed in Table 8.1. In both cases the weight fraction of toluene in the solutions was about 0.2. The agreement, between the predicted relaxation times and C values and the analyses given in Table 8.1 are excellent. The relaxation time of toluene, 6.5×10^{-12} sec. in both instances, is almost the same as the mean relaxation time for toluene in p-xylene and cyclohexane using much larger weight fractions at 25°C.. However, a more accurate appraisal of the data can be obtained from the ε'' against $\log \omega$ plots, Fig. 8.7, which show that a toluene relaxation time of 9.0×10^{-12} sec. provides an almost equally good fit to the experimental curve. Thus these measurements fail to provide an accurate value for the relaxation time of toluene in relatively dilute solution, due to the small contribution it makes to the total absorption, and any increase in the toluene concentration would only serve to defeat the object of the experiments.

All the foregoing discussion has been concered with alkylbenzenes, and therefore the substituent groups have

Fig 8.7 Plot of ε'' against Log ω

(a) Toluene-Acridine in p-Xylene at 25°C

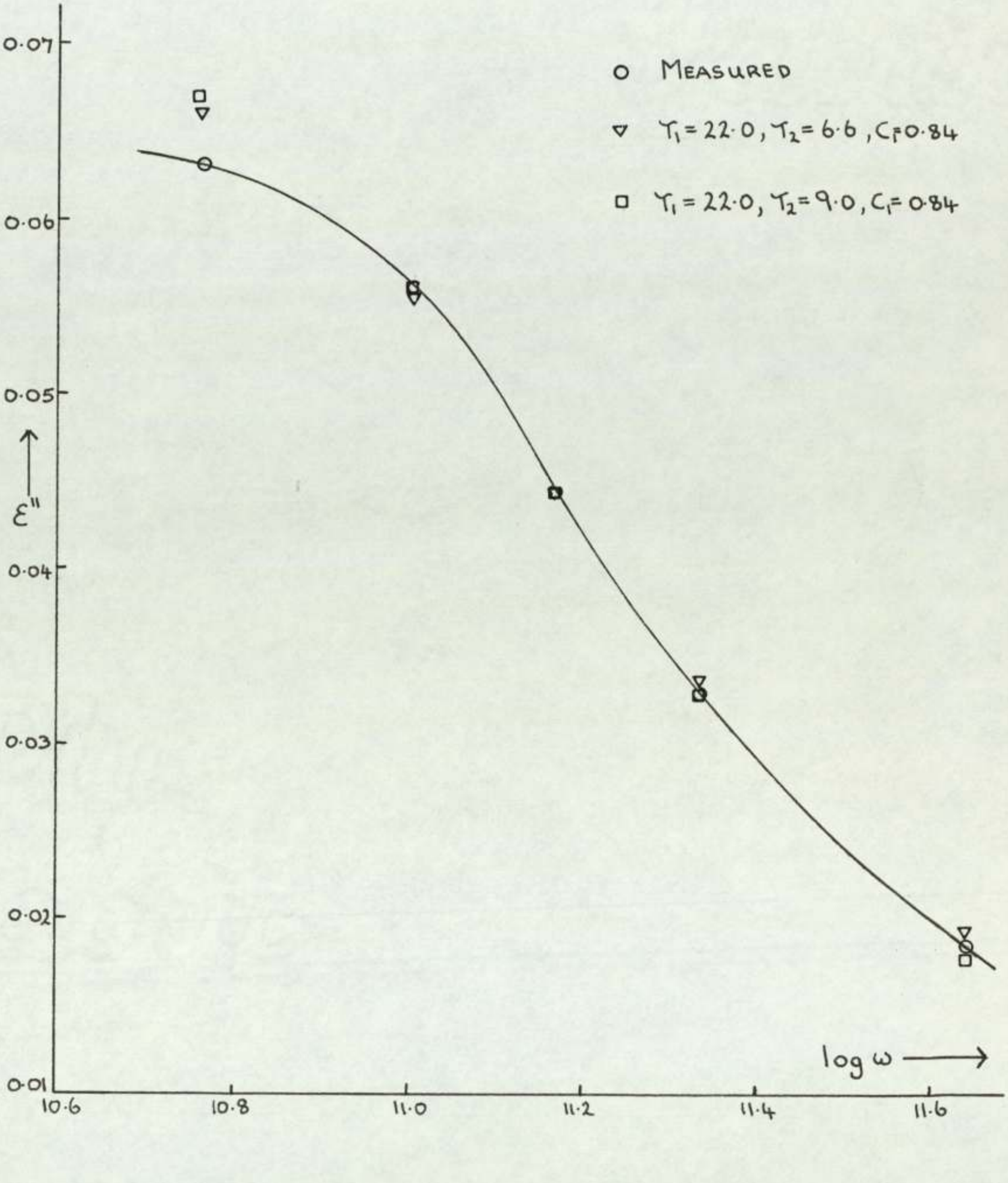
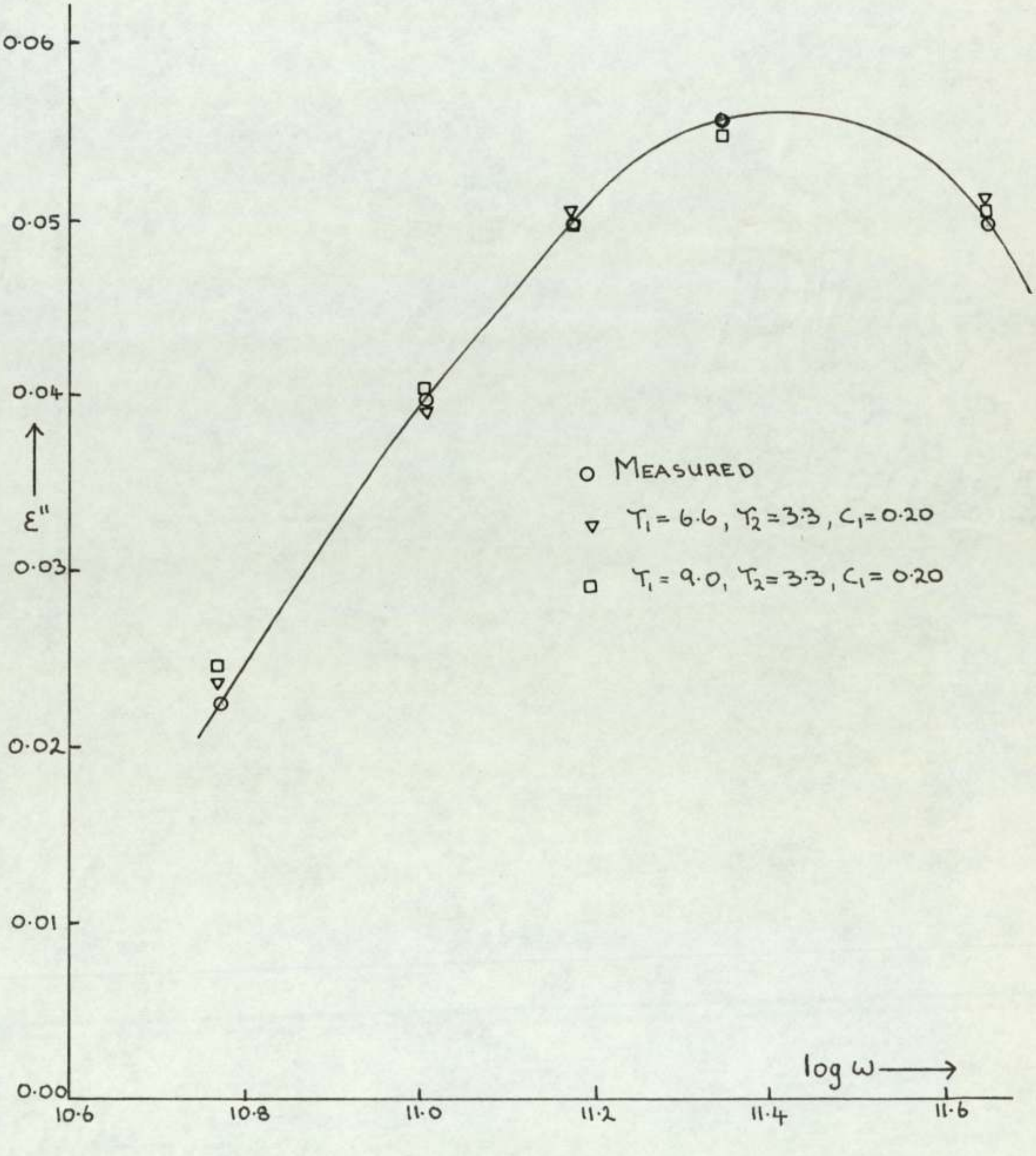


Fig 8.7(b) TOLUENE - TETRAHYDROPYRAN IN CYCLOHEXANE AT 25°C



been attached to a conjugated system. The methyl group in 4-methylcyclohexene is not attached to a conjugated system, and thus there is no possibility of overlap of the methyl-group orbitals with any π-electrons of the alicyclic ring, and an intramolecular relaxation process is not expected. The dielectric absorption of this compound at 25°C., having an apparent dipole moment of 0.29D, may be characterised by a single relaxation time of 5.6×10^{-12} sec.. The molecular relaxation time of an alicyclic molecule would be shorter than that for an analogous aromatic because the puckering in the former would give rise to a more spherical molecule, and thus the volume swept out during molecular re-orientation will be smaller than for a planar aromatic molecule. Thus the observed relaxation time for 4-methylcyclohexene can be attributed to molecular re-orientation, and may be compared with interpolated relaxation times of 6.1×10^{-12} and 7.7×10^{-12} sec., for fluoro- and chlorobenzene respectively in p-xylene at 25°C.[82]. Thus the τ_2 process for the monoalkylbenzenes would seem to be dependent on their conjugated nature.

