Dielectric Studies of Organic Molecules and the Determination of Energy Barriers

by

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Summary

The relaxation times of polar molecules have been determined by the measurement of the dielectric absorption of dilute solutions of the polar solute molecules in a non-polar solvent at microwave frequencies, by a bridge method. The study was applied to molecules that contain rotating polar groups so that a group, as well as a molecular, relaxation time was evaluated. By measuring the relaxation times at several temperatures the enthalpies of activation to molecular and group rotation were determined.

Among the compounds studied was acetophenone, which was examined in three solvents, and for which an energy barrier to acetyl group rotation of approximately 2 kcal/mole was obtained. Several other aromatic and also aliphatic molecules containing acetyl groups were investigated and the resulting relaxation time data correlated with the structures of the compounds. An intensive study was also carried out on aromatic molecules containing methoxy groups and the way in which the group relaxation time and energy barrier to rotation was affected by other substituents in the benzene ring noted.

Dielectric studies have also been made on molecules of the type $X-C_6H_4-X$, where X is a rotating polar group, and for these only group rotation is observed. Since group relaxation is the only relaxation mechanism the relaxation time can be determined with an accuracy of $\pm$ 5% whereas when molecular and group relaxation processes are both taking place

the accuracy is approximately ± 10% on the relaxation times.

In addition to the derivation of the relaxation times of polar molecules the dipole moments have also been determined and these include several for which no previous value existed. The derived dipole moments have proved useful in assessing the distribution of charge within the molecules.

The possible causes of the short relaxation times of diphenylether and its substituted derivatives are discussed. Selected molecules were chosen for study so that an estimation of the most likely causes could be made.

Preface.

The work described in this thesis was carried out at The University of Aston in Birmingham from October 1964 to September 1967 under the supervision of S.Walker M.A., D.Sc., D.Phil., F.R.I.C., whom I would like to thank for his encouragement and many helpful discussions.

I would also like to thank Professor F.M.Page B.A., Sc.D., Ph.D., and A.Holt B.A., B.Sc., Ph.D., F.R.I.C., with whom I have had interesting and useful discussions.

My sincere thanks are also due to M.D.Magee B.Sc., Ph.D., who provided the programmes for the Elliott 803 computer and to Mr.B.K.Morgan for his invaluable technical assistance.

D.B.Farmer.
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Contents.

Chapter 1

Experimental Methods and Basic Theory

1. 1. The Measurement of Dielectric Constant and Loss Factor.

Relaxation of Polarization.[1-5]

Relaxation may be defined as the time lag in the response of a system to a change in the physical forces to which it is subjected and its existence becomes apparent when its rate is not far from the rate of change of the applied forces. If the system under study is a solution of polar molecules in a non-polar solvent and the applied force is an alternating field then, for frequencies greater than about 10^8c/s, there is a time lag between the response of the dipole to the behaviour of the alternating field. The polar molecules of the system under the influence of the field move toward an equilibrium distribution in molecular orientation with a corresponding dielectric polarization. The relaxation time is related to the build up of polarization in a static field by the equation

$$P = P_\infty \left(1 - e^{-t/\tau}\right) \qquad 1.1$$

where P is the orientation polarization at time t, P_∞ is the final orientation polarization when equilibrium has been reached at time $t=\infty$, and τ is the relaxation time. The relaxation time depends upon viscosity of solvent, temperature, size and shape of the molecule and intermolecular forces that may exist between the polar solute molecule and the solvent molecules and is of the order 10^{-12} to 10^{-10} sec for the

molecules studied in this thesis.

In addition to the orientation of the permanent dipoles there will, at microwave frequencies (10^8c/s to 10^{12}c/s), be contributions to the total polarization caused by induced displacements of atoms relative to one another and electrons relative to the positive nuclei. These latter two types of polarization are known as atom and electron polarization respectively. Thus

$$P_T = P_E + P_A + P_O \qquad 1.2.$$

where P_T is the total polarization, P_E is the electron polarization, P_A is the atom polarization and Po is the orientation polarization.

If the frequency is increased to approximately 10^{12}c/s the oscillations of the field will be too fast for the polar molecules to rotate before the field direction is reversed and hence the orientation polarization will be zero. The atom polarization contribution will also disappear if the frequency is increased to approximately 10^{15}c/s and then only the electron polarization will remain. At microwave frequencies the atom and electron oscillations will be in phase with the applied field and therefore there will be no absorption of energy from the field due to these processes. Only rotational relaxation processes are observed and the study of these is the subject of this thesis.

FIG. 1.1 (a) DIAGRAM OF CURRENT (I) AGAINST VOLTAGE (E) OUT OF PHASE BY 90°.

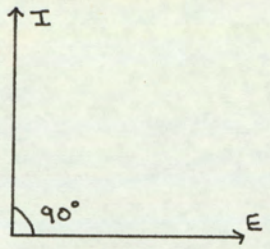


FIG. 1.1 (b) DIAGRAM OF CURRENT (I) AGAINST VOLTAGE (E) OUT OF PHASE BY $(90-\delta)^{\circ}$.

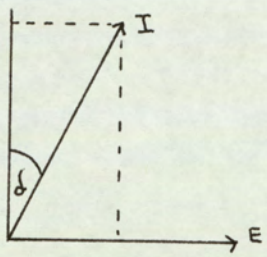
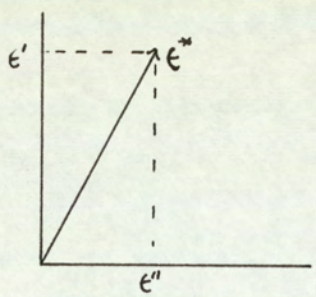


FIG. 1.1 (c) COMPLEX DIELECTRIC CONSTANT (ϵ^*) WITH COMPONENTS THE REAL DIELECTRIC CONSTANT (ϵ') AND LOSS FACTOR (ϵ'').



Dielectric Constant and Loss.

At frequencies less than about 10^8 c/s there is no lag between the orientation of small polar molecules and the variations of the alternating voltage and it follows that the displacement current in the dielectric will be exactly 90^o out of phase with the former, the former leading the latter. In a phase diagram (Fig.1.1.a) it is seen that there is no component of the current (I) in step with the e.m.f. (E) so the Joule heating in the system measured by the product E x I is zero. If the frequency of the applied e.m.f. is continuously increased up to microwave values the rotation of the molecules will, at some stage, begin to lag behind the voltage oscillations and two important effects will accompany this lag. First, owing to the phase displacement, δ, (Fig.1.1.b) in the dipole rotations the current acquires a component ($I \times \sin \delta$) in step with the voltage and a dissipation of energy, as Joule heating, occurs in the medium; secondly, owing to the inability of the dipole to follow the field, the dielectric constant falls to that of a non-polar material which arises solely from the atomic and electronic polarizabilities. It is the first factor which gives rise to the term 'dielectric loss' and the latter to the dispersion of the dielectric constant.

The behaviour of the dielectric constant can also

be represented by a phase diagram (Fig.1.1.c) in which the total or complex dielectric constant (ϵ^*) has two components at those frequencies for which loss occurs in the medium: this is represented by

$$\epsilon^* = \epsilon' - i\epsilon'' \qquad 1.3.$$

where ϵ' is the real dielectric constant, ϵ'' is the loss factor and is a measure of the ability of the medium to dissipate energy and $i=\sqrt{-1}$.

The loss tangent is defined by

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \qquad 1.4.$$

Attenuation and Phase Shift.

The electric field at a given point in the waveguide varies sinusoidally with the angular frequency ω so that it may be represented by the real part of $E_o e^{i\omega t}$ where E_o is the electric field strength at time t=0. The field strength at a distance x down the waveguide is given by

$$E_x = E_o^{i\omega t} e^{-\gamma x} \qquad 1.5.$$

where $\gamma = \alpha^* + i\beta$

or $$E_x = E_o e^{i(\omega t - \beta x)} e^{-\alpha^* x} \qquad 1.6.$$

Thus the phase of the propagated wave changes by βx and its amplitude decreases by the factor $e^{-\alpha^* x}$ as it traverses a length x of the waveguide. Consequently, β is called the phase constant and α^* the attenuation constant.

The units are radians cm^{-1} for β and nepers cm^{-1} for α^*.

Determination of ϵ' and ϵ'' from α^* and β.

The basic equation is

$$\gamma = \alpha^* + i\beta = \frac{2\pi}{\lambda_0}\left[\left(\frac{\lambda_0}{2a}\right)^2 - \epsilon' + i\epsilon''\right] \qquad 1.7.$$

where λ_0 is the wavelength in cm of the radiation in vacuum and 'a' is the inner broad-side width of the cross-section of the waveguide.

From equation 1.7. it can be shown that

$$\epsilon'' = \left(\frac{\lambda_0^2}{4\pi^2}\right) 2\alpha^*\beta \qquad 1.8.$$

$$\epsilon' = (\beta^2 - \alpha^{*2})\frac{\lambda_0^2}{4\pi^2} + \left(\frac{\lambda_0}{2a}\right)^2 \qquad 1.9.$$

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

Apparatus. The Bridge Method.[6,7]

The range of frequency which may be propagated along a waveguide of a given cross-section is summarized in Table 1.1. for the bands used in this work, and the letter employed to designate the band is also given. The small variations of frequency on a particular waveband are barely permissible for accurate measurement of phase shift and attenuation owing to the variable behaviour of the measuring components at the different frequencies. Each band was therefore operated at one frequency.

FIG. 1.2 BLOCK DIAGRAM OF THE BRIDGE APPARATUS

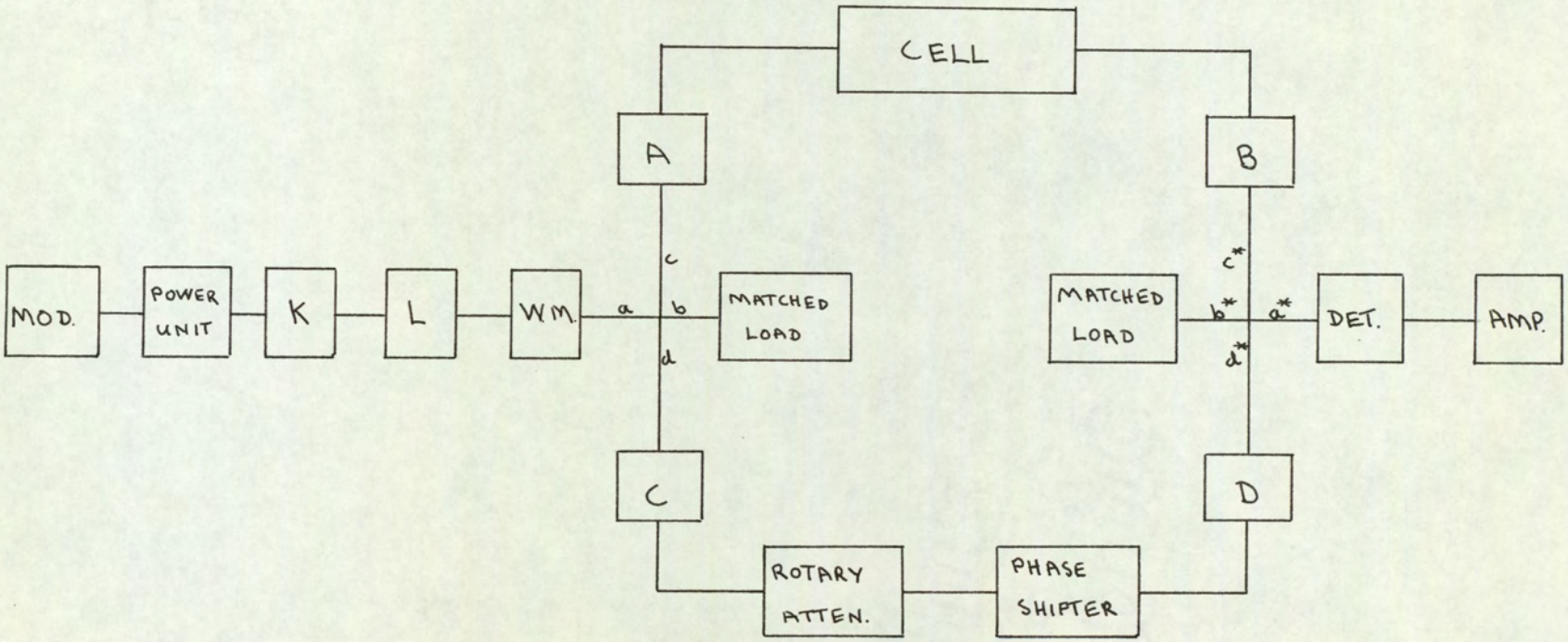


Table 1.1. Waveguide Internal Cross-Section Dimension, Frequency Range of Propagation, Frequency Used and Letter Employed to Characterize Band.

Waveguide internal cross-section dimension (inches)	Frequency range in Gc/s	Frequency employed in Gc/s	Letter characterizing waveband
0.122 x 0.061	60.0-90.0	70	O
0.280 x 0.140	26.5-40.0	34.86 & 35.11	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	6.7	C

A block diagram of the bridge circuit as used for Q, K, P, X, and C bands is given in Fig.1.2. The four arms of each magic T are labelled a, b, c and d. The individual items in the bridge were, excepting the cell, obtained from various manufacturers. The cells were made by the engineers of the Chemistry Department from rectangular waveguide.

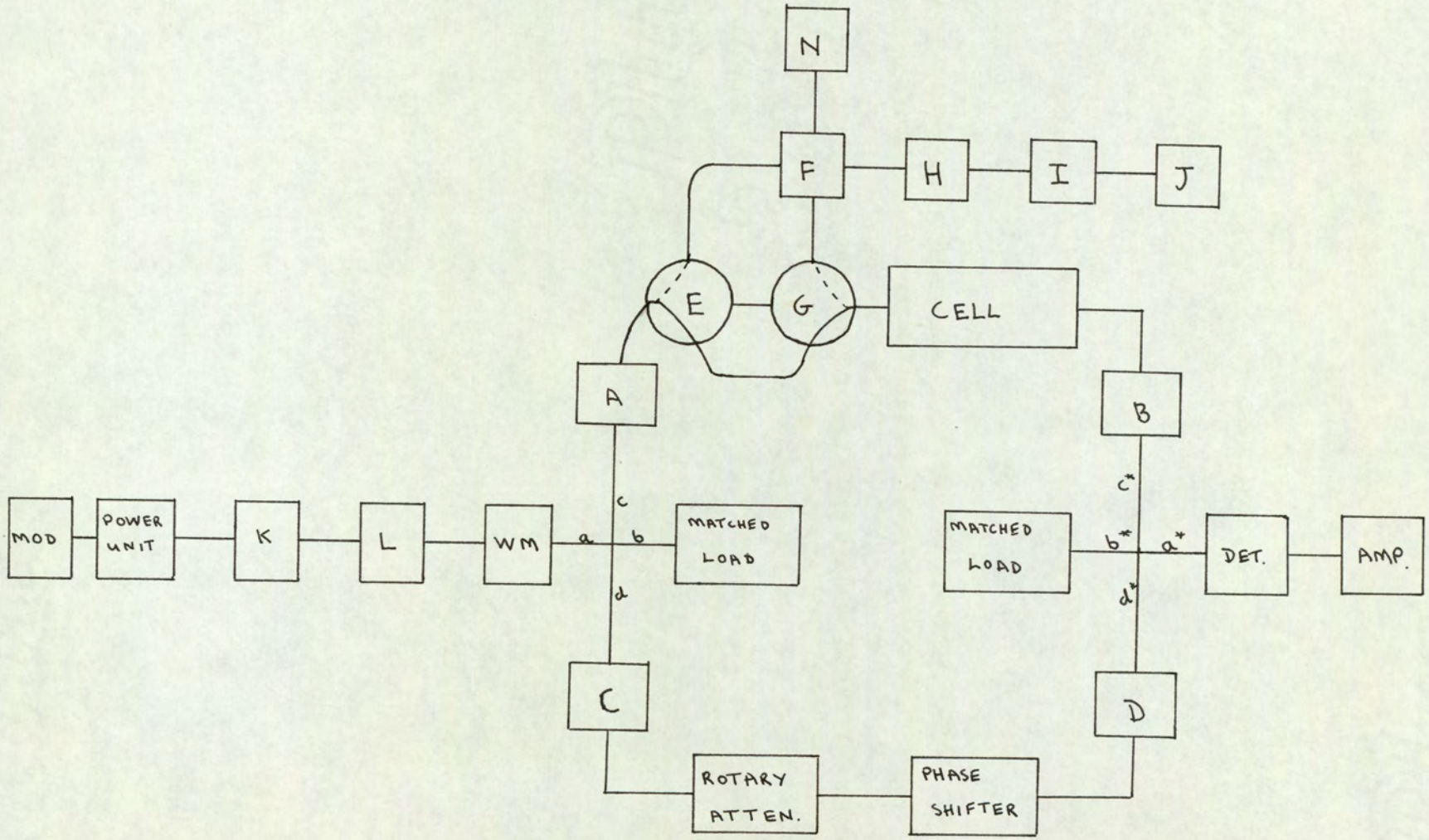
The monochromatic microwave radiation is generated by a klystron (K) (to which square-wave reflector modulation of 1000c/s is applied) and propagated along a rectangular waveguide. The attenuator or isolator (L) protects the klystron from variations of power caused by reflections from other components in the line. It is usual practice to put between 5 and 15 decibels attenuation between the klystron and the load to decouple them. The wavemeter

consists of a subsiduary chamber coupled to the waveguide. The length of this chamber is adjusted in length until it becomes resonant with the frequency of the energy flowing in the waveguide when a decrease in signal is noted inside the guide by a dip of the needle on the amplifier. Since the wavemeter has a calibrated scale the frequency can be read directly and if necessary the klystron can be adjusted to give the frequency that is required.

At 'a' the power is split into two equal halves by the magic T, one half passing through the cell containing the solution and the other half along the side of the bridge through the calibrated variable attenuator and phase shifter. Any power passing along arm 'b' is absorbed with no reflection by the matched load. The polar solution in the cell shifts the phase and attenuates the wave. The procedure is then to alter the phase and attenuation in the other side of the bridge and to achieve the condition in which, when the waves combine, the fields have been restored to equal anti-phase conditions at the junctions of the arms c^* and d^* of the output magic T. With the fields so adjusted the vector sum in output arm a^* is zero and the bridge is balanced. The high gain, low noise amplifier and voltmeter connected to the crystal detector then registers zero reading.

For very dilute solutions, where the attenuation is low, it is particularly desirable to minimise reflections.

FIG. 1.3 BLOCK DIAGRAM OF THE 4·3m.m. BRIDGE APPARATUS



It is found that by the introduction of isolators at points A, B, C and D reflections are minimised. This is assessed by determining the standing wave ratio at 'c*' and 'd*' using a standing wave indicator with minimum probe depth.

The standing wave ratio, ρ , is defined as

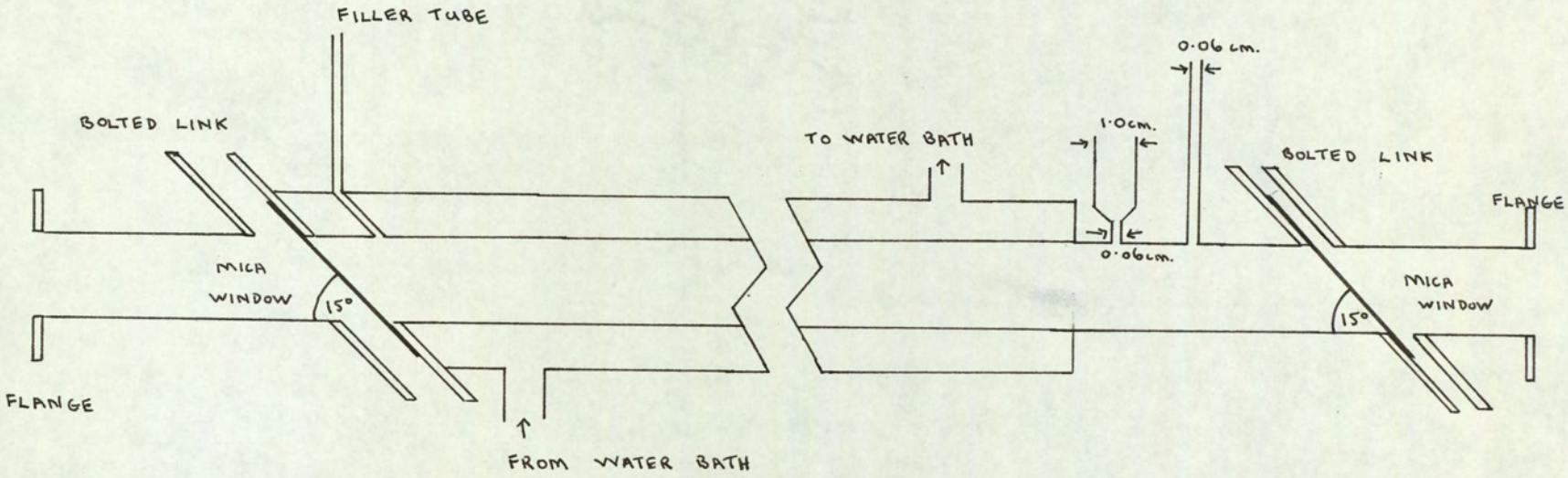
$$\rho = \frac{a_1 + a_2}{a_1 - a_2} \qquad 1.10$$

where a_1 is the amplitude of the incident wave and a_2 that of the reflected wave. Ideally a_2 ought to be zero and ρ equal to 1 but a value of less than 1.1 for ρ is acceptable in practice. Unfortunately the use of a standing wave indicator at 4.3 mm wavelength (O-band) is open to objection for the most accurate measurements. The block diagram of the 4.3 mm bridge circuit is shown in Fig.1.3. where the items E, F, G, H, I, J and N are employed in the assessment of ρ. An impedance meter N is used from which the standing wave ratio may be assessed from

$$\rho = \frac{1+|M|}{1-|M|} \qquad 1.11$$

in which M is the modulus reading on the impedance meter. F is a hybrid-T and when the impedance in the arm FN and FG is equal then the vector sum output in arm FHI is zero; this is detected by the crystal I which is connected to a high gain, low noise amplifier and voltmeter (J). H is a

FIG. 1.4. DIAGRAM OF THE CELL



slide screw tuner which is employed to match I to the magic T. E and G are waveguide switches and the dotted lines indicate the path of a wave when the standing wave ratio is being measured in front of the cell. This is carried out for each length of solution for which the attenuation and phase shift are determined, since for certain lengths of solution the reflections can be appreciable. As the waveguide itself is significantly attenuating, the value of ρ immediately in front of the cell window is not determined. In fact it is the changes of ρ which are followed and any attenuation or phase shift readings corresponding to appreciably higher values of ρ are rejected. The basic bridge circuit is incorporated in the 4.3 mm apparatus and the procedure for determining the attenuation and phase shift readings is identical to that employed for the other bands.

The bridge circuit is set up on a board inclined at $\sim 15^{\circ}$ to the horizontal, the klystron being at the lower end. Basic details of the cell are shown in Fig.1.4. Mica windows are employed of $\sim$0.001 to 0.002 cm thickness and inclined at 15° to the direction of wave propagation so that the electric field component is introduced gradually into the cell and consequently reflections of the wave are minimised.

The cell is surrounded by a water jacket around which water is circulated from a thermostatted bath which

has a temperature control of ± 0.01°C. The cell is filled through a narrow metal tube of 0.03 to 0.06 cm inner diameter which enters the cell-remaining flush with the wall-in the middle of the broad side of the guide close to the bottom window for Q, K and P bands and at the upper end of the cell for X and C bands. The cells are washed with a volatile solvent and dried by blowing air through them from a pump.

A water-jacketted 'Agla' micrometer syringe is employed for filling the cells of O, Q and K bands. The syringe is filled from a water-jacketted container. Due to its small size the O-band cell had to be modified. Additions of solution to the cell are made from an 'Agla' micrometer syringe through a very small hole in the centre of the waveguide at the upper end of the cell. To reduce the amount of liquid creeping up the cell an inclination of $\sim 40^{\circ}$ was employed on the bench supporting the apparatus. A short tube fits close to the bottom window and is sealed by a soldered needle when measurements are being taken. It is unsealed afterwards in order to drain the cell. The cells of P, X and C bands are filled from a grade A burette which is fitted with a water jacket. The burette of P-band is connected to the filler tube by a short length of polythene tubing.

The solution is run in until the mica window is covered. The bridge is balanced and attenuation and

phase shift readings are taken. Enough solution is added to give a phase shift of 360° and the readings are again taken. This is continued until sensitivity is lacking which will vary with the type of solution and its concentration. C-band has a total capacity of ~200 mls and if the solute has a low dipole moment then a comparitively large volume of solute has to be used if measurements on this band are to be made. In cases where only a few mls of solute are available measurements on C-band have to be omitted.

The solution is added in equal amounts to give a 360°phase shift each time because the phase shifter itself introduces attenuation which varies according to the setting. The phase shifter is calibrated by measuring its attenuation at settings of 10° intervals and it is found that for those settings about which small variations in the 360° phase shift occur the attenuation is not significantly altered.