Phenylacetylene is a highly conjugated molecule and yet it's dielectric absorption in cyclohexane solution at 25°C., in the most dilute solution, is characterised by a relaxation time, $\sim 13 \times 10^{-12}$ sec., of a magnitude expected for it's shape and size. Conversely phenyltrimethylsilane, a molecule in which the phenyl-Si bond contains appreciable double bond character, exhibits non-Debye absorption and has a mean relaxation time much shorter than for rigid molecules of similar shape and size. Dipole moment studies[1] have shown phenylacetylene to have a moment of 0.7D, which is slightly greater than the microwave value of $\sim$ 0.6D, and that the dipole moment of p-methylphenylacetylene is 1.0D, which indicates that the acetylene group is the negative end of the moment. The zero distribution coefficient, in dilute solution, does not conflict with the intramolecular relaxation hypothesis, since the π-electron cloud of the substituent group is cylindrical, and therefore no variation of overlap with the π-electrons of the ring is anticipated for rotation about the aryl- acetylenic bond. The non-zero distribution coefficient obtained for the more concentrated solution may well be the result of variations in local environment experienced by the re-orientating solute molecules. It was not possible to analyse the dielectric data for this solution in terms of reasonable τ_1 and τ_2 values, however, if the distribution is valid it would provide evidence against an intramolecular process for the monoalkylbenzenes.

Allylbenzene is unique amongst the compounds under discussion in that the $-CH{=}CH_2$ group moment does not act along the major axis of the molecule, but is inclined at an angle to it. Models show that rotation of this group is relatively unhindered and thus an intramolecular relaxation process would be anticipated irrespective of an oscillation of charge mechanism. The mean relaxation time for allylbenzene is short by comparison with other molecules of similar shape and size such as benzotrichloride and isopropylbenzene (Table 8.1), and the considerable distribution coefficient would suggest a contribution from a short relaxation time process, and the apparent dipole moment is in agreement with the literature value of 0.52D. However, the dielectric absorption data has not been analysed since, as the later discussion will suggest, it is possible that the absorption may be characterised by three relaxation processes; molecular re-orientation, intramolecular rotation and an intermolecular process.

It is expected that the alkyl-aryl bond in styrene will have appreciably more double bond character than those in the monoalkylbenzenes, and thus an intramolecular relaxation process is to be expected for this molecule, if the hypothesis for the monoalkylbenzenes is valid. The mean relaxation time for styrene is short by comparison with the relaxation time for the smaller bromobenzene molecule, and the Cole-Cole plot obtained from the dielectric data reveals a large distribution coefficient. Literature values of the dipole moments of styrene[127,131] are 0.13 to 0.18D, and may be compared with the microwave value of 0.14D.

Petro and Smyth[127] measured pure liquid styrene and obtained a relaxation time of 6.4×10^{-12} sec. at 20°C., and a zero distribution coefficient. These workers noted the anomalously short relaxation time, and pointed out that the vinyl group is larger than the methyl group, and that styrene has a viscosity 32% larger than toluene. In explaining this anomaly they suggested that since the molecule is in a planar configuration, as a result of resonance, closer packing with corresponding increased viscosity would result, and the molecules could relax with comparatively little interference from molecules in adjacent planes. Such an argument is not supported by the results for the planar phenylacetylene molecule, which is of a similar size to styrene, but its absorption is characterised by a relaxation time much longer than that for styrene.

The dielectric data for styrene can be accounted for in terms of contributions from a molecular re-orientation process and a short relaxation time process. The former is 16.0×10^{-12} sec., and may be compared with the interpolated relaxation time obtained for the rigid iodobenzene in p-xylene at 25°C. which is 15.2×10^{-12} sec.[82]. The value of μ_2 obtained from $c_1/c_2 = \mu_1^2/\mu_2^2$ for styrene is ~ 0.15D which is half that obtained for toluene. If the vinyl group were m-directing, then on the basis of the results of

Groves and Sugden[132], the mesomeric moment of the op-directing toluene would be greater. Electrophilic substitution with styrene occurs preferentially in the vinyl group, and there appears to be no data available concerning the directing power of the vinyl group. However, the dipole moments of styrene and 4-methylstyrene have been reported as 0.2 and 0.6D respectively[1], indicating that the vinyl group is the negative end of the moment. Groves and Sugden calculated mesomeric moments of 0.97 and 0.29 for chloro- and nitrobenzene respectively, and thus it would appear that these moments are related to the electrophilic nature of the substituent, and not the conjugation of the molecule, and on such an argument the μ_2 values for toluene and styrene may be reasonable for an intramolecular process. For styrene rotation about the vinyl-aryl bond would involve steric inhibition of resonance, and a longer τ_2 value might be predicted because of the increased energy barrier, expected for such a process, compared with toluene.

For indane in cyclohexane, and pure liquid benzocyclobutene, the dielectric absorption at 25°C. may be characterised by a single relaxation time of 12.6×10^{-12} sec. in both cases. In both molecules the substituent groups are fixed, and thus an intramolecular relaxation process is not possible, and these results would offer support to the intramolecular process for the monoalkylbenzenes.

Conversely, tetralin shows a non-zero distribution coefficient at 15 and 25°C. in cyclohexane solution which is inconsistent for a rigid molecule, and though α is zero at 50°C. a second relaxation time is possible due to the small C_2 and τ_1/τ_2 values (see Table 1.4). These results indicate that the τ_2 process observed for the monoalkylbenzenes may be associated with some mechanism other than rotation about the alkyl-aryl bond. Rampolla and Smyth[33] measured pure liquid tetralin at 20°C. and found it's absorption to be characterised by a single relaxation time, 29.3×10^{-12} sec., they also calculated the apparent dipole moment to be 0.59D which compares favourably with those reported in Table 8.1. The difference between the relaxation times in the pure liquid and in cyclohexane may be attributed to the differences in viscosity which are 2.22 and 1.15 c.p. respectively.

Plots of τ_0 and τ_1 against the molar volume at 25°C., are shown in Fig. 8.8 and 8.9 respectively, for a variety of substituted benzene compounds. For these molecules of similar shape and viscosity such plots should provide a reasonable correlation of the relaxation times.

The plots involving τ_0, the mean relaxation time, can be considered in terms of two curves, the one of steepest slope is obtained for molecules whose dielectric absorption is characterised by a single relaxation time. For the