The attenuation in nepers is plotted against the length of added solution in cms. The slope is α^* the attenuation constant. The length of liquid is knowm from the volume added and the cross-section of the waveguide.

The phase shift in radians is plotted against length of added liquid. The slope is β_{MEAS} . The value of β_{MEAS} is not that of the solution, however, because an equivalent volume of air has been displaced and this too

has a significant phase shift.

Thus

$$\beta_{SOLN} = \beta_{MEAS} + \beta_{AIR} \qquad 1.12$$

β_{AIR} is not a constant for any wavelength and is obtained from the equation

$$\beta_{AIR} = \frac{2\pi}{\lambda_g} \qquad 1.13$$

where λ_g is the wavelength in the guide. λ_g is determined from the relationship

$$\left(\frac{1}{\lambda_o}\right)^2 = \left(\frac{1}{\lambda_g}\right)^2 + \left(\frac{1}{\lambda_c}\right)^2 \qquad 1.14$$

where λ_o is the free space wavelength and is determined from the measured frequency of radiation, and λ_c is the cut off wavelength and is equal to twice the inner broad-side width of the waveguide.

From eqn. 1.14, if $\lambda_o = \lambda_c$, then $(1/\lambda_g)^2 = 0$. This means that the guide wavelength is infinitely long and no propagation can take place. For any free space wavelength less than λ_c eqn. 1.14 can be solved for a real value of λ_g and so propagation is possible.

The slopes of the plots were evaluated from the equation of least mean squares

$$\text{Slope} = \frac{\sum xy - \bar{x}\sum y}{\sum x^2 - \bar{x}\sum x} \qquad 1.15$$

where x = volume added, y = attenuation or phase change. ϵ'' and ϵ' were then obtained by substitution of α'' and β_{SOLN}

into equations 1.8 and 1.9. A calculation of ϵ' and ϵ'' from the experimental data by manual methods is very time consuming. A computer programme has therefore been written which calculates ϵ' and ϵ'', from the input data of volume of liquid added, attenuation and total phase change, in a few seconds. An Elliott 803 computer was used for this purpose. A typical example of input data is shown in Table 1.2.

Table 1.2. Example of Input Data, Resulting from Measurements on X-band, for Computer Programmed to Determine ϵ' and ϵ'' .

Number of experimental points (6)

Total volume of solution in cell (mls)	Attenuation (db)	Phase change (deg)
0	2.37	0
13.6	3.85	361
27.2	5.20	724
40.8	6.75	1086.5
54.4	8.08	1447.5
68.05	9.53	1810.5

From this input data the computer calculates ϵ' and ϵ'' to be 2.088 and 0.0364 respectively.

Static Dielectric Constant ϵ_o.

The static dielectric constants were measured at 2 Mc/s using a heterodyne beat apparatus. The instrument used was a Wiss-Tech-Werkstatten Dipolmeter, Type DM01.

The cell was calibrated with air, pure cyclohexane and p-xylene.

Correction Applied to ϵ' and ϵ'' .

The volume of the liquid retained by the filler tube fitted to Q and K bands (see Fig.1.3.) caused a small consistent error in the measurement of the dielectric constant for determinations on these bands. The error in the measured loss factor was negligible. To account for the error on ϵ' the apparent dielectric constant of pure cyclohexane was measured by the microwave bridge method on Q and K bands and subsequent measurements of solutions were corrected by $+\left[\epsilon_{o\,\text{cyclohexane}} - \epsilon'_{\text{cyclohexane}}\right]$. These corrections to ϵ'_{MEAS} were +0.012 and +0.005 on Q and K bands respectively.

1,4-Dioxan, p-xylene and carbon tetrachloride had small but detectable dielectric absorption and corrections for this were made to measurements on solutions employing these solvents. The dielectric constants and loss factors of the same batch of solvents as used in making the solutions were determined at the same temperature and frequency used for the subsequent solution measurements. The measured dielectric constants and loss factors of the solutions were then corrected by $+\left[\epsilon_{o\,\text{solvent}} - \epsilon'_{\text{solvent}}\right]$ and $-\epsilon''_{\text{solvent}}$ respectively, where $\epsilon'_{\text{solvent}}$ and $\epsilon''_{\text{solvent}}$ were determined at the same frequency as the solution values.

Density.

The densities of the solution, when required, were determined using a pyknometer similar to that employed by Cumper, Vogel and Walker.[8] Its volume was about 10 ml and the weights were reproducible to 0.1 mg.

Refractive Index.

The refractive indices were measured on a Bellingham and Stanley refractometer of the Pulfrich type reading to ± 0.00001.

Infrared Spectra.

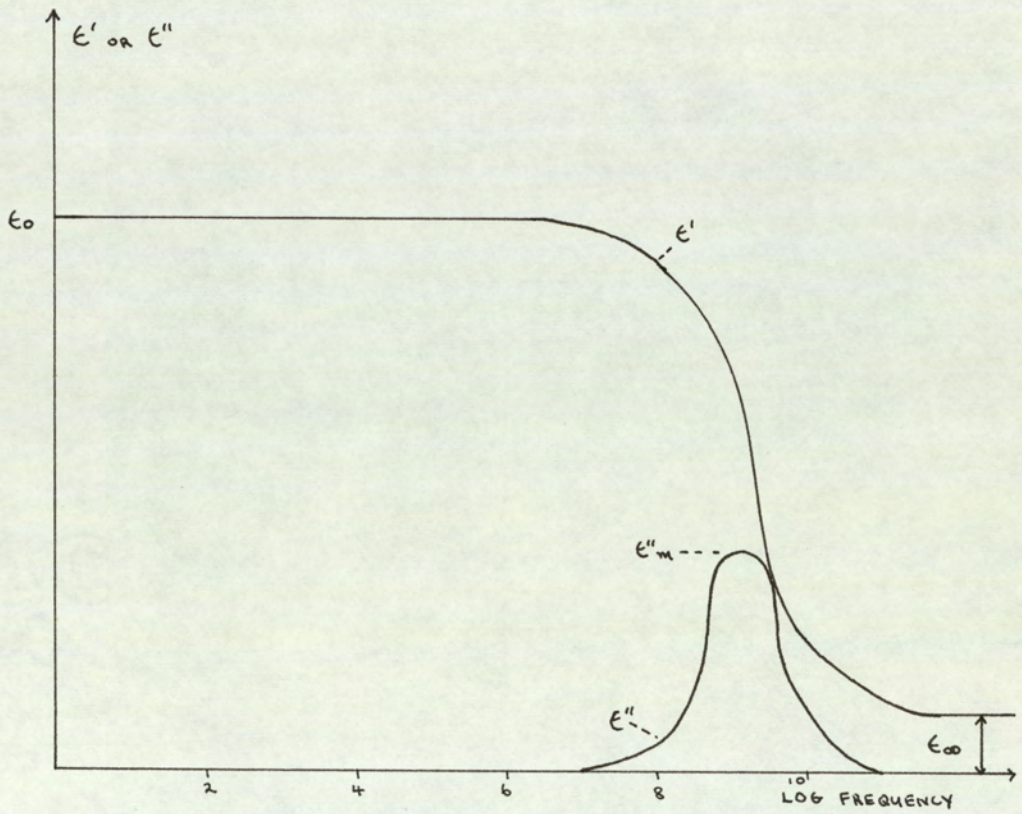
The infrared spectra were recorded on a Perkin-Elmer 225 Grating Infrared Spectrophotometer.

1.2. Representation and Analysis of Dielectric Data.

The dependence of dielectric constant and loss on the frequency of measurement was first treated by Debye.[9] In this theory the difference between the values ϵ_o (the static dielectric constant at low frequencies) and ϵ_∞ (the smaller limiting value at higher frequencies) is attributed to dipole polarization. The orientation of polar molecules in an alternating current field is opposed by the effects of thermal agitation and molecular interactions. Debye represents the second effect in terms of viscous damping, the molecules being regarded as spheres in a continuous medium. The theoretical analysis in this case leads to the equation

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_o - \epsilon_\infty}{1 + i\omega\tau} \qquad 1.16$$

FIG. 1.5. DEPENDENCE OF DIELECTRIC CONSTANT (ϵ') AND LOSS FACTOR (ϵ'') UPON THE LOGARITHM OF FREQUENCY.



which can be written

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_o - \epsilon_\infty} = \frac{1}{1+(\omega\tau)^2} \qquad 1.17$$

$$\frac{\epsilon''}{\epsilon_o - \epsilon_\infty} = \frac{\omega\tau}{1+(\omega\tau)^2} \qquad 1.18$$

where ω is the angular frequency and τ is the relaxation time.

From eqn. 1.18 it can be shown that ϵ'' approaches zero both for small and for large values of $\omega\tau$ while it is a maximum if

$$\omega\tau = 1 \qquad 1.19$$

For this value of $\omega\tau$ eqn. 1.18 gives

$$\epsilon''_m = \frac{\epsilon_o - \epsilon_\infty}{2} \qquad 1.20$$

and 1.17 gives

$$\epsilon'_m = \frac{\epsilon_o + \epsilon_\infty}{2} \qquad 1.21$$

Eqn. 1.17 requires that ϵ' decrease from ϵ_o to ϵ_∞ with increasing frequency and eqn. 1.18 requires that ϵ'' change from a small value through a maximum, such that $\omega\tau = 1$, to a small value again. The frequency dependence given by eqns. 1.17 and 1.18 is represented graphically in Fig.1.5. The experimental data are not readily analysed by such a representation, however, due to the difficulty in assessing the maximum of the ϵ'' against log frequency curve when the

FIG. 1.6.a. COLE-COLE PLOT FOR A SYSTEM CHARACTERIZED BY ONE RELAXATION TIME.

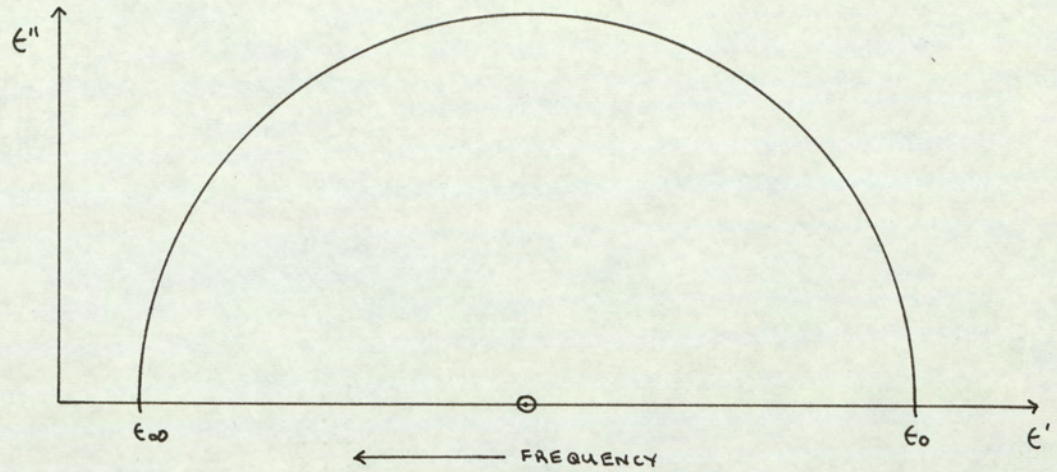
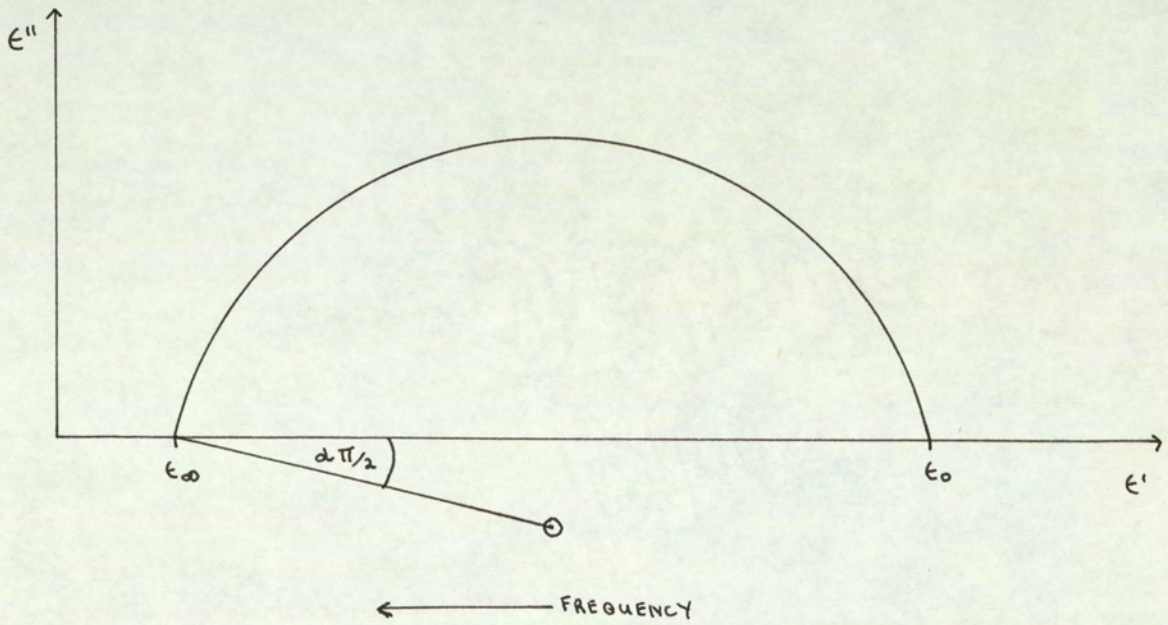


FIG. 1.6.b. COLE-COLE PLOT FOR A SYTEM CHARACTERIZED BY A DISTRIBUTION OF RELAXATION TIMES.



experimental points are not evenly distributed about the maximum. A more convenient representation of the dielectric data is obtained from a consideration of the equation derived from the combination of eqns. 1.17 and 1.18 and eliminating $\omega\tau$ between them, viz

$$(\epsilon'')^2 + \left[\epsilon' - \frac{(\epsilon_0 + \epsilon_\infty)}{2}\right]^2 = \left[\frac{(\epsilon_0 - \epsilon_\infty)}{2}\right]^2 \qquad 1.22$$

Here ϵ' and ϵ'' are values of those variables at the same frequency. The equation is of the form $x^2 + y^2 = r^2$ i.e. it represents a semi-circle. A plot of ϵ'' against ϵ' is known as the Cole-Cole plot.[10] For systems characterized by a single relaxation time the centre of the semi-circle lies on the abscissa (Fig.1.6.a). In many cases however the centre of the semi-circle is found to lie below the abscissa axis and the diameter drawn through the centre from the ϵ_∞ point makes an angle $\alpha\pi/2$ radians with the abscissa axis (Fig.1.6.b). In these cases the dielectric data is not represented by a single relaxation time but by a distribution of relaxation times. A useful empirical formula due to Cole and Cole[10] is

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} \qquad 1.23$$

where τ_0 is the mean or most probable relaxation time and α (the distribution constant) is a numerical factor with values between 0 and 1 measuring the departures from a single relaxation time (i.e. $\alpha = 0$). From eqn. 1.23 the

real and imaginary parts, ϵ' and ϵ'', of the complex dielectric constant as a function of frequency are given by

$$\epsilon' - \epsilon_\infty = \frac{(\epsilon_0 - \epsilon_\infty)\left[1 + (\omega\tau_0)^{1-\alpha} \sin\left(\alpha\frac{\pi}{2}\right)\right]}{1 + 2(\omega\tau_0)^{1-\alpha} \sin\left(\alpha\frac{\pi}{2}\right) + (\omega\tau_0)^{2(1-\alpha)}} \qquad 1.24$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)(\omega\tau_0)^{1-\alpha} \cos\left(\alpha\frac{\pi}{2}\right)}{1 + 2(\omega\tau_0)^{1-\alpha} \sin\left(\alpha\frac{\pi}{2}\right) + (\omega\tau_0)^{2(1-\alpha)}} \qquad 1.25$$

Equations 1.24 and 1.25 reduce to the Debye expression for $\alpha = 0$. For values of 'α' greater than zero the dispersion region is broader and the maximum value of ϵ'' corresponding to $\omega\tau = 1$ is decreased. τ_0, α, and ϵ_∞ are evaluated by using a computer programme, incorporating eqns. 1.24 and 1.25, which minimises the square of the difference between the calculated values of ϵ' and ϵ'' and the experimental values at the same frequency.

Equations 1.24 and 1.25 assume a symmetrical distribution of relaxation times around a most probable value. A number of mean relaxation times, however, have been observed which are much shorter than would be estimated for molecular rotation alone and this shortening has therefore been attributed to a contribution from an intra-molecular or group relaxation process with a short relaxation time in addition to the normal orientation process. This shortening of the mean relaxation time below that expected for molecular rotation is one of the main criteria in assessing whether the molecule is non-rigid.

For systems that have several discrete relaxation times contributing to the dielectric absorption Budó[11] has shown that the complex reduced dielectric constant should have the form

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_{i=1}^{\infty} \frac{C_i}{1 + i\omega\tau} \qquad 1.26$$

where Ci is the relative weight of the contribution of each relaxation process of relaxation time τ_i to the dielectric absorption as a whole and

$$\sum C_i = 1 \qquad 1.27$$

Hence, for systems with two mutually independent relaxation times the dielectric data may be represented by the equations

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{C_1}{1 + (\omega\tau_1)^2} + \frac{C_2}{1 + (\omega\tau_2)^2} \qquad 1.28$$

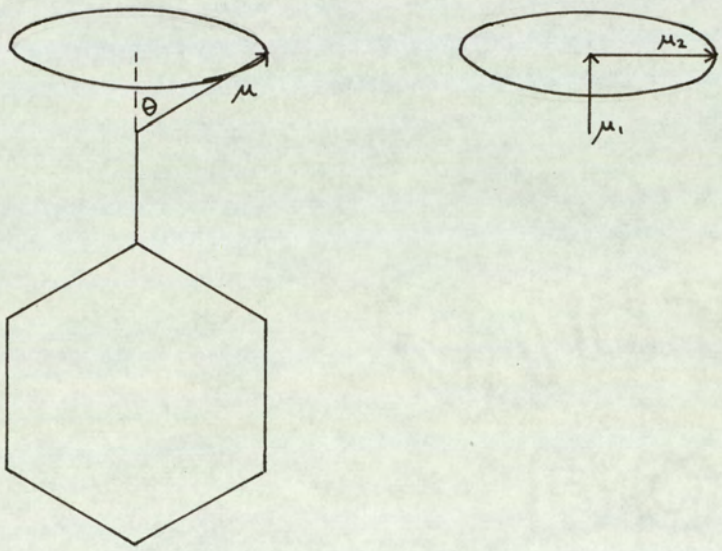
$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{C_1\omega\tau_1}{1 + (\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1 + (\omega\tau_2)^2} \qquad 1.29$$

where τ_1 is the molecular relaxation time, τ_2 is the group relaxation time and C_1 and C_2 are the relative weights of each relaxation term where $C_1 + C_2 = 1$. Bergmann[12,13] has proposed a graphical method, incorporating eqns. 1.28 and 1.29, for determining τ_1, τ_2, and C_1 from the dielectric data. An alternative procedure, and the one that has been used most often in this study, is to insert estimates of τ_1, τ_2 and C_1 together with the dielectric experimental data into a computer programmed to evaluate ϵ' and ϵ'' from eqns.

1.28 and 1.29. The computer then continuously minimises the square of the difference between calculated and measured values of ϵ' and ϵ'' until a minimum deviation is reached. Values of τ_1, τ_2 and C_1 corresponding to this minimum deviation are then outputted.

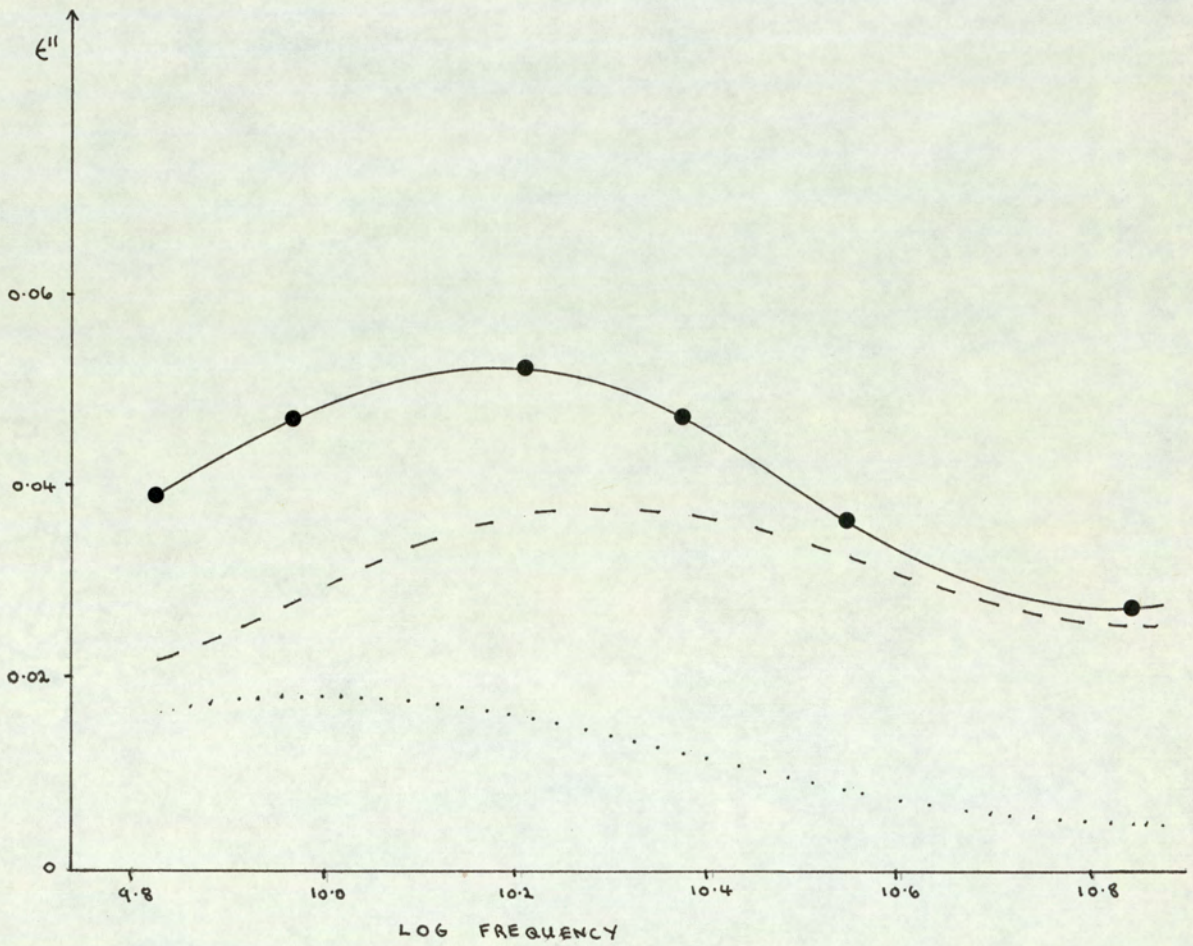
Fig.1.7. represents a molecule whose resultant dipole moment (μ) is not along a symmetry axis.

Fig.1.7. Molecular Dipole Moment (μ) and its Two Components (μ_1 and μ_2) for a Molecule where the Molecular Dipole Moment is not along a Symmetry Axis.



In this particular case the molecule consists of a polar group attached to a benzene ring. If the moment (μ) subtends an angle θ with the $C_1 - C_4$ axis of the molecule then it can be resolved into two components (i) $\mu_1 = \mu \cos\theta$ along the $C_1 - C_4$ axis (ii) $\mu_2 = \mu \sin\theta$ perpendicular to this axis. The component μ_1 is associated with molecular rotation and,

FIG. 1.8 EXPERIMENTAL LOSS CURVE (—), CALCULATED LOSS CURVE DUE TO MOLECULAR RELAXATION CONTRIBUTION (····), CALCULATED LOSS CURVE DUE TO INTRAMOLECULAR RELAXATION CONTRIBUTION (---) FOR ACETOPHENONE IN CYCLOHEXANE AT 25°C.



if group relaxation can take place, μ_2 with group rotation. The weight factors are related to these dipole components and the resultant dipole moment by the equations[14]

$$C_1 = \left(\frac{\mu_1}{\mu}\right)^2 \qquad 1.30$$

$$C_2 = \left(\frac{\mu_2}{\mu}\right)^2 \qquad 1.31$$

From 1.30 and 1.31

$$\frac{C_1}{C_2} = \left(\frac{\mu_1}{\mu_2}\right)^2 \qquad 1.32$$

Hence if θ is evaluated and μ is known then C_1 and C_2 may be determined. If $\theta = 90^\circ$ then $\mu_1 = 0$ and hence $C_2 = 1$ and only group relaxation will be observed. For many of the molecules examined in this work θ has been evaluated by either a vector summation of the individual bond moments or from a consideration of the dipole moments of the para-substituted derivatives of the compound in question. Examples of the use of these methods in determining θ are given in the relevant chapters.