Fig 8.8 PLOT OF τ_0 AGAINST MOLAR VOLUME AT 25°C FOR SOME SUBSTITUTED BENZENE COMPOUNDS

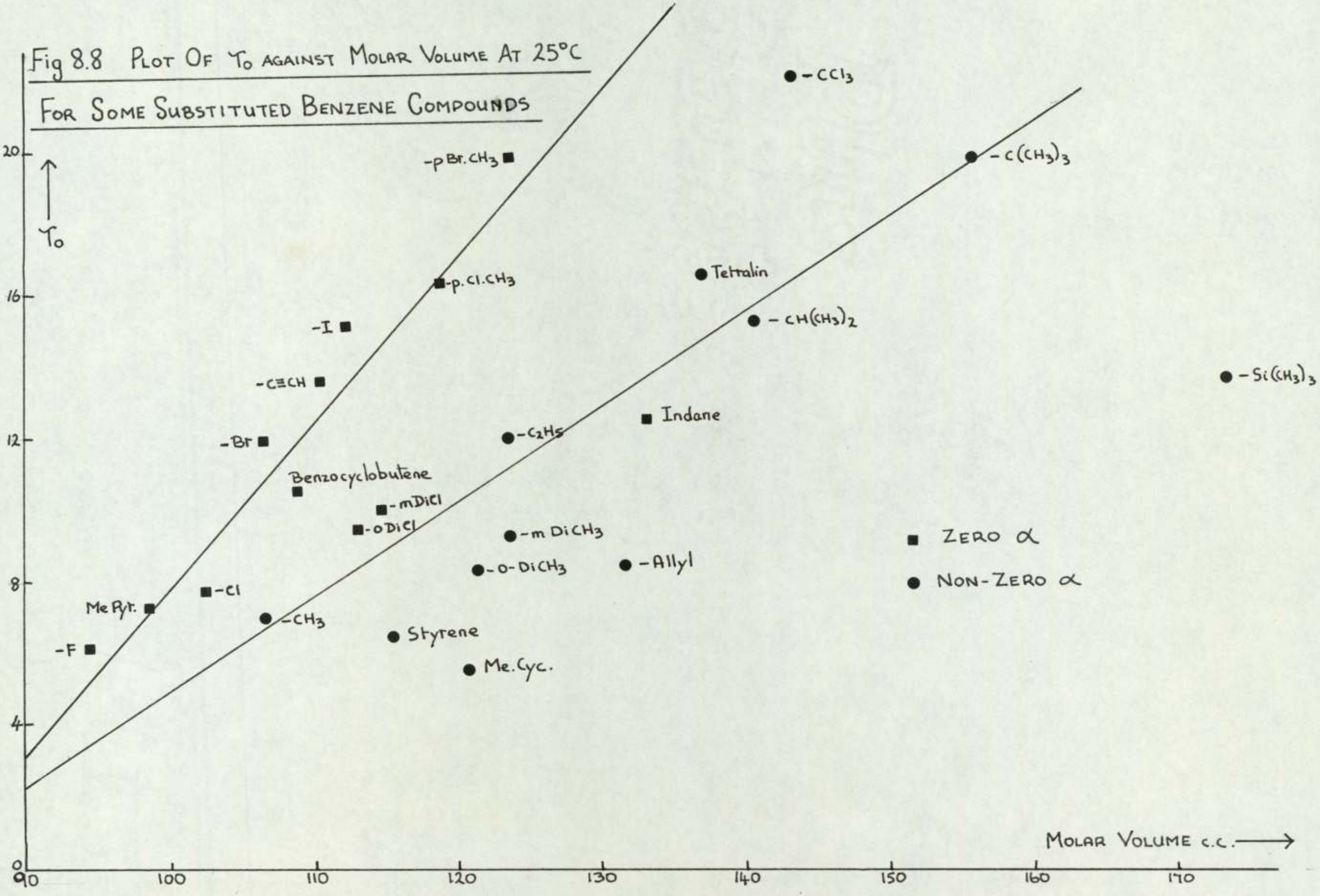
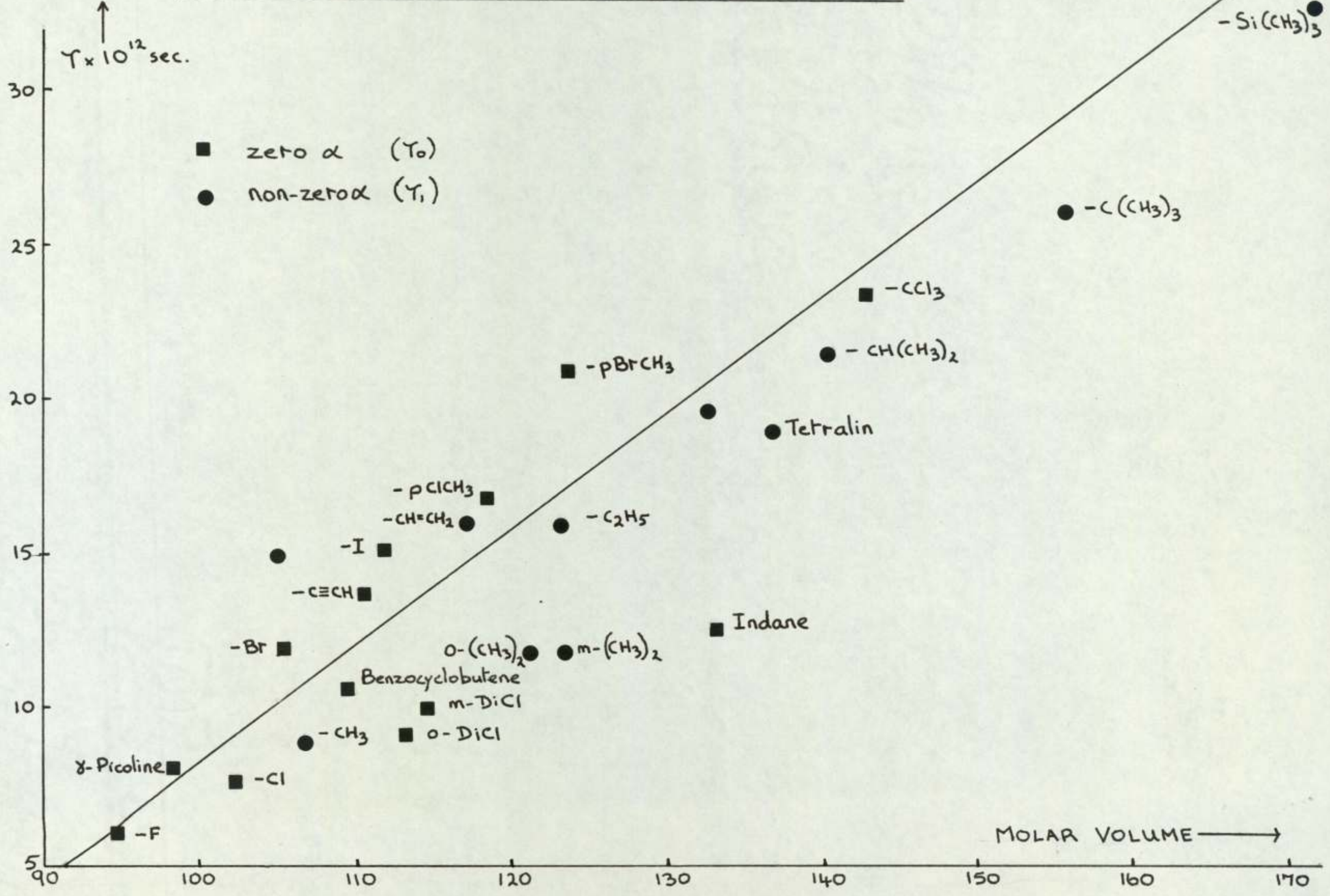


Fig 8.9 MOLECULAR RELAXATION TIME AGAINST MOLAR VOLUME at 25°C



compounds whose dielectric absorption reveals a non-zero distribution coefficient a more random distribution about a second less steep curve is obtained, which suggests particularly for allylbenzene, styrene and phenyltrimethylsilane, a contribution to the dielectric absorption from a short relaxation time process. Though straight lines have been drawn for comparison, it is possible that the points lie on a curve and thus the mean relaxation times for t-butylbenzene and phenyltrimethylsilane are probably not as short as this plot suggests.

The plot of τ_1 against molar volume is useful in the assesment of the analyses in terms of the τ_1 values. The error in these values is about ± 15%, and considering this and the likelihood that molar volumes are not an exact means of correlation, the agreement between the τ_1 and the τ_0 values, (which refer to rigid molecules whose dielectric absorption are characterised by a zero distribution coefficient) on this plot, are reasonable. The values for the rigid ortho- and meta-dichlorobenzene and the xylenes appear to be short. This apparent anomaly can be explained if the volume swept out by molecular re-orientation is considered. For the quinoline family and 4-methylpyridine, discussed in chapter 2, it was suggested that re-orientation was predominantly about the axis perpendicular to the plane of the ring, and the molecular relaxation time for such molecules is related to the length of the molecule. Thus, for ortho and meta substituted benzenes, the molecular relaxation times will be similar, and only slightly longer than those for the monosubstituted compounds, and will appear short by comparison with their total volume, and the relaxation times for the monosubstituted and the para-disubstituted compounds. Similarly, the apparently short relaxation times for benzocyclobutene, for which Hassell's value in cyclohexane solution has been used, and tetralin may also be explained. For indane the τ_0 value is anomalously short, and this may suggest that there is a contribution from a short relaxation process, even though the distribution coefficient is zero.

The results reported in this chapter confirm that a short relaxation time process contributes to the dielectric absorption of styrene, allylbenzene, phenyltrimethylsilane, toluene, ethyl-, isopropyl- and t-butylbenzene. In addition there is evidence that a short relaxation time process contributes to the dielectric absorption for indane, tetralin and phenylacetylene. The results for benzotrichloride, 4-methylcyclohexene and benzocyclobutene indicate that they are rigid molecules whose dielectric absorption may be characterised by a single molecular relaxation time.

Several objections to an intramolecular relaxation process are summarised below.

(i) The enthalpies of activation for toluene, ethyl-, isopropyl- and t-butylbenzene are all indistinguishable from zero, which is not consistent with the increased steric factors along the series. Furthermore, the potential energies, in the gas phase, for methyl group rotation in ortho- and meta-xylene are reported to be 2.0 and 0.5 kcal/mole. respectively[107], which is inconsistent with possible analyses for both compounds in terms of a τ_2 value of $\sim 5 \times 10^{-12}$ sec..

(ii) The τ_2 value for phenyltrimethylsilane is much shorter than that for t-butylbenzene although the substituent group in the former is larger.

(iii) The dielectric absorption of phenylacetylene at the higher weight fraction shows a non-zero distribution coefficient.

(iv) For an intramolecular relaxation process, involving methyl group rotation, it is reasonable to assume that the contribution from such a process to the absorption would increase with increasing number of substituent methyl groups. The maximum absorption given by the τ_2 process, which is determined by C_2 and $\varepsilon_0 - \varepsilon_\infty$, for the pure liquids which have been measured are listed in Table 8.3, for a range of C_2 values including those given by the computer analyses (C_{obt}). The loss for toluene (i.e. from C_{2obt} to $C_2 = 0.3$ which is the smallest acceptable value) is appreciably

Table 8.3 Maximum Loss Associated with the τ_2 Process for some Alkylbenzenes in the Pure Liquid at 25°C..

				ε''_{max}				
Compound	τ_2	$\varepsilon_0-\varepsilon_\infty$	C_{obt}	$C_2=0.5$	$C_2=0.3$	$C_2=0.1$	C_{obt}	μ_D
Toluene	4.3	0.1205	0.45	0.03012	0.01808	0.00604	0.02717	0.35
Ethylbenzene	6.2	0.1551	0.40	0.03877	0.02327	0.00778	0.03109	0.37
Isopropylbenzene	8.4	0.1471	0.20	0.03677	0.02207	0.00738	0.01477	0.40
t-Butylbenzene	9.2	0.1198	0.25	0.02995	0.01797	0.00600	0.01501	0.39
Styrene	3.3	0.0230	0.48	0.00575	0.00345	0.00115	0.00553	0.14
Phenyltrimethylsilane	5.0	0.0453	0.40	0.01132	0.00679	0.00227	0.00908	0.23
Benzene	1.0	-	1.00	-	-	-	0.006	0.10
p-Xylene	2.5	-	1.00	-	-	-	0.0065	0.12
Mesitylene	5.0	-	1.00	-	-	-	0.008	0.14

greater than for p-xylene and mesitylene, and those for the latter two are similar to that for benzene, which is inconsistent with methyl group rotation on the basis of the above argument relating to the number of methyl groups. In addition Hassell obtained $C_2 = 0.25$ for m-xylene which is less than that for toluene and since the dipole moment of the former is $\sim$ 0.32D, which is very similar to that of $\sim$0.35D for toluene, the analyses are not consistent with an intramolecular process.

(v) Tetralin and indane are rigid molecules but the former shows a significant distribution coefficient at 15 and 25°C., and the mean relaxation time for indane appears to be short.