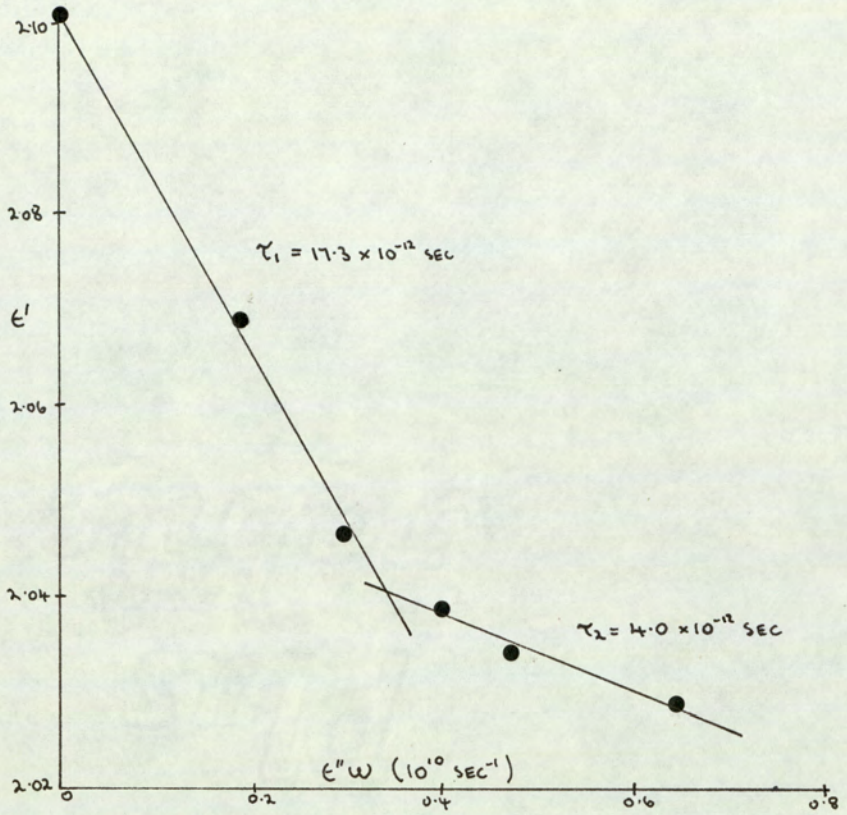
Fig.1.8. represents the relative contributions to the total dielectric loss from the molecular and intra-molecular processes in the form of an ϵ'' against log frequency curve. The individual losses are calculated from the equations

$$\frac{\epsilon_1''}{\epsilon_0 - \epsilon_\infty} = \frac{C_1 \omega \tau_1}{1 + (\omega \tau_1)^2} \qquad 1.33$$

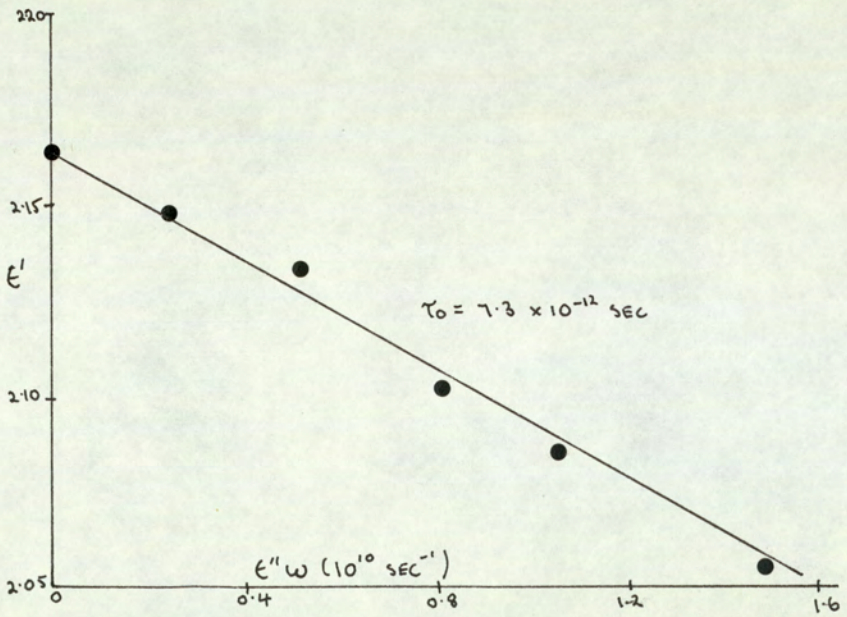
FIG. 1.9. PLOTS OF ϵ' AGAINST $\epsilon'' w$

(a) METHOXY PENTAFLUOROBENZENE IN CYCLOHEXANE AT 25°C

$w_2 = 0.03781$



(b) p-DIMETHOXYBENZENE IN CYCLOHEXANE AT 25°C. $w_2 = 0.06586$



$$\frac{\epsilon''_2}{\epsilon_0 - \epsilon_\infty} = \frac{C_2 \omega \tau_2}{1+(\omega \tau_2)^2} \qquad 1.34$$

for the system acetophenone in cyclohexane at 25°C where $\tau_1 = 17.2 \times 10^{-12}$ sec, $\tau_2 = 7.8 \times 10^{-12}$ sec, $C_1 = 0.33$ and $\epsilon_0 - \epsilon_\infty = 0.1142$.

An alternative graphical method of interpreting the dielectric data has been suggested by Cole.[15] The real and imaginary parts of eqn.1.16 obtained after multiplication by $(1+i\omega\tau)$ yield the equations

$$\epsilon' = \epsilon_0 - \tau(\epsilon''\omega) \qquad 1.35$$

$$\epsilon' = \epsilon_\infty + (1/\tau)(\epsilon''/\omega) \qquad 1.36$$

Equation 1.35 is more useful since it makes use of ϵ_0 which is known with considerable accuracy. From eqn.1.35 it can be seen that a plot of ϵ' against $\epsilon''\omega$ is of slope $-\tau$. Examples of this type of plot are shown in Fig.1.9. If two dispersion regions exist then a plot of ϵ' against $\epsilon''\omega$ gives two straight lines with relaxation times τ_1 and τ_2 corresponding to the two slopes. The value of τ_1 obtained is usually low while that of τ_2 is high because of the effect of the overlap of the two absorption regions on the slopes of the two lines.[16] This method of evaluating τ_1 and τ_2 also appears to be less accurate than that employing eqns.1.28 and 1.29 and has not been used extensively in this thesis.

In the previous description of relaxation times

it has been assumed that $\mu_2 (= \mu \sin\theta)$ is to be associated only with group rotation and that no molecular relaxation occurs about the projection of the $C_1 - C_4$ axis. Fong,[17] however, has suggested that molecular, as well as group, relaxation can occur about this axis and that therefore τ_2 as derived from equations 1.28 and 1.29 is not the true group relaxation time. He suggests that both molecular and intramolecular mechanisms are occuring simultaneously in the orientation of μ_2 and that the true group relaxation time (τ_g) should be derived from the equation

$$\frac{1}{\tau_2} = \frac{1}{\tau_1} + \frac{1}{\tau_g} \qquad 1.37$$

The equation in this form appears erroneous however since if $\tau_1 = \tau_g$ then $\tau_2 = \tau_1/2$ i.e. the observed relaxation time is only half that resulting from each of the two contributing processes. Use of the equation[11, 18-20]

$$\frac{1}{\tau_2} = \frac{1}{2}\left(\frac{1}{\tau_1} + \frac{1}{\tau_g}\right) \qquad 1.38$$

will remove this anomaly since if $\tau_1 = \tau_g$ then $\tau_2 = \tau_1$. However, it is unlikely that two relaxation processes could occur about the same axis since the process with the shorter relaxation time would require a smaller free energy of activation for the orientation process. For molecular relaxation to take place about the $C_1 - C_4$ axis the group would have to be held rigidly in place during the molecular relaxation period. This would seem unlikely if τ_2 was

less than τ_1 as is normally the case. Considering these objections to the use of eqns. 1.37 and 1.38 and the fact that the bulk of relaxation time data in the literature in recent years has been in the τ_1, τ_2 form it has been felt undesirable to modify τ_2 and therefore this is taken as the group relaxation time.

Molecular Relaxation Time and Internal Field.

The macroscopic relaxation time is the relaxation time obtained from the Cole-Cole arc plot. Debye[9] related the macroscopic relaxation time (τ_m) to the molecular or microscopic relaxation time (τ_μ) by the expression

$$\tau_m = \frac{\epsilon_o + 2}{\epsilon_\infty + 2} \cdot \tau_\mu \qquad 1.39$$

Powles,[21] and later Glarum,[22] obtained the relation

$$\tau_m = \frac{3\epsilon_o}{2\epsilon_o + \epsilon_\infty} \tau_\mu \qquad 1.40$$

Experimental measurements by Miller and Smyth[23] showed this relationship to be approximately true.

In the case of dilute solutions of polar compounds in non-polar solvents the difference $(\epsilon_o - \epsilon_\infty)$ is about 0.2 or less. This leads to a correction in eqn. 1.40 which is less than the experimental error in the macroscopic relaxation time. Therefore the difference in τ_m and τ_μ has been neglected and no internal field corrections have been applied to the relaxation times.

Dielectric Relaxation as a Chemical Rate Process.

The rate at which the portion of the dielectric polarization arising from the orientation of dipoles comes into equilibrium with an applied field is found to change considerably with temperature. In all the systems examined both the molecular and intramolecular relaxation times are found to shorten with an increase in temperature. This suggests that a molecule or group is forced to wait until it has acquired, by thermal fluctuations, a considerable amount of energy in excess of the average thermal energy in the medium before it can rotate from one equilibrium position to another. At higher temperatures more energy will be available and therefore the time required to reach equilibrium with the applied field will be shorter. The energy barrier separating the two mean equilibrium positions has been related to the relaxation time by a rate expression derived from transition state theory as[4,24]

$$\frac{1}{\tau} = \kappa \frac{kT}{h} e^{-\Delta G^{\ddagger}/RT} \qquad 1.41$$

where h is the Planck constant, $\Delta G^{\ddagger}$ is the molar free energy of activation for dipole relaxation, T is the absolute temperature and κ is the transmission coefficient normally taken to be 1 and corresponds with the case of the re-orienting unit which each time it is excited to the top of the energy barrier continues to move in the same direction. Plots of $\Delta G^{\ddagger}$ against τ, deduced from eqn.1.41, are shown in

FIG. 1.10. PLOT OF FREE ENERGY OF ACTIVATION ($\Delta G^{\ddagger}$) AGAINST RELAXATION TIME (τ) AT 15°C AND 60°C.

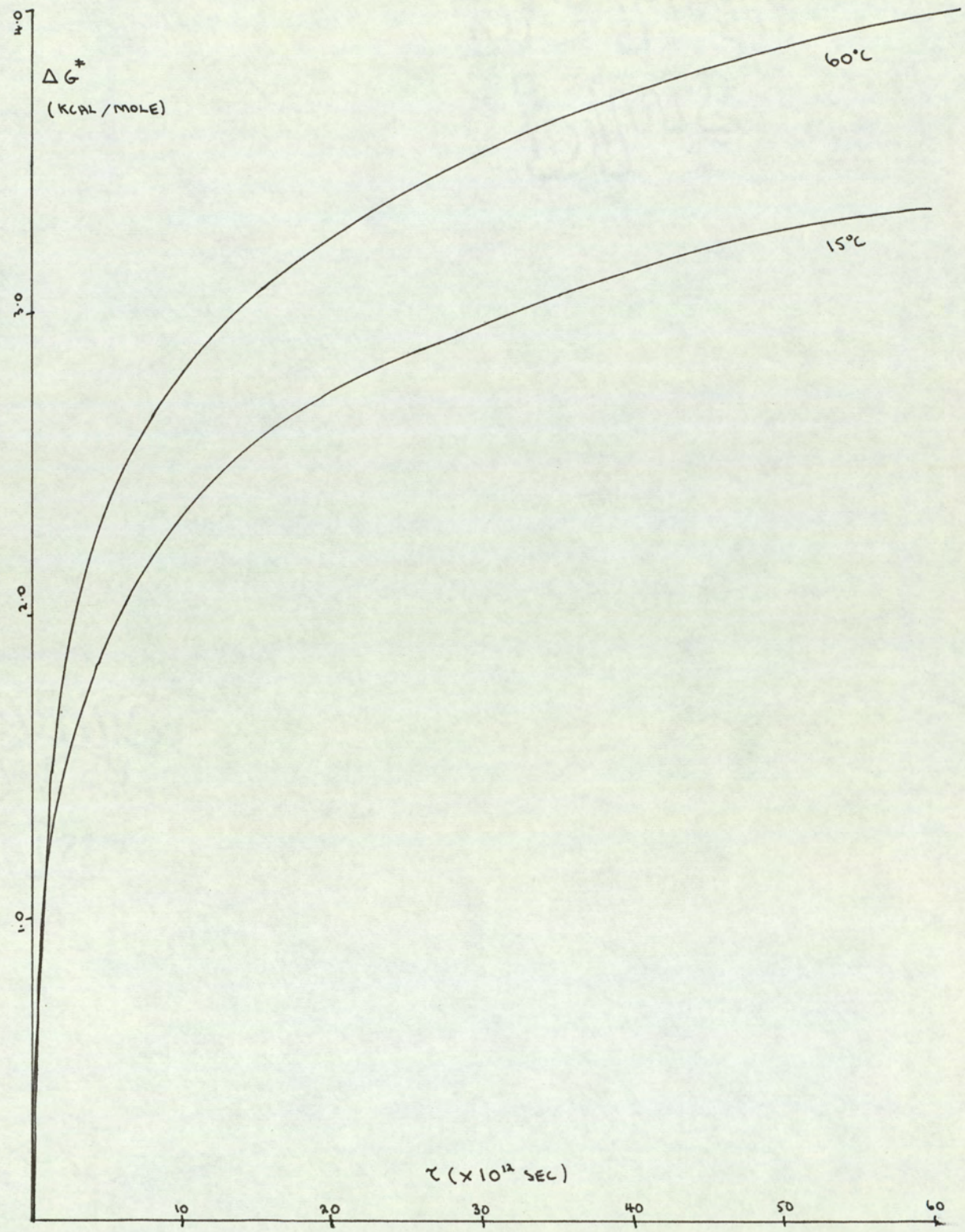


Fig.1.10 for temperatures of 15 and 60°C.

Since

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}, \qquad 1.42$$

at constant pressure, eqn.1.41 may be rewritten

$$\tau = \frac{h}{kT} e^{\Delta H^{\ddagger}/RT} e^{-\Delta S^{\ddagger}/R} \qquad 1.43$$

where $\Delta H^{\ddagger}$ is the enthalpy and $\Delta S^{\ddagger}$ the entropy of activation for dipole relaxation. Differentiation of eqn.1.43 leads to

$$\log_{10} \tau T = \frac{1}{T} \frac{\Delta H^{\ddagger}}{2.303R} + \left[\log_{10} \frac{h}{k} - \frac{\Delta S^{\ddagger}}{2.303R} \right] \qquad 1.44$$

Hence a plot of $\log_{10} \tau T$ against $1/T$ is a straight line of slope $\Delta H^{\ddagger}/2.303R$ and therefore $\Delta H^{\ddagger}$ is determined. Since $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ are both now known $\Delta S^{\ddagger}$ may be determined from eqn.1.42.

If both molecular and group relaxation processes are present then the enthalpy of activation for each of these processes may be determined from the appropriate $\log \tau T$ against $1/T$ plot. The energy barrier to molecular rotation may be attributed to viscous friction and intermolecular forces. Group rotation will also meet an energy barrier due to viscous friction and intermolecular forces but there may be additional effects present which will raise the energy barrier. These could include conjugation of the π-electrons in the group with those of the benzene nucleus, steric hindrance to group rotation and intramolecular hydrogen bonding.

The barrier heights of re-orientating polar groupings in model compounds which are related to the corresponding polymers could well have an important influence on the glass transition temperature (Tg) in the polymers. Tg is a fundamental parameter in characterizing a polymer and it is desirable to be able to predict the effect on the magnitude of Tg when the molecular structure is modified. Therefore an accurate determination of ΔH_2^*, the enthalpy of activation to group rotation, could be extremely useful in helping to achieve this aim.

Small negative values have been observed for the entropies of activation and this can be attributed to an activated state showing an increased order (e.g. mutual alignment of the molecules).

Dipole Moments.

For solutions of high weight fraction (ω_2), the apparent dipole moments have been evaluated from the Debye equation

$$\mu = 0.012812 \left[\frac{3T(\epsilon_0 - \epsilon_\infty)}{c(\epsilon_0+2)(\epsilon_\infty+2)} \right]^{\frac{1}{2}} \qquad 1.45$$

in which c is the concentration in moles/ml and T the absolute temperature.

$$c = \frac{\omega_2 d_{12}}{M_2} \qquad 1.46$$

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

For dilute solutions, the dipole moments have been evaluated by extrapolation to infinite dilution at which

$$(\epsilon_0 + 2)(\epsilon_\infty + 2) = (\epsilon_1 + 2)^2 \qquad 1.47$$

and $d_{12} = d_1$, where ϵ_1 is the static dielectric constant of the solvent and d_1 the density of the solvent. Eqn.145 then becomes

$$\mu = 0.012812 \left[\frac{3T(\epsilon_0 - \epsilon_\infty) M_2}{(\epsilon_1 + 2)^2 \omega_2 d_1} \right]^{1/2} \qquad 1.48$$

This procedure, unlike the Halverstadt-Kumler[25] or Guggenheim[26] approaches, does not involve any atomic polarization approximations and may therefore explain the tendency to obtain slightly lower moments by the microwave procedure.

1.3. Purification of Materials.

Solvents.

The distillation of all solvents was through a two foot column packed with glass rings. Cyclohexane, p-xylene and 1,4-dioxan were purified by refluxing over sodium followed by distillation. They were stored in well closed amber bottles over sodium wire.

Carbon tetrachloride and decalin were first of all dried , and then distilled, over anhydrous calcium chloride and 15% of the volume was rejected as a first fraction.

Solutes.

The purification of solutes is summarized in Table 1.3. The solutes are listed in subsections (a) to (d) each of which contains the compounds discussed in Chapters 2 to 5 respectively of this thesis.

Liquids were dried over a suitable drying agent when necessary and distilled on a 30 theoretical plate spinning band column. A small, constant boiling point, centre fraction was collected and the purity confirmed by gas-liquid chromatography.

Solids were recrystallised twice or until a constant melting point was obtained. They were dried over a suitable agent in a vacuum dessicator.

Table 1.3. Purification of Solutes.

Solute	Solid Solvent for recrystallisation	M.Pt. (°C)	Liquid Drying Agent	B.Pt. (°C)
a) Acetophenone			$MgSO_4$	202
ω,ω,ω-Trifluoro-acetophenone			$MgSO_4$	152
4-Acetylpyridine				211
Cyclohexylmethyl-ketone				180
p-Methoxyacetophenone	Petroleum Ether	37		
2-Acetonaphthone	Petroleum Ether	56		
b) Anisole			$CaSO_4$	152

Solute	Solid		Liquid	
	Solvent for recrystallisation	M.Pt. (^{o}C)	Drying Agent	B.Pt. (^{o}C)
p-Bromoanisole			$CaSO_4$	212
p-Methylanisole			$CaSO_4$	175
Methoxypentafluoro-benzene			$CaSO_4$	152
Pentafluorobenzene				85
Difluoromethyl phenyl ether	Pure sample submitted by R.A.E. Farnborough			
Difluoromethyl pentafluorophenyl ether	''	''	''	
2-Methoxynaphthalene	Absolute Ethanol	72		
Trifluoromethoxy-benzene				102
c)4-Benzoylpyridine	Petroleum Ether	72		
Benzophenone	Petroleum Ether	49		
Decafluorobenzo-phenone	Petroleum Ether	90		
Diethylether			Na wire	34
Diethylketone			$MgSO_4$	99
Dicyclohexylketone				161/25mm
m-Dibenzoylbenzene	Petroleum Ether	103		
d)p-Dimethoxy-benzene	Petroleum Ether	55		
α,α'-Dichloro-p-xylene	Petroleum Ether	98		

Solute	Solid Solvent for recrystallisation	M.Pt. (°C)	Liquid Drying Agent	B.Pt. (°C)
p-Diacetylbenzene	Absolute Ethanol	112		
Benzyl chloride			Na_2SO_4	177
p-phenylenediamine	Absolute Ethanol	147		
p-Dibenzoylbenzene	Petroleum Ether	160		
Dibenzoyl	Petroleum Ether	95		
Diacetyl			$MgSO_4$	90
Tetrafluorohydro-quinone	Used as received from manufacturer			

1.4. Assessment of the Bridge Apparatus.

An assessment of the accuracy of measurements on a number of the bands has been made previously.[7,27] The results obtained from these measurements were found to be in good agreement with existing values in the literature.

One of the main sources of error in determining the relaxation times and dipole moments of polar molecules by the microwave bridge method is in the evaluation of ϵ_∞. This especially applies to systems which have short relaxation times and for which the experimental points obtained will lie on the right hand side of the Cole-Cole plot making a long extrapolation to ϵ_∞ necessary. In order to minimise this source of error a bridge method has been developed at the relatively low wavelength of 4.3mm

(O-band). The length of extrapolation on the Cole-Cole plot to obtain ϵ_∞ is therebye considerably reduced by having a point at this wavelength .

The 4.3 mm bridge apparatus has been described earlier in this chapter. The main procedure employed to assess the O-band ϵ'' and ϵ' values has been to examine whether it lay on the Cole-Cole plot expressed in the form of a'' (ordinate axis) against a' (abscissa) in which a'' is the slope of ϵ'' against ω_2 (weight fraction of solute) and a' the slope of ϵ' against ω_2 where the slopes are determined by the method of least mean squares. The relevant equations for the parameters in this form of the Cole-Cole plot are

$$\epsilon'' = a'' \omega_2 \qquad 1.49$$

$$\epsilon' = \epsilon_1 + a' \omega_2 \qquad 1.50$$

$$\epsilon_0 = \epsilon_1 + a_0 \omega_2 \qquad 1.51$$

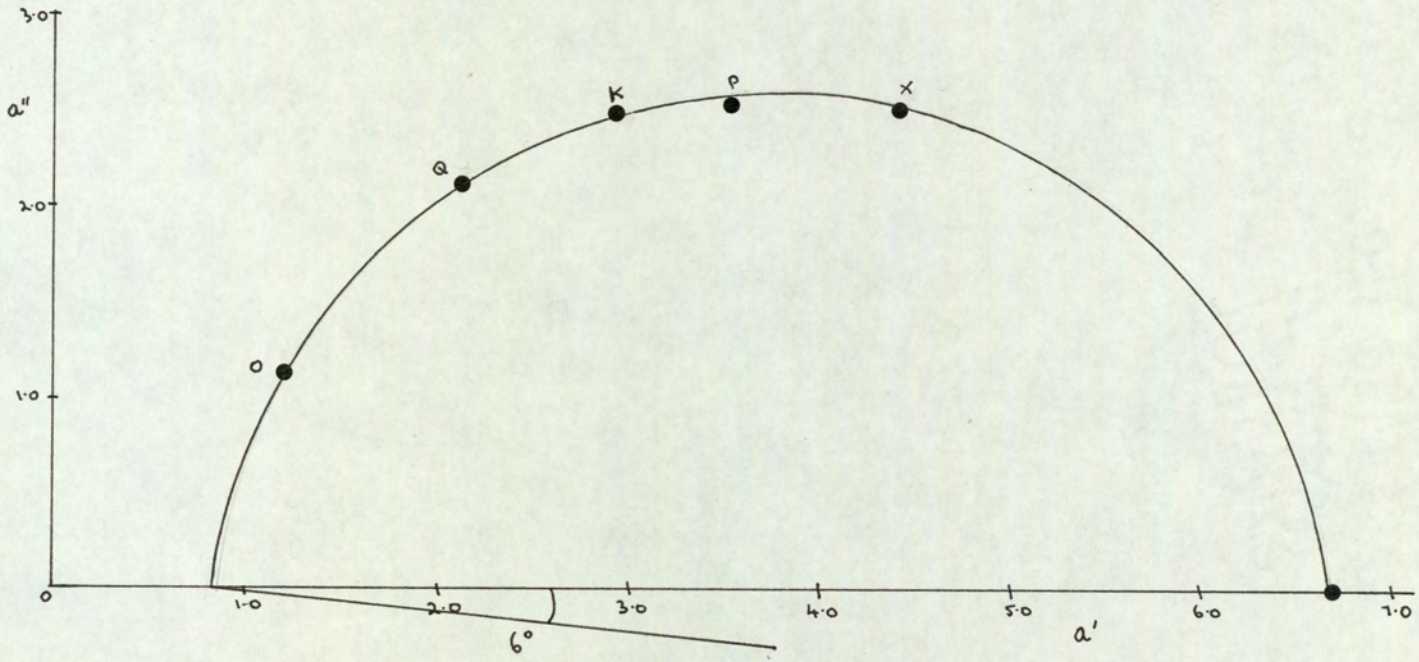
These equations apply to dilute solutions of a polar solute in a non-polar solvent.