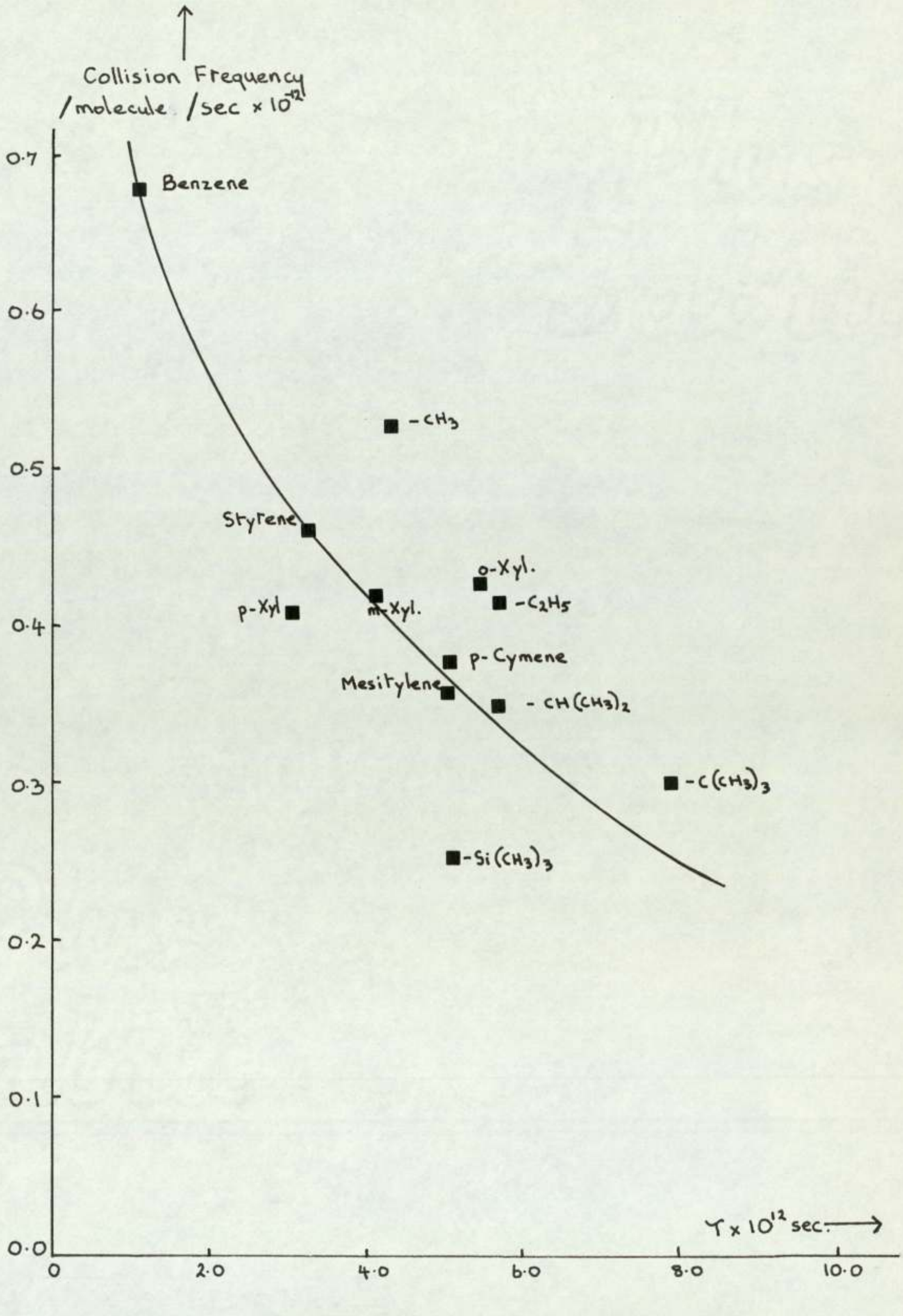
The results discussed in the previous chapter suggest that an alternative mechanism may provide a more satisfactory explanation of the short relaxation times observed for the monoalkylbenzene compounds.

A collision induced dipole, and a relaxation time related to the frequency between collisions, would explain the apparent independence of temperature shown by the τ_2 process for the monoalkylbenzenes, since, for the temperature range which has been used, the collision frequency would not show any significant variation. In order to ascertain the number of collisions per second experienced by the molecules in question, in the pure liquid state at 25°C., numerical values have been substituted into Eq. 7.5. The collision diameter was taken to be 4 Å in every case since the van der Waals radius of the phenyl group is ~ 2 Å. The results are compared with the τ_2 values in Fig. 8.10.

An exact relationship between τ_2 and the collision frequency is not anticipated because of the inaccuracy of the former and the approximate nature of the latter. In addition it is probable that a favourable orientation of the colliding molecules may be required for a collision to be fruitful. However, the plot (Fig. 8.10) shows a reasonable agreement for various molecules, and values of $1/\tau_2$ compare favourably with the collision frequencies. Thus for the molecules represented in this plot the relaxation times are consistent with a collision process.

For a collision process it might be expected that the dielectric absorption for indane and benzocyclobutene should be characterised by two relaxation times, one associated with molecular re-orientation, and a short relaxation time related to the collision frequency, and a non-zero distribution coefficient. This apparent anomaly may be explained if the contribution to the dielectric absorption from the short relaxation time process was small, and it's magnitude was not sufficiently different from that for molecular re-orientation. For tetralin at 50°C. a zero distribution coefficient was observed, but it was possible to analyse the data in terms of two relaxation

Fig 8.10 PLOT OF COLLISION FREQUENCY AGAINST RELAXATION TIME



times, and the non-zero distribution coefficients at 15 and 25°C. may be due to the increased τ_1/τ_2 ratio at these lower temperatures (Table 1.4), since τ_1 increases and τ_2 remains constant with decreasing temperature. The mean relaxation times for indane and benzocyclobutene at 25°C. are similar to that for tetralin at 50°C..

Indane and tetralin have similar dipole moments and both were measured in cyclohexane solution, thus for a collision induced dipole the τ_2 and C_2 values for these two compounds would be of similar magnitude, and by analogy with tetralin at 50°C. a zero distribution coefficient for indane at 25°C. is anticipated. Benzocyclobutene was measured in the pure liquid at 25°C. and for toluene τ_2 is longer in the pure liquid than in cyclohexane solution, and thus the zero distribution coefficient for benzocyclobutene may be explained by a small τ_1/τ_2 ratio.

The collision frequencies (Fig. 8.10) were based on the values for the pure liquid i.e. the number of molecules per c.c., and in solution N will decrease and it might be expected that the frequency of collision between solute molecules should also decrease. However, the solute molecules will collide with solvent molecules and it is not inconceivable that such collisions would be fruitful. The absorption for cyclohexane alone is negligible and it is anticipated that cyclohexane-alkylbenzene collisions would result in a smaller induced moment than for alkylbenzene - alkylbenzene collisions, which is in agreement with the C_2 values for toluene not exhibiting any apparent increase with dilution.

The τ_2 values for toluene in the pure liquid, p-xylene, carbontetrachloride and cyclohexane are 4.3, 4.2, 3.6 and $\sim 2 \times 10^{-12}$ sec. respectively. Thus the magnitude of τ_2 would appear to be related to the electron donor capacity of the solvent molecules. This behaviour may be explained in terms of a collision process if the molecular pairs are considered in terms of interaction between the available electrons of one and the alkylgroup hydrogens of the other. Thus for toluene it is reasonable to expect the degree of interaction and therefore the lifetime of the molecular pair to be greater with p-xylene and toluene and to be the least for cyclohexane.

Hassell and Walker[51] found that London dispersion energies were the dominating factor in intermolecular interactions between toluene, ethyl-, isopropyl- and t-butylbenzene. In addition the order of magnitude of these forces were similar to those reported in chapter 7, and such that the free energies of activation for the τ_2 process could be due to a rate process involving London dispersion forces. The polarizabilities and ionization energies, for the remaining molecules in this chapter, are similar to those for the compounds also studied by Hassell and Walker. Thus such a rate process might explain all the results which can be interpreted by a collision process. Furthermore, the shortening of the τ_2 value for toluene with dilution may be interpreted in terms of decreased dipolar forces. However, the negligible absorption for cyclohexane is a strong point against a process involving London forces.

Comparison of the μ_2 values for the τ_2 process for monoalkylbenzenes (Table 8.3) with the maximum loss for benzene, p-xylene, p-cymene and mesitylene (Fig. 7.1) is interesting. It is apparent that the maximum loss calculated for the monoalkylbenzenes, styrene excepted, from the Cobt values, are much greater than for the benzene family. However, this type of behaviour is to be anticipated for a collision induced dipole, since for the dipolar molecules it is probable that the induced dipole will contain, in addition to an induced moment of similar origin to those for the symmetrical molecules, a contribution from a dipole-dipole induced moment. The latter may be calculated, by assuming the alkylbenzene dipole lies symmetrically along the sixfold axis of symmetry of a neighbouring molecule, from:

$$\mu_{ind} = \frac{2\mu\partial(\varepsilon+2)}{3\varepsilon r^3} \qquad 8.2$$

which is the equation employed by Frank[133] when $\theta = 0$, and r is the intermolecular distance, ε is the dielectric

Table 8.4 Induced Moments Calculated from Eq. 8.2 for Various Values of the Intermolecular Distance (r) and the Molecular Dipole Moment (μ).

$r(\text{Å}) =$	3.5	4.0	4.5	5.0
μ_0				
0.10	0.03	0.02	0.01	0.01
0.15	0.04	0.03	0.02	0.02
0.20	0.06	0.04	0.03	0.02
0.25	0.07	0.05	0.03	0.03
0.30	0.09	0.06	0.04	0.03
0.35	0.10	0.07	0.05	0.04
0.40	0.12	0.08	0.06	0.04
0.45	0.13	0.09	0.06	0.05
0.50	0.15	0.10	0.07	0.05
0.55	0.16	0.11	0.08	0.06
0.60	0.18	0.12	0.08	0.06
0.80	0.24	0.15	0.12	0.08
1.60	0.47	0.31	0.22	0.16

Table 8.5 Values of μ_2 Obtained from $c_1/c_2 = \mu_1^2/\mu_2^2$ for a Range of μ_1 and C_2 Values.