In order to check whether the Cole-Cole plot itself is satisfactory, the electric dipole moment is evaluated from the equation

$$\mu = \left[\frac{27\, kT\, M_2 (a_0 - a_\infty)}{4\pi N d_1 (\epsilon_1 + 2)^2} \right]^{\frac{1}{2}} \qquad 1.52$$

where the symbols have their usual meaning.

FIG 1.11. COLE-COLE PLOT FOR ACETOPHENONE IN CYCLOHEXANE AT 25°C.



The dielectric absorption of acetophenone in cyclohexane was measured at 25°C on O, Q, K, P and X bands by the bridge method and the results are given in Fig.1.11 in the $\alpha'' - \alpha'$ form of a Cole-Cole plot. Eight solutions were employed in each of these determinations of α', α'' and α_o.

It is seen that the O-band point falls on the Cole-Cole plot established by measurements at several wavelengths which therefore suggests that the method is successful. The computed mean relaxation time (τ_o) of 10.7×10^{-12}sec compares with a value in benzene of 11.8×10^{-12}sec at the same temperature[19] and in carbon tetrachloride of 11.9×10^{-12}sec at 19.5°C.[28] Small increments in relaxation times from measurements in these solvents over those in cyclohexane are quite normal which suggests that the value in the latter solvent is reasonable. The calculated dipole moment of 2.87D compares with literature values between 2.80 and 2.99D in benzene.[29] The majority of these values lie between 2.91 and 2.96D but since in most cases no allowance has been made for the atomic polarization contribution these slightly higher values would be expected.

The 4.3 mm procedure has also been applied to several other systems, such as tetrahydrofuran, thiacyclopentane and cyclopentanone, the solvent in each case being cyclohexane.[30] For all these solutes the absorption at 4.3 mm is near the maximum of the Cole-Cole plot and the

point was invaluable in formulating the plot.

It is not to be supposed that the 4.3 mm bridge method is as accurate and repeatable as the other type of bridge procedure employed at higher wavelengths. For the latter approach it is possible to make good Cole-Cole $\epsilon'' - \epsilon'$ plots from measurements at one concentration and to establish a sufficient degree of accuracy to obtain two relaxation times from the analysis. This is not to be recommended for the 4.3 mm ϵ'' and ϵ' data if the loss is less than 0.02. For losses greater than this however measurements at one concentration have proved sufficient to determine ϵ' and ϵ'' with an accuracy of $\pm$ 0.01 on ϵ' and $\pm$ 0.002 on ϵ''.

The accuracy of ϵ' on the other bands has been assessed to be $\pm$ 0.006 on Q-band and $\pm$ 0.003 on K, P, X and C bands. The error on ϵ'' is not greater than $\pm$ 0.002 on all the bands. Other methods than the bridge method may be less accurate; for example, one of the most successful methods in the literature is an impedance method used by Smyth for which the errors quoted are $\pm$ 2% on ϵ' and $\pm$ 5% on ϵ'' in the most favourable case.[31]

The accuracy of the mean relaxation time (τ_o) is of the order of $\pm$ 5% while that of τ_1 and τ_2 is approximately $\pm$ 10% provided that the weight factor on a particular relaxation mechanism is in excess of 0.2.[32]

Chapter 2

Determination of the Energy Barriers to Acetyl Group Rotation in Aromatic and Aliphatic Molecules.

Introduction.

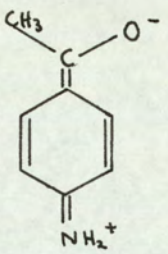
The energy barrier to acetyl group rotation in an aromatic compound will be dependent upon the degree of conjugation between the π-electrons of the aromatic nucleus and the carbonyl carbon atom. If conjugation occurs to such an extent that the energy barrier to group rotation is associated with a frequency lower than that in the microwave region then a relaxation time characteristic only of a molecular relaxation process will be observed. If, however, the energy barrier to acetyl group rotation is small (0→3 kcal/mole) then a shortening of the relaxation time, below that normally associated with molecular rotation, will be apparent. Analysis of the dielectric data in terms of two relaxation times, for measurements at a number of temperatures, will then enable the enthalpies of activation for molecular and intramolecular relaxation ($\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$) to be determined.

Smyth and co-workers have examined relaxation mechanisms in a number of compounds which contain acetyl groups and have obtained $\Delta H_2^{\ddagger}$ values of 1.1→1.5 kcal/mole.[33,34] The resonance energy contribution to this energy barrier could be approximately 0.8 kcal/mole as quoted by Wheland[35] for the additional resonance energy of acetophenone relative to benzene. Pauling's[36] value, however, for this additional resonance energy is 7.0 kcal/mole, which would suggest a high energy barrier to group rotation.

The main object of this study is to ascertain first

of all whether acetyl group rotation is taking place in the compounds investigated and having decided on this to calculate the enthalpies of activation to both molecular and group rotation. Since measurements, in most cases, are at five or six microwave frequencies the accuracy of the $\Delta H^{\ddagger}$ values is usually better than $\pm$ 0.5 kcal/mole, depending upon the weight factor on each individual relaxation process. In addition to the determination of energy barriers to rotation, dipole moment results have been employed to calculate the magnitude and direction of bond and group moments in some of the molecules investigated.

The position of the infrared carbonyl stretching frequency in substituted acetophenones has been shown to indicate the way in which the degree of conjugation is affected by a substituent, relative to acetophenone.[37] For example, the amino group in p-aminoacetophenone will release charge into the ring to stabilise the resonance form (1) which will reduce the double bond character of the C=O bond and lower its stretching frequency relative to acetophenone.



(1)

Since the direction of electron release is such as to enhance the mesomeric effect of the acetyl group then a higher energy

barrier to acetyl group rotation, relative to group rotation in acetophenone, might be expected. The shift for p-nitro-acetophenone, however, is positive and suggests that the mesomeric and inductive effects are reinforcing to withdraw electrons from the ring. In this case the effect of the nitro group will be to diminish the mesomeric withdrawal of charge by the acetyl group and hence a smaller energy barrier to acetyl group rotation, relative to that in acetophenone, would be expected. As the direction of flow of charge should effect the energy barrier to group rotation a knowledge of the infrared carbonyl stretching frequency of the compounds investigated in this chapter (see Table 2.3.) has proved useful in the elucidation of some of the results.

The relaxation processes of acetophenone were examined in solution in cyclohexane, p-xylene and decalin at several temperatures and the $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ values were determined. Enthalpies of activation have also been calculated for 4-acetylpyridine, ω,ω,ω-trifluoroacetophenone and cyclohexylmethylketone. The compounds 2-acetonaphthone and p-methoxyacetophenone were studied at a single temperature. p-Diacetylbenzene has also been studied at four temperatures but the results for this compound are discussed in Chapter 5.

Table 2.1. Relaxation times, distribution parameter (α), static dielectric constant (ϵ_0), dielectric constant at very high frequency (ϵ_∞) and dipole moment (μ) for solutions of weight fraction w_2 at temperature t °C for molecules containing acetyl groups or substituted acetyl groups.

t (°C)	w_2	τ_0	τ_1	τ_2	C_1	α	ϵ_0	ϵ_∞	μ (D)
			$\times 10^{12}$ sec						
				Acetophenone/cyclohexane					
15	0.02030	11.5	18.2	8.9	0.33	0.04	2.1688	2.047	2.84
25	0.02030	10.2	17.2	7.8	0.33	0.05	2.1472	2.033	2.82
25	0-0.03	10.7	19.0	8.0	0.33	0.06	6.674(a_0)	0.845(a_∞)	2.87
40	0.02168	8.0	13.9	6.0	0.33	0.03	2.1199	2.006	2.84
50	0.02046	7.0	11.6	5.3	0.33	0.02	2.0927	1.991	2.83
				Acetophenone/p-xylene					
15	0.01828	14.3	24.5	10.8	0.33	0.02	2.4288	2.293	2.83
25	0.01967	12.8	22.0	9.7	0.33	0.03	2.4166	2.277	2.84
40	0.02239	10.2	16.6	7.9	0.33	0.02	2.3979	2.252	2.82
50	0.02163	9.0	14.4	6.8	0.33	0.02	2.3655	2.234	2.80
60	0.01685	7.8	12.5	6.0	0.33	0.01	2.3091	2.214	2.76
				Acetophenone/decalin					
15	0.02070	20.1	31.4	15.4	0.33	0.03	2.3440	2.201	2.76
25	0.02263	17.5	28.1	13.4	0.33	0.03	2.3342	2.188	2.74

t (°C)	w_2	τ_0	τ_1 $\times 10^{12}$ sec	τ_2	c_1	α	ϵ_0	ϵ_∞	μ (D)
			Acetophenone/decalin (cont.)						
40	0.02263	13.1	20.2	10.3	0.33	0.02	2.2991	2.163	2.74
50	0.01914	11.8	19.2	9.1	0.33	0.02	2.2566	2.145	2.76
60	0.02070	10.1	16.3	7.7	0.33	0.02	2.2489	2.128	2.83
			4-Acetylpyridine/p-xylene						
15	0.02438	16.1				0.04	2.4218	2.299	2.34
25	0.02347	14.2				0.03	2.3901	2.281	2.30
40	0.02216	11.2				0	2.3469	2.254	2.27
60	0.02734	9.0				0	2.3272	2.225	2.26
			4-Acetylpyridine/decalin						
40	0.02348	11.6				0.02	2.2442	2.154	2.22
			ω,ω,ω-Trifluoroacetophenone/cyclohexane						
15	0.03516	21.8	24.9	9.2	0.85	0.04	2.2571	2.046	3.41
25	0.04868	19.9	21.8	7.4	0.91	0.03	2.3201	2.040	3.43
40	0.02541	15.6	15.6	2.5	0.98	0.01	2.1342	2.002	3.40
			ω,ω,ω-Trifluoroacetophenone/p-xylene						
15	0.03345	24.7	30.9	10.0	0.8	0.07	2.5496	2.284	3.52
25	0.04002	22.3	26.5	11.1	0.78	0.03	2.5757	2.287	3.44

t (°C)	w_2	τ_0	τ_1	τ_2	c_1	α	ϵ_0	ϵ_∞	μ (D)
			$\times 10^{12}$ sec						
				ω,ω,ω-Trifluoroacetophenone/p-xylene (cont.)					
40	0.02463	16.4	19.2	11.1	0.71	0.02	2.4056	2.245	3.40
60	0.03002	13.1	13.1		1.0	0	2.3900	2.216	3.37
				2-Acetonaphthone/p-xylene					
25	0.02379	32.8	40.9	13.3	0.8	0.06	2.4176	2.277	3.08
				p-Methoxyacetophenone/p-xylene					
25	0.01659	26.9	50.4	15.4	0.51	0.10	2.4137	2.272	3.48
				Cyclohexylmethylketone/p-xylene					
15	0.01640	9.9	24.8	8.8	0.15	0.03	2.3901	2.293	2.59
25	0.01707	9.0	34.4	8.2	0.13	0.04	2.3753	2.280	2.58
40	0.01767	7.6	10.5	7.2	0.16	0	2.3442	2.256	2.53
50	0.01894	6.9	9.4	6.4	0.20	0	2.3271	2.239	2.51
60	0.01997	5.9	12.4	5.4	0.10	0	2.3105	2.219	2.49

Table 2.2. Free Energies ($\Delta G^{\ddagger}$), Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta S^{\ddagger}$) of Activation for Molecular and Intramolecular Relaxation.

t (°C)	$\Delta G_1^{\ddagger}$	$\Delta H_1^{\ddagger}$	$\Delta S_1^{\ddagger}$	$\Delta G_2^{\ddagger}$	$\Delta H_2^{\ddagger}$	$\Delta S_2^{\ddagger}$
	—KCAL/MOLE—		CAL/DEG/MOLE	— KCAL/MOLE —		CAL/DEG/MOLE
			Acetophenone/cyclohexane			
15	2.68	1.8	-3.0	2.28	2.2	-0.2
25	2.76	''	-3.2	2.29	''	-0.3
40	2.80	''	-3.2	2.28	''	-0.2
50	2.79	''	-3.1	2.23	''	-0.1
			Acetophenone/p-xylene			
15	2.86	2.2	-2.2	2.39	1.9	-1.7
25	2.96	''	-2.5	2.43	''	-1.8
40	2.91	''	-2.2	2.45	''	-1.8
50	2.94	''	-2.2	2.45	''	-1.7
60	2.95	''	-2.2	2.47	''	-1.7
			Acetophenone/decalin			
15	2.99	2.2	-2.7	2.59	2.3	-0.9
25	3.05	''	-2.8	2.62	''	-1.0
40	3.03	''	-2.6	2.60	''	-0.9
50	3.11	''	-2.8	2.64	''	-1.0
60	3.14	''	-2.8	2.62	''	-0.9
			4-Acetylpyridine/p-xylene			
15				2.61	1.9	-2.4
25				2.64	''	-2.4
40				2.67	''	-2.4
60				2.74	''	-2.5

t (°C)	$\Delta G_1^{\neq}$	$\Delta H_1^{\neq}$	$\Delta S_1^{\neq}$	$\Delta G_2^{\neq}$	$\Delta H_2^{\neq}$	$\Delta S_2^{\neq}$
	— KCAL/MOLE —		CAL/DEG/MOLE	—	KCAL/MOLE —	CAL/DEG/MOLE
	ω,ω,ω-Trifluoroacetophenone/cyclohexane					
15	2.86	1.8	-3.7			
25	2.91	"	-3.7			
40	2.87	"	-3.4			
	ω,ω,ω-Trifluoroacetophenone/p-xylene					
15	2.99	2.2	-2.7			
25	3.02	"	-2.7			
40	3.00	"	-2.3			
60	2.98	"	-2.3			
	Cyclohexylmethylketone/p-xylene					
15				2.27	1.3	-3.4
25				2.32	"	-3.4
40				2.39	"	-3.4
50				2.41	"	-3.4
60				2.39	"	-3.2

Table 2.3. Values of the Infrared Carbonyl Stretching Frequencies for the Compounds Discussed in this Chapter. The Solvent is Carbon Tetrachloride in each Case.