$C_2 =$	0.1	0.2	0.3	0.4	0.5
μ_1					
0.15	0.05	0.08	0.10	0.12	0.15
0.20	0.07	0.10	0.13	0.16	0.20
0.25	0.08	0.13	0.16	0.20	0.25
0.30	0.10	0.15	0.20	0.25	0.30
0.35	0.12	0.18	0.23	0.29	0.35
0.40	0.13	0.20	0.26	0.33	0.40
0.45	0.15	0.23	0.30	0.37	0.45
0.50	0.17	0.25	0.33	0.41	0.50
0.55	0.18	0.28	0.36	0.45	0.55
0.60	0.20	0.30	0.39	0.49	0.60
0.80	0.26	0.40	0.52	0.66	0.80
1.60	0.53	0.80	1.05	1.31	1.60

constant and α the polarizability. Table 8.4 gives values of μ_{ind} for a range of dipole moments and intermolecular distances, and these were evaluated for a dielectric constant and a polarizability of 2.3 and 1.0×10^{-23} c.c. respectively. The results may then be compared for the various alkylbenzenes for all of which ε is roughly 2.3 and the polarizabilities along the axis perpendicular to the plane of the ring for molecules such as toluene, p-xylene, mesitylene and chlorobenzene are 0.901, 1.075, 1.247 and 0.818×10^{-23} c.c. respectively[108]. The van der Waals radius of the phenyl group is 2 Å and the relevant results in Table 8.4 are probably for $r = 3.5 - 5.0$ Å.

It is considered reasonable that the magnitude of a collision induced moment for the monoalkylbenzenes might have contributions from that for the symmetrical molecules (0.1 to 0.2D) plus the dipole induced moment. In order to compare collision induced moments with those associated with the τ_2 process for the alkylbenzenes the values of μ_2, obtained from the relationship $c_1/c_2 = \mu_1^2/\mu_2^2$, have been calculated for a range of μ_1 and c_2 values and the results are shown in Table 8.5. Thus from c_2 given by the computer analysis and inspection of Tables 8.4 and 8.5 it is apparent that the μ_2 values for styrene, phenyltrimethylsilane, tetralin, toluene, ethyl-, isopropyl- and t-butylbenzene are of the order that might reasonably be expected for a collision induced moment.

The dipole moments of toluene, ethyl-, isopropyl- and t-butylbenzene are almost the same, whereas the maximum loss associated with the τ_2 process (Table 8.3) for the last two are less than for toluene and ethylbenzene. However, the van der Waals radii of - CH_3 and $-C_2H_5$ groups are similar to the half thickness of a phenyl ring. Conversely, the larger size of the isopropyl- and t-butyl- groups may hinder their approach to a neighbouring molecule, and r (Eq. 8.2) might be increased and hence μ_{ind} decreased for these two compared with toluene and ethylbenzene.

By analogy with cyclohexane and from Tables 8.4 and 8.5 the contribution to the dielectric absorption from an induced dipole moment would be small for 4-methylcyclohexene, and a zero distribution coefficient is anticipated.

A dipole moment value of 1.6D has been included in Tables 8.4 and 8.5 for comparison. For the halobenzenes, which have dipole moments of that order, an induced moment of $\sim$ 0.4 - 0.5D and a C_2 value $<$0.1 would be expected, and thus the zero distribution coefficients observed for these compounds in p-xylene solution[82] are not unexpected.

In conclusion the available evidence would favour a collision induced dipole mechanism, rather than an intramolecular relaxation process, as an interpretation of the dielectric absorption data for the alkyl substituted benzenes. However, the precise origin of the induced moments are not yet established.

APPENDIX

Table 1. Experimental Results Discussed in Chapter 2.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Quinoline	50	70.00	2.006	0.0284	2.006	0.0287
in Cyc.		35.09	2.035	0.0428	2.026	0.0435
w_2 0.03866		23.98	2.047	0.0475	2.043	0.0466
		16.20	2.067	0.0441	2.060	0.0431
		9.313	2.069	0.0317	2.077	0.0313
Quinoline	25	70.00	2.288	0.0266		
in p-Xylene		34.86	2.307	0.0477		
w_2 0.03780		23.98	2.315	0.0587		
		16.20	2.349	0.0639		
		9.313	2.380	0.0560		
Quinoline	50	35.09	2.256	0.0497		
in p-Xylene		23.98	2.294	0.0567		
w_2 0.03780		16.20	2.314	0.0523		
		9.313	2.332	0.0422		
Isoquinoline	25	35.09	2.055	0.0521		
in Cyc.		23.98	2.061	0.0627		
w_2 0.03582		16.20	2.110	0.0687		
		9.313	2.141	0.0620		
		6.697	2.150	0.0514		

Table 1. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Isoquinoline	50	70.00	1.998	0.0310	2.002	0.0323
in cyc.		35.09	2.031	0.0516	2.024	0.0514
w_2 0.03328		23.98	2.047	0.0586	2.044	0.0576
		16.20	2.074	0.0554	2.066	0.0559
		9.313	2.084	0.0436	2.090	0.0426
Isoquinoline	25	70.00	2.285	0.0282		
in Cyc.		34.86	2.297	0.0485		
w_2 0.03647		23.98	2.319	0.0653		
		16.20	2.350	0.0804		
		9.313	2.390	0.0827		
Isoquinoline	50	70.00	2.255	0.0258		
in p-Xylene		35.09	2.271	0.0466		
w_2 0.03088		16.20	2.307	0.0608		
		9.313	2.335	0.0565		
Phthalazine	50	35.09	1.990	0.0290	2.000	0.0288
in Cyc.		23.98	2.015	0.0310	2.016	0.0309
		16.20	2.031	0.0275	2.024	0.0290
		9.313	2.037	0.0220	2.036	0.0212

Table 1. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Phthalazine	25	70.00	2.296	0.0296		
in p-Xylene		34.86	2.302	0.0561		
w_2 0.01301		23.98	2.321	0.0755		
		16.20	2.346	0.0968		
		9.313	2.395	0.1141		
Phthalazine	50	35.09	2.282	0.0639		
in p-Xylene		23.98	2.293	0.0827		
w_2 0.01301		16.20	2.316	0.0978		
		9.313	2.373	0.0973		
Acridine	50	35.09	1.997	0.0119		
in p-Xylene		23.98	1.997	0.0150		
w_2 0.02608		16.20	2.008	0.0181		
		9.313	2.012	0.0204		
Acridine	25	34.86	2.313	0.0300	2.316	0.0293
in p-Xylene		23.98	2.322	0.0412	2.322	0.0407
w_2 0.05807		16.20	2.332	0.0556	2.334	0.0548
		9.313	2.360	0.0690	2.365	0.0711

Table 1. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Acridine	50	70.00	2.255	0.0133	2.253	0.0152
in p-Xylene		35.09	2.256	0.0278	2.260	0.0283
w_2 0.04802		23.98	2.268	0.0367	2.268	0.0377
		16.20	2.286	0.0475	2.282	0.0464
		9.313	2.313	0.0499	2.309	0.0496
5,6-Benzo-	25	35.09	2.310	0.0258		
quinoline		23.98	2.312	0.0346		
in p-Xylene		16.20	2.323	0.0446		
w_2 0.05516		9.313	2.345	0.0664		
		6.697	2.359	0.0737		
4-Methyl-	50	70.00	2.000	0.0438	2.004	0.0451
pyridine		35.09	2.040	0.0614	2.037	0.0609
in Cyc.		23.98	2.061	0.0615	2.060	0.0597
w_2 0.02380		16.20	2.082	0.0496	2.080	0.0509
		9.313	2.096	0.0337	2.097	0.0343
4-Methyl-	25	70.00	2.293	0.0362		
pyridine		35.09	2.314	0.0603		
in p-Xylene		23.98	2.334	0.0734		
w_2 0.02310		16.20	2.366	0.0766		
		9.313	2.403	0.0676		

Table 2. Experimental Results Discussed in Chapter.3.

Solution	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
1,4-Thioxan	34.86	2.424	0.0451	2.441	0.0461
	23.98	2.444	0.0481	2.453	0.0466
w_2 1.0000	16.20	2.462	0.0475	2.466	0.0470
d 1.1099	9.313	2.493	0.0415	2.487	0.0456
1,4-Thioxan	34.86	2.410	0.0408	2.423	0.0401
in Cyc.	23.98	2.434	0.0428	2.436	0.0440
w_2 0.9691	16.20	2.448	0.0467	2.451	0.0456
d 1.0965	9.313	2.468	0.0374	2.473	0.0402
1,4-Thioxan	34.86	2.391	0.0427	2.399	0.0417
in Cyc.	23.98	2.405	0.0421	2.411	0.0443
w_2 0.9363	16.20	2.420	0.0465	2.426	0.0448
d 1.0800	9.313	2.450	0.0362	2.447	0.0388
1,4-Thioxan	34.86	2.353	0.0377	2.364	0.0369
in Cyc.	23.98	2.364	0.0386	2.376	0.0395
w_2 0.8668	16.20	2.379	0.0408	2.389	0.0399
d 1.0482	9.313	2.406	0.0302	2.407	0.0343
1,4-Thioxan	34.86	2.264	0.0293	2.276	0.0284
in Cyc.	23.98	2.272	0.0286	2.286	0.0295
w_2 0.7107	16.20	2.295	0.0285	2.297	0.0285
d 0.9836	9.313	2.305	0.0200	2.303	0.0228

Table 2. Continued.

Solution	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
1,4-Thioxan	34.86	2.375	0.0352	2.390	0.0349
in Nujol	23.98	2.408	0.0376	2.402	0.0384
w_2 0.8740	16.20	2.414	0.0388	2.416	0.0386
d 1.0710	9.313	2.434	0.0308	2.434	0.0319
1,4-Thioxan	34.86	2.354	0.0292	2.365	0.0296
in Nujol	23.98	2.362	0.0323	2.374	0.0312
w_2 0.7827	16.20	2.380	0.0317	2.384	0.0320
d 1.0469	9.313	2.398	0.0261	2.398	0.0292
1,4-Thioxan	34.86	2.331	0.0267	2.340	0.0266
in Nujol	23.98	2.348	0.0285	2.348	0.0282
w_2 0.7109	16.20	2.353	0.0276	2.358	0.0284
d 1.0247	9.313	2.375	0.0237	2.371	0.0245
Tetrahydropyran	70.00	2.075	0.0489	2.064	0.0484
in Cyc.	34.86	2.092	0.0491	2.098	0.0491
w_2 0.04823	23.98	2.111	0.0404	2.113	0.0412
	16.20	2.122	0.0315	2.123	0.0312
	9.313	2.131	0.0207	2.130	0.0192

Table 2. Continued.

Solution	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Pentamethylene	70.00	2.072	0.0542	2.068	0.0537
Sulphide	34.86	2.100	0.0610	2.108	0.0616
in Cyc.	23.98	2.123	0.0554	2.129	0.0548
w_2 0.05255	16.20	2.144	0.0426	2.145	0.0432
	9.313	2.159	0.0268	2.156	0.0274
s-Trioxan	70.00	2.070	0.0368	2.061	0.0364
in Cyc.	34.86	2.083	0.0343	2.086	0.0347
w_2 0.02031	23.98	2.093	0.0279	2.096	0.0284
	16.20	2.101	0.0224	2.102	0.0211
	9.313	2.107	0.0133	2.106	0.0129
s-Trioxan	70.00	2.063	0.0433	2.064	0.0431
in Cyc.	34.86	2.095	0.0406	2.094	0.0420
w_2 0.02297	23.98	2.103	0.0377	2.106	0.0347
	16.20	2.117	0.0241	2.114	0.0260
	9.313	2.119	0.0157	2.120	0.0159

Table 3. Experimental Results Discussed in Chapter 4.

Solution	T°C.	Frequency (G.c./sec.)	$\varepsilon'_{\text{MEAS}}$	$\varepsilon''_{\text{MEAS}}$	$\varepsilon'_{\text{CALC}}$	$\varepsilon''_{\text{CALC}}$
Cyclopentanone in Cyc. w_2 0.00944	25	70.00	2.053	0.0334	2.042	0.0290
		34.86	2.058	0.0350	2.062	0.0326
		23.98	2.064	0.0307	2.072	0.0308
		16.20	2.083	0.0247	2.082	0.0264
		9.313	2.093	0.0154	2.090	0.0170
Cyclopentanone in Cyc. w_2 0.01149	25	70.00	2.051	0.0385	2.050	0.0353
		34.86	2.069	0.0429	2.064	0.0387
		23.98	2.091	0.0384	2.085	0.0365
		16.20	2.098	0.0293	2.097	0.0313
		9.313	2.112	0.0203	2.107	0.0201
Cyclopentanone in Cyc. w_2 0.01438	25	70.00	2.060	0.0496	2.065	0.0471
		34.86	2.072	0.0517	2.095	0.0489
		23.98	2.106	0.0484	2.110	0.0442
		16.20	2.118	0.0362	2.122	0.0366
		9.313	2.134	0.0234	2.133	0.0247
Cyclopentanone in Cyc. w_2 0.01437	40	70.00	2.042	0.0495	2.047	0.0479
		34.86	2.067	0.0500	2.075	0.0447
		23.98	2.087	0.0415	2.079	0.0392
		16.20	2.098	0.0321	2.088	0.0315
		9.313	2.106	0.0186	2.107	0.0206

Table 3. Continued.

Solution	T°C.	Frequency (g.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Cyclopentanone in Cyc. w_2 0.01432	60	70.00	2.006	0.0417	2.013	0.0427
		34.86	2.028	0.0404	2.037	0.0386
		23.98	2.043	0.0342	2.048	0.0331
		16.20	2.056	0.0248	2.055	0.0260
		9.313	2.064	0.0156	2.063	0.0166
Cyclohexanone in Cyc. w_2 0.01241	25	70.00	2.046	0.0357	2.043	0.0351
		34.86	2.066	0.0462	2.069	0.0464
		23.98	2.082	0.0438	2.086	0.0448
		16.20	2.105	0.0390	2.101	0.0377
		9.313	2.114	0.0248	2.113	0.0251
Cycloheptanone in Cyc. w_2 0.01554	25	70.00	2.049	0.0348	2.050	0.0341
		34.86	2.070	0.0446	2.075	0.0457
		23.98	2.087	0.0456	2.092	0.0445
		16.20	2.108	0.0366	2.107	0.0378
		9.313	2.117	0.0252	2.119	0.0254
Cyclooctanone in Cyc. w_2 0.01919	25	70.00	2.032	0.0292		
		34.86	2.041	0.0432		
		23.98	2.066	0.0483		
		16.20	2.095	0.0486		
		9.313	2.109	0.0357		

Table 4. Experimental Results Discussed in Chapter 5.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}
1,1-Dichloro-	25	70.00	2.026	0.0204
ethane in Cyc.		34.86	2.038	0.0193
w_2 0.01482		23.98	2.049	0.0160
		16.20	2.055	0.0107
		9.313	2.062	0.0084
1,1-Dichloro-	25	70.00	2.043	0.0297
ethane in Cyc.		34.86	2.052	0.0281
w_2 0.02151		23.98	2.068	0.0224
		16.20	2.075	0.0169
		9.313	2.084	0.0098
1,1-Dichloro-	25	70.00	2.055	0.0426
ethane in Cyc.		34.86	2.073	0.0399
w_2 0.03050		23.98	2.088	0.0329
		16.20	2.099	0.0247
		9.313	2.110	0.0154
1,1-Dibromo-	25	70.00	2.036	0.0202
ethane in Cyc.		34.86	2.040	0.0218
w_2 0.03169		23.98	2.046	0.0212
		16.20	2.058	0.0156
		9.313	2.065	0.0120

Table 4. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}
1,1-Dibromo-	25	70.00	2.042	0.0273
ethane in Cyc.		34.86	2.041	0.0280
w_2 0.04079		23.98	2.051	0.0254
		16.20	2.070	0.0208
		9.313	2.083	0.0137
1,1-Dibromo-	25	70.00	2.050	0.0446
ethane in Cyc.		34.86	2.075	0.0480
w_2 0.06909		23.98	2.091	0.0444
		16.20	2.110	0.0356
		9.313	2.129	0.0245
1,2-Dichloro-	25	70.00	2.074	0.0352
ethane in Cyc.		34.86	2.085	0.0297
w_2 0.05157		23.98	2.094	0.0250
		16.20	2.105	0.0153
		9.313	2.106	0.0105
1,2-Dichloro-	25	70.00	2.120	0.0706
ethane in Cyc.		34.86	2.155	0.0578
w_2 0.1014		23.98	2.167	0.0491
		16.20	2.173	0.0335
		9.313	2.186	0.0205

Table 4. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}
1,1,1-Trichloroethane in Cyc. w_2 0.03969	25	70.00	2.055	0.0346
		34.86	2.066	0.0351
		23.98	2.074	0.0284
		16.20	2.085	0.0212
		9.313	2.099	0.0136
1,1,1-Trichloroethane in Cyc. w_2 0.04241	25	70.00	2.048	0.0364
		34.86	2.075	0.0375
		23.98	2.083	0.0306
		16.20	2.094	0.0236
		9.313	2.104	0.0144
1,1,1-Trichloroethane in Cyc. w_2 0.05281	25	70.00	2.068	0.0477
		34.86	2.096	0.0474
		23.98	2.103	0.0393
		16.20	2.110	0.0301
		9.313	2.128	0.0187
1,1,2-Trichloroethane in Cyc. w_2 0.06323	25	70.00	2.040	0.0325
		34.86	2.067	0.0383
		23.98	2.083	0.0330
		16.20	2.092	0.0288
		9.313	2.101	0.0181

Table 4. Continued.

Solution	$T^{o}C.$	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
1,1,2-Tri-	25	70.00	2.053	0.0439		
chloroethane		34.86	2.080	0.0503		
in Cyc.		23.98	2.100	0.0453		
w_2 0.08175		16.20	2.114	0.0372		
		9.313	2.129	0.0246		
1,1,1,2-Tetra-	25	70.00	2.051	0.0424	2.055	0.0418
chloroethane		34.86	2.078	0.0541	2.086	0.0552
in Cyc.		23.98	2.103	0.0533	2.106	0.0532
w_2 0.1035		16.20	2.127	0.0451	2.124	0.0448
d 0.8153		9.313	2.140	0.0287	2.138	0.0298
1,1,2,2-Tetra-	15	70.00	2.059	0.0422		
chloroethane		34.86	2.080	0.0628		
in Cyc.		23.98	2.106	0.0701		
w_2 0.1089		16.20	2.136	0.0701		
		9.313	2.179	0.0584		
1,1,2,2-Tetra-	25	70.00	2.048	0.0427		
chloroethane		34.86	2.070	0.0631		
in Cyc.		23.98	2.101	0.0695		
w_2 0.1107		16.20	2.125	0.0668		
d 0.8175		9.313	2.159	0.0505		

Table 4. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}
1,1,2,2-Tetra-	40	70.00	2.006	0.0251
chloroethane		34.86	2.028	0.0331
in Cyc.		23.98	2.040	0.0358
w_2 0.06416		16.20	2.050	0.0315
		9.313	2.067	0.0226
1,1,2,2-Tetra-	40	70.00	2.022	0.0432
chloroethane		34.86	2.047	0.0571
in Cyc.		23.98	2.083	0.0635
w_2 0.1089		16.20	2.095	0.0564
		9.313	2.124	0.0405
1,1,2,2-Tetra-	50	70.00	1.988	0.0252
chloroethane		34.86	1.997	0.0336
in Cyc.		23.98	2.027	0.0340
w_2 0.06416		16.20	2.040	0.0273
		9.313	2.050	0.0181
1,1,2,2-Tetra-	50	70.00	2.010	0.0444
chloroethane		34.86	2.041	0.0581
in Cyc.		23.98	2.066	0.0608
w_2 0.1089		16.20	2.086	0.0492
		9.313	2.103	0.0346

Table 4. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Pentachloro-	25	34.86	2.037	0.0190	2.038	0.0181
ethane		23.98	2.046	0.0207	2.044	0.0215
in Cyc.		16.20	2.056	0.0215	2.053	0.0224
w_2 0.1004		9.313	2.066	0.0198	2.064	0.0185
Pentachloro-	25	70.00	2.053	0.0215	2.055	0.0217
ethane		34.86	2.067	0.0360	2.068	0.0361
in Cyc.		23.98	2.080	0.0417	2.081	0.0419
w_2 0.1918		16.20	2.098	0.0431	2.098	0.0426
d 0.8659		9.313	2.122	0.0339	2.118	0.0342
Pentachloro-	25	34.86	2.069	0.0413	2.076	0.0406
ethane in Cyc.		23.98	2.088	0.0462	2.092	0.0466
w_2 0.2081		16.20	2.117	0.0455	2.110	0.0468
d 0.8744		9.313	2.133	0.0368	2.131	0.0370
1,1,2,2-Tetra-	25	70.00	2.061	0.0169	2.060	0.0153
bromoethane		34.86	2.068	0.0286	2.068	0.0276
in Cyc.		23.98	2.078	0.0357	2.077	0.0349
w_2 0.1778		16.20	2.096	0.0408	2.092	0.0403
d 0.8870		9.313	2.103	0.0407	2.112	0.0379

Table 5. Experimental Results Discussed in Chapter 6.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}
1,1-Dichloro-	25	70.00	2.304	0.0395
ethane		34.86	2.328	0.0497
in p-Xylene		23.98	2.344	0.0489
w_2 0.03005		16.20	2.366	0.0395
		9.313	2.376	0.0290
1,1-Dibromo-	25	70.00	2.293	0.0326
ethane		34.86	2.297	0.0430
in p-Xylene		23.98	2.323	0.0481
w_2 0.05628		16.20	2.343	0.0457
		9.313	2.364	0.0341
1,2-Dichloro-	25	70.00	2.319	0.0580
ethane		34.86	2.356	0.0719
in p-Xylene		23.98	2.387	0.0741
w_2 0.06529		16.20	2.429	0.0682
		9.313	2.442	0.0474
1,1,1-Tri-	25	70.00	2.299	0.0378
chloroethane		34.86	2.314	0.0407
in p-Xylene		23.98	2.328	0.0408
w_2 0.04265		16.20	2.349	0.0323
		9.313	2.354	0.0220

Table 5. Continued.

Solution	$T^{o}C.$	Frequency (G.c./sec.)	$\mathcal{E}'_{MEAS}$	$\mathcal{E}''_{MEAS}$	$\mathcal{E}'_{CALC}$	$\mathcal{E}''_{CALC}$
1,1,1,2-Tetrachloroethane in p-Xylene w_2 0.1379	25	70.00	2.302	0.0383	2.308	0.0370
		34.86	2.316	0.0619	2.328	0.0656
		23.98	2.340	0.0827	2.351	0.0813
		16.20	2.394	0.0918	2.383	0.0904
		9.313	2.435	0.0795	2.431	0.0814
1,1,2,2-Tetrachloroethane in p-Xylene w_2 0.1133	25	70.00	2.293	0.0433		
		34.86	2.308	0.0620		
		23.98	2.318	0.0742		
		16.20	2.357	0.0936		
		9.313	2.395	0.1059		
1,1,2,2-Tetrabromoethane in p-Xylene w_2 0.1614	15	70.00	2.307	0.0139		
		34.86	2.314	0.0209		
		23.98	2.311	0.0289		
		16.20	2.324	0.0411		
		9.313	2.343	0.0549		
1,1,2,2-Tetrabromoethane in p-Xylene w_2 0.1643	25	70.00	2.288	0.0142		
		34.86	2.290	0.0222		
		23.98	2.301	0.0321		
		16.20	2.305	0.0376		
		9.313	2.337	0.0543		

Table 5. Continued.

Solution	$T^{o}C.$	Frequency (G.c./sec.)	$\varepsilon'_{\text{MEAS}}$	$\varepsilon''_{\text{MEAS}}$	$\varepsilon'_{\text{CALC}}$	$\varepsilon''_{\text{CALC}}$
1,1,2,2-Tetra-	37.5	34.86	2.278	0.0249		
bromoethane		23.98	2.285	0.0337		
in p-Xylene		16.20	2.292	0.0430		
w_2 0.1633		9.313	2.326	0.0524		
1,1,2,2-Tetra-	50	70.00	2.249	0.0134	2.252	0.0129
bromoethane		34.86	2.249	0.0224	2.256	0.0246
in p-Xylene		23.98	2.267	0.0356	2.263	0.0333
w_2 0.1619		16.20	2.270	0.0416	2.274	0.0427
		9.313	2.305	0.0491	2.299	0.0495
Pentachloro-	25	70.00	2.297	0.0308	2.301	0.0242
ethane		34.86	2.308	0.0466	2.310	0.0464
in p-Xylene		23.98	2.315	0.0634	2.321	0.0632
w_2 0.2726		16.20	2.339	0.0814	2.342	0.0822
		9.313	2.377	0.0944	2.390	0.0982
1,1-Dichloro-	25	70.00	2.314	0.0382		
ethane		34.86	2.332	0.0456		
in p-Xylene		23.98	2.346	0.0463		
+ D.B.O		16.20	2.365	0.0420		
w_2 0.02912		9.313	2.373	0.0277		

Table 5. Continued.

Solution	$T^{o}C.$	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}
1,1,1-Tri-	25	70.00	2.309	0.0408
chloroethane		34.86	2.321	0.0468
in p-Xylene		23.98	2.342	0.0423
+ D.B.O.		16.20	2.357	0.0399
w_2 0.04725		9.313	2.374	0.0262
1,1,2-Tri-	25	70.00	2.294	0.0257
chloroethane		34.86	2.302	0.0349
in p-Xylene		23.98	2.315	0.0429
+ D.B.O.		16.20	2.340	0.0471
w_2 0.05220		9.313	2.362	0.0426
1,1,1,2-Tetra-	25	70.00	2.268	0.0244
chloroethane		34.86	2.296	0.0376
in p-Xylene		23.98	2.313	0.0442
+ D.B.O.		16.20	2.340	0.0452
w_2 0.07332		9.313	2.356	0.0430
1,1,2,2-Tetra-	25	70.00	2.294	0.0258
chloroethane		34.86	2.295	0.0301
in p-Xylene		23.98	2.301	0.0369
+ D.B.O.		16.20	2.321	0.0464
w_2 0.06164		9.313	2.330	0.0525

Table 5. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}
Pentachloro-ethane in p-Xyl.+ D.B.O. w_2 0.1191	25	34.86	2.302	0.0184
		9.313	2.323	0.0388

Table 6. Experimental Results Discussed in Chapter 8.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Toluene	25	35.09	2.290	0.0424	2.297	0.0429
in p-Xylene		23.98	2.305	0.0455	2.312	0.0446
w_2 0.7863		16.20	2.331	0.0398	2.328	0.0413
d 0.8620		9.313	2.345	0.0303	2.344	0.0308
Toluene	25	70.00	2.271	0.0205	2.274	0.0192
in Mesitylene		35.09	2.283	0.0257	2.287	0.0274
w_2 0.5055		23.98	2.296	0.0307	2.297	0.0291
d 0.8594		16.20	2.306	0.0265	2.308	0.0271
		9.313	2.326	0.0199	2.319	0.0200
Toluene +	25	35.09	2.304	0.0333	2.306	0.0340
Acridine in		23.98	2.309	0.0442	2.315	0.0442
p-Xylene		16.20	2.324	0.0569	2.329	0.0550
		9.313	2.356	0.0630	2.358	0.0658
Toluene +	25	35.09	2.130	0.0559	2.137	0.0562
Tetrahydropyran		23.98	2.148	0.0497	2.155	0.0491
in Cyclohexane		16.20	2.172	0.0391	2.168	0.0387
		9.313	2.172	0.0391	2.168	0.0387

Table 6. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}
Benzotrichloride in Cyclohexane w_2 0.07387	15	70.00	2.052	0.0165
		34.86	2.059	0.0268
		23.98	2.065	0.0379
		16.20	2.076	0.0506
		9.313	2.107	0.0679
Benzotrichloride in Cyclohexane w_2 0.06200	25	34.86	2.038	0.0257
		23.98	2.044	0.0345
		16.20	2.054	0.0448
		9.313	2.079	0.0562
Benzotrichloride in Cyclohexane w_2 0.07315	37.5	70.00	2.022	0.0200
		34.86	2.027	0.0324
		23.98	2.039	0.0439
		16.20	2.052	0.0558
		9.313	2.080	0.0655
Benzotrichloride in Cyclohexane w_2 0.07244	45	35.09	2.015	0.0333
		23.98	2.024	0.0448
		16.20	2.040	0.0557
		9.313	2.073	0.0638
		6.690	2.091	0.0616

Table 6. Continued.

Solution	T^{o}C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Benzotri-	50	70.00	2.003	0.0198		
chloride in		34.86	2.011	0.0354		
Cyclohexane		23.98	2.025	0.0467		
w_2 0.07381		16.20	2.035	0.0560		
		9.313	2.067	0.0627		
Benzotri-	25	70.00	2.288	0.0246		
chloride in		34.86	2.294	0.0338		
p-Xylene		23.98	2.300	0.0483		
w_2 0.07167		16.20	2.317	0.0642		
		9.313	2.343	0.0792		
Ethylbenzene	15	35.09	2.300	0.0447	2.296	0.0458
w_2 1.0000		23.98	2.304	0.0572	2.310	0.0555
d 0.8644		16.20	2.330	0.0620	2.329	0.0636
		9.313	2.381	0.0607	2.382	0.0621
		6.700	2.381	0.0607	2.382	0.0621
Ethylbenzene	37.5	35.09	2.262	0.0489	2.261	0.0500
w_2 1.0000		23.98	2.280	0.0599	2.278	0.0579
d 0.8513		16.20	2.299	0.0597	2.299	0.0613
		9.313	2.332	0.0568	2.329	0.0560
		6.700	2.342	0.0480	2.343	0.0480

Table 6. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Ethylbenzene	50	35.09	2.246	0.0487	2.241	0.0492
w_2 1.0000		23.98	2.266	0.0593	2.259	0.0570
d 0.8404		16.20	2.284	0.0572	2.281	0.0587
		9.313	2.314	0.0499	2.309	0.0493
		6.700	2.319	0.0425	2.320	0.0401
Isopropyl-	15	35.09	2.263	0.0358	2.265	0.0361
benzene		23.98	2.272	0.0452	2.275	0.0448
w_2 1.0000		16.20	2.288	0.0532	2.288	0.0543
d 0.8661		9.313	2.320	0.0670	2.315	0.0659
		6.700	2.335	0.0667	2.336	0.0678
Isopropyl-	37.5	35.09	2.232	0.0388	2.234	0.0387
benzene		23.98	2.248	0.0490	2.245	0.0490
w_2 1.0000		16.20	2.263	0.0580	2.263	0.0582
d 0.8469		9.313	2.296	0.0616	2.295	0.0611
Isopropyl-	50	35.09	2.212	0.0413	2.212	0.0412
benzene		23.98	2.232	0.0508	2.226	0.0515
w_2 1.0000		16.20	2.248	0.0594	2.246	0.0585
d 0.8363		9.313	2.274	0.0561	2.277	0.0562
		6.700	2.292	0.0491	2.292	0.0487

Table 6. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
t-Butylbenzene	15	35.09	2.176	0.0175	2.177	0.0172
in Cyclohexane		23.98	2.177	0.0228	2.181	0.0223
w_2 0.6757		16.20	2.187	0.0264	2.188	0.0276
d 0.8411		9.313	2.206	0.0347	2.201	0.0344
t-Butylbenzene	37.5	35.09	2.147	0.0193	2.149	0.0190
in Cyclohexane		23.98	2.150	0.0241	2.154	0.0246
w_2 0.6840		16.20	2.169	0.0300	2.163	0.0299
d 0.8202		9.313	2.178	0.0339	2.179	0.0338
		6.700	2.198	0.0329	2.185	0.0335
t-Butylbenzene	45	35.09	2.138	0.0206	2.138	0.0200
in Cyclohexane		23.98	2.141	0.0248	2.144	0.0259
w_2 0.6800		16.20	2.160	0.0316	2.153	0.0312
d 0.8140		9.313	2.170	0.0338	2.171	0.0335
		6.700	2.179	0.0307	2.181	0.0308
t-Butylbenzene	50	35.09	2.126	0.0216	2.125	0.0215
in Cyclohexane		23.98	2.133	0.0251	2.134	0.0250
w_2 0.6757		16.20	2.149	0.0303	2.142	0.0304
d 0.8089		9.313	2.163	0.0297	2.158	0.0309
		6.700	2.169	0.0305	2.166	0.0279

Table 6. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Benzocyclo-	25	70.00	2.433	0.0433	2.430	0.0437
butene		34.86	2.448	0.0655	2.445	0.0640
w_2 1.0000		23.98	2.463	0.0815	2.465	0.0824
d 0.957		16.20	2.471	0.0877	2.498	0.0970
Indane	25	34.86	2.251	0.0528	2.237	0.0504
in Cyclohexane		23.98	2.260	0.0646	2.253	0.0649
w_2 0.5718		16.20	2.274	0.0751	2.278	0.0764
d 0.8692		9.313	2.308	0.0767	2.321	0.0754
Tetralin	15	70.00	2.212	0.0252	2.212	0.0255
in Cyclohexane		34.86	2.220	0.0401	2.223	0.0411
w_2 0.5293		23.98	2.228	0.0549	2.232	0.0529
d 0.8751		16.20	2.244	0.0676	2.247	0.0674
		9.313	2.284	0.0828	2.284	0.0847
Tetralin	25	34.86	2.187	0.0411	2.206	0.0410
in Cyclohexane		23.98	2.208	0.0573	2.217	0.0548
w_2 0.5412		16.20	2.220	0.0672	2.234	0.0704
d 0.8673		9.313	2.276	0.0811	2.275	0.0846

Table 6. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Tetralin	50	34.86	2.172	0.0481	2.171	0.0487
in Cyclohexane		23.98	2.185	0.0616	2.185	0.0601
w_2 0.5293		16.20	2.204	0.0691	2.207	0.0700
d 0.8440		9.313	2.245	0.0705	2.245	0.0705
4-Methyl-	25	70.00	2.095	0.0393	2.105	0.0293
cyclohexene		35.09	2.117	0.0415	2.126	0.0413
w_2 1.0000		23.98	2.146	0.0408	2.142	0.0417
d 0.7963		16.20	2.157	0.0375	2.156	0.0365
		9.313	2.167	0.0241	2.169	0.0251
Phenylacetylene	25	35.09	2.090	0.0186	2.094	0.0190
in Cyclohexane		23.98	2.100	0.0254	2.100	0.0249
w_2 0.2001		16.20	2.114	0.0297	2.110	0.0301
d 0.7964		9.313	2.126	0.0309	2.127	0.0309
Phenylacetylene	25	70.00	2.260	0.0356	2.253	0.0322
in Cyclohexane		35.09	2.271	0.0582	2.268	0.0592
w_2 0.5668		23.98	2.286	0.0758	2.285	0.0778
d 0.8478		16.20	2.316	0.0955	2.313	0.0945
		9.313	2.362	0.1026	2.365	0.1022

Table 6. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Styrene	25	35.09	2.402	0.0091	2.414	0.0085
w_2 1.0000		23.98	2.414	0.0087	2.417	0.0087
d 9012		16.20	2.418	0.0074	2.419	0.0088
		9.313	2.419	0.0071	2.423	0.0081
Allylbenzene	25	70.00	2.130	0.0235	2.142	0.0233
in Cyclohexane		35.09	2.150	0.0287	2.158	0.0292
w_2 0.4008		23.98	2.165	0.0295	2.166	0.0296
d 0.8149		16.20	2.178	0.0294	2.174	0.0297
		9.313	2.186	0.0279	2.186	0.0297
Phenyltri-	15	35.09	2.323	0.0121	2.335	0.0123
methylsilane		23.98	2.335	0.0119	2.338	0.0129
w_2 1.0000		16.20	2.344	0.0150	2.341	0.0135
d 0.8741		9;313	2.356	0.0142	2.346	0.0152
Phenyltri-	37.5	35.09	2.303	0.0116	2.303	0.0115
methylsilane		23.98	2.305	0.0127	2.307	0.0123
w_2 1.0000		16.20	2.308	0.0116	2.311	0.0124
d 0.8538		9.313	2.321	0.0126	2.316	0.0125

Table 6. Continued.

Solution	T°C.	Frequency (G.c./sec.)	ε'_{MEAS}	ε''_{MEAS}	ε'_{CALC}	ε''_{CALC}
Phenyltri-	50	35.09	2.287	0.0117	2.282	0.0110
methylsilane		23.98	2.287	0.0117	2.285	0.0118
w_2 1.0000		16.20	2.289	0.0104	2.289	0.0118
d 0.8425		9.313	2.299	0.0125	2.294	0.0104

Published Work

The following papers have been published from the work reported in this thesis.

1. Conformational Studies of 1,4-Dioxan, 1,4-Dithian and 1,4-Thioxan.
   J. Crossley, A. Holt and S. Walker.
   Tetrahedron, 21, 3141, (1965).

2. Two Relaxation Processes of Cyclopentanone, Tetrahydrofuran and Thiacyclopentane.
   J. Crossley, S.W. Tucker and S. Walker.
   Trans.Far.Soc., 62, 576, (1966).

3. Relaxation Processes of Some Haloethanes in Cyclohexane Solution.
   J. Crossley and S. Walker.
   J.Chem.Phys., 45, 4733, (1966).

Suggestions For Further Work

For the quinoline family of compounds the molecular relaxation times are independent of the direction of the dipole vector within the molecule, and molecular re-orientation is predominantly about the axis perpendicular to the plane of the ring. The extention of this study to include the anthracene analogues i.e. 1-aza-, 2-aza- and 2,3-diaza--anthracene, together with the data for acridine should prove a useful basis for further investigation of the effects which influence molecular relaxation times.

The work reported in chapters 3 and 4 indicated that the microwave method is a useful means of detecting non-rigidity in saturated cyclic systems containing polar groups, especially for molecules which may exist in both polar and non-polar conformations. Relatively large dipole moments ($> 1D$) have been reported for molecules such as thianthrene and 1,4-cyclohexanedione, and measurement of these should indicate whether the dipole moments are related to, either large atomic polarization contributions, or the existence of large proportions of polar conformations. If the latter were true it may be possible to examine the energy barriers between conformational isomers in such ring systems.

The sensitivity of relaxation times to intermolecular forces was well illustrated for the haloethanes in cyclohexane and p-xylene solution, and these results suggest that the work may be usefully extended to include a variety of alkyl-X compounds. Furthermore, by employing compounds with a greater electron donor capacity than p-xylene, a profitable study might ensue.

A collision induced dipole mechanism presents a new area of research, and measurement of a large number of non-polar and weakly polar ($\mu < 0.5D$) aromatic and aliphatic liquids would be invaluable in facilitating a correct assignment of the origin of the absorption, and the factors which influence the relaxation times.

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