Compound	$\nu_{C=O}$ (cm^{-1})	Compound	$\nu_{C=O}$ (cm^{-1})
Acetophenone	1691[a]	2-Acetonaphthone	1688[c]
4-Acetylpyridine	1706[b]	ω,ω,ω-Trifluoroacetophenone	1725[c]
Cyclohexylmethyl-ketone	1713[c]	ω,ω,ω-Trichloroacetophenone	1717[b]
p-Methoxyaceto-phenone	1685[c]	ω,ω,ω-Tribromoacetophenone	1704[b]

(a) Ref. 37. (b) Ref. 38. (c) This work.

Discussion.

For the molecule acetophenone the resultant moment (μ) is not along a symmetry axis and can be represented by two components (Fig.1.7.) namely μ_1 which is along the projection of the C_1-C_4 axis and can orientate along with the whole molecule and μ_2 perpendicular to that axis which rotates with the frequency of group rotation. In such a case, for frequencies where $\omega\tau \ll 1$,

$$\tau(eff) = \left(\frac{\mu_1}{\mu}\right)^2 \tau_1 + \left(\frac{\mu_2}{\mu}\right)^2 \tau_2 \qquad 2.1$$

where τ(eff) is the measured or effective relaxation time at long wavelengths and $\mu^2 = \mu_1^2 + \mu_2^2$. Fischer[39] estimated τ_1 by using an expanded version of the Debye equation

$$\tau_1 = 4\pi\eta\,(a.b.c)\,s/\kappa T \qquad 2.2$$

where a, b, c are the semi-axes of the rotational ellipsoid and s is a small numerical factor (1.5→2.0) taking account of the direction of the dipole axis with respect to the axes of inertia. For acetophenone an angle of 50° [19] was taken for the direction of the molecular dipole moment to the C_1-C_4 axis and hence $\mu_1 = \mu\cos 50^\circ$ and $\mu_2 = \mu\sin 50^\circ$. The relation 2.1 then enables τ_2 in principle to be calculated from τ(eff). For his qualitative conclusions however Fischer merely compares τ(eff) with τ_1 and where the former is markedly shorter he declares that rotation is possible for the substituted group.

Fischer[19] measured acetophenone in both benzene and

carbon tetrachloride at 25°C and τ(eff) was determined to be 11.8 and 13.0×10^{-12} sec respectively. His calculated values for the molecular relaxation times were 11.2 and 13.8×10^{-12} sec in benzene and carbon tetrachloride respectively[19] and his conclusion, presumably based on the results in carbon tetrachloride, is that there is some weak indication of intramolecular rotation in acetophenone. This approach by Fischer has certain limitations however since τ(eff) was determined at the single wavelength of 4.5m and hence no indication of the dependence of ϵ'' upon frequency is possible. Therefore if the weight factor on the group relaxation process is small this process could pass completely undetected. In addition, the calculation of the relaxation time expected for molecular rotation from eqn. 2.2 could be subject to considerable error due to the difficulty in assessing a, b and c and also s (the form factor). τ_1 may be more accurately assessed from a consideration of the relaxation times of rigid molecules of similar size to the molecule in question. Furthermore it is desirable to carry out measurements at frequencies where the contribution to the total dielectric loss by the group relaxation process is considerable. Such a condition is realised by measuring the dielectric absorption at frequencies extending to 70 Gc/sec.

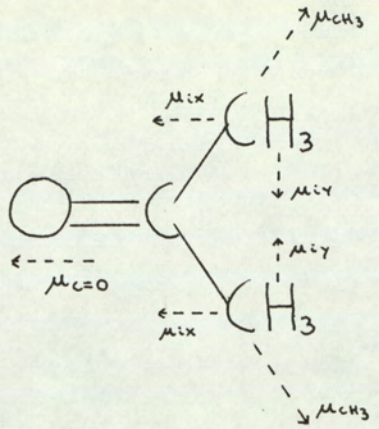
Measurements on acetophenone were made in three solvents, cyclohexane, p-xylene and decalin, at five or six frequencies. The mean relaxation time of acetophenone in

cyclohexane at 25°C, obtained from the $\epsilon'-\epsilon''$ plot, is 10.2×10^{-12} sec which compares with a molecular relaxation time of 16.2×10^{-12} sec for ethylbenzene in cyclohexane at 25°C.[27] Courtauld models suggest that acetophenone is larger than ethylbenzene and hence a contribution from an intramolecular process must be present in acetophenone to shorten the relaxation time. If acetophenone were rigid, with the acetyl group locked in the plane of the ring, then it would rotate in a planar configuration and have a shorter molecular relaxation time than if the group was rotating while molecular rotation was taking place. Courtauld models suggest that a planar, rigid, form of acetophenone is larger than bromobenzene by about 10% but this would then be incompatible with the mean relaxation times of 11.5 and 10.2×10^{-12} sec for acetophenone in cyclohexane at 15°C and 25°C respectively and that of bromobenzene which is 12.0×10^{-12} sec in cyclohexane at 20°C.[27] It seems apparent therefore that acetophenone is non-rigid due to a contribution from a group relaxation process and it is now necessary to determine the weight factor on this process.

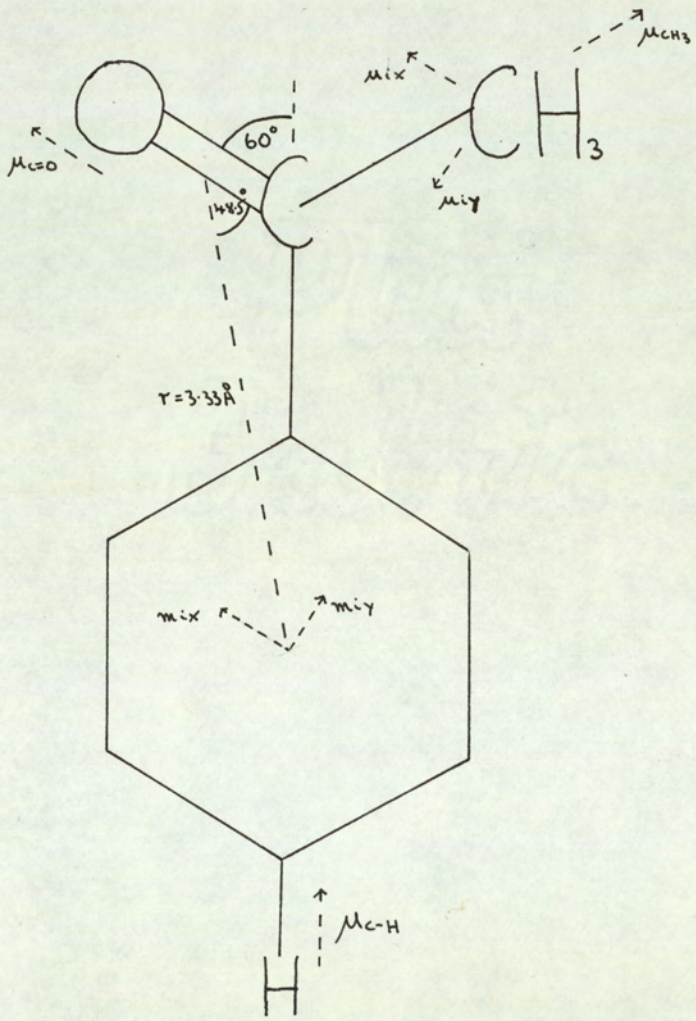
In order to calculate the weight factor (C) on a particular relaxation process it is first of all necessary to determine the angle (θ) that the molecular dipole moment (μ) subtends with the projection of the $C_1 - C_4$ axis. Two methods have been employed to determine this angle (i) from bond moment calculations (ii) from group moment calculations.

FIG. 2.1 LOCATION OF BOND AND INDUCED MOMENTS IN

(a) ACETONE



(b) ACETOPHENONE



The first of these will now be considered.

For the molecule acetophenone the molecular dipole moment will be a resultant of the primary C=O, C-CH_3 and H-C bond moments. In addition there will be secondary contributions due to (a) the inductive effect by the carbonyl group on the phenyl and methyl groups and (b) a mesomeric release of charge from the phenyl ring into the acetyl group. In order to calculate the C=O bond moment the moment of acetone (μ =2.85D)[40] will be considered. This moment is a resultant of the carbonyl group moment, two methyl group moments and an inductive moment due to the effect of the carbonyl group on the methyl groups. The C-$\hat{C}$-C angle is taken as 110°.[40] Groves and Sugden[40] have worked out the moment induced in each of the methyl groups by the carbonyl group to be 0.125·$\mu_{c=o}$ (μ_{ix}) along an axis parallel to the C=O bond (see Fig.2.1.a). The moments induced along an axis perpendicular to the C=O bond, in each methyl group, are 0.271·$\mu_{c=o}$ (μ_{iy}) but the effect of these cancels out by symmetry. The CH_3 moment is taken to be 0.3D[41] with the negative end of the dipole directed towards the hydrogen atoms. Hence, for acetone, the resultant moment (μ) =2.85D= $\mu_{c=o}$ +0.25·$\mu_{c=o}$ -2x0.3cos$\left(\frac{110^o}{2}\right)$ whereby $\mu_{c=o}$ =2.55D.

In acetophenone the C=O bond moment will induce a moment in the methyl group and in the phenyl ring. The moment induced along an axis parallel to the C=O bond in the methyl group is 0.125 $\mu_{c=o}$ =0.32D (μ_{ix}). There will also

be a moment perpendicular to this axis, induced in the methyl group, of $0.271\,\mu_{C=O} = 0.69D$ (μ_{iy}). The induced moments in the phenyl ring (m_{ix} and m_{iy}) may be calculated by the method of Frank.[42] Let the angle between the C=O direction and the projection of the C_1-C_4 axis of the ring be 60°. The polarizability of the benzene ring is assumed to act at the centre with an average value of 1.0×10^{-23} cm^3.[43] The C-C distance in the ring is taken as 1.40 Å and the $C_{aliphatic}-C_{aromatic}$ distance as 1.50 Å.[43] The C=O moment is assumed to act at the point of contact of the carbon and oxygen atoms i.e. at 0.70 Å from the carbon nucleus.[43] The equations employed are

$$m_{ix} = \mu\gamma\left[(\epsilon+2)/3\epsilon_0\right]\left[(3\cos^2\phi-1)/r^3\right] \qquad 2.3$$

$$m_{iy} = \mu\gamma\left[(\epsilon+2)/3\epsilon_0\right]\left[3\sin\phi\cos\phi/r^3\right] \qquad 2.4$$

where m_{ix} is the moment induced, parallel to the C=O bond direction, at the centre of the ring; m_{iy} is the moment induced, perpendicular to the C=O bond direction, at the centre of the ring; μ is the magnitude of the primary dipole ($\mu_{C=O} = 2.55D$); ϕ is the angle between the direction of the C=O bond and the line of length r joining the point of contact of the carbon and oxygen atoms to the polarizable centre ($\phi = 131.5^{\circ}$ and $r = 3.33$ Å from a vector diagram); γ is the polarizability of the ring at its centre; ϵ is the dielectric constant of the material intervening between the point in question and the primary dipole and ϵ_0 is the dielectric

constant of the polarizable material. Values for these dielectric constants are uncertain but a value of 2.264 (the dielectric constant of p-xylene at 25°C) should introduce little error into the results. Inserting the above values into eqns.2.3 and 2.4 gives m_{ix} =0.10D and m_{iy} =0.50D. The location of the bond and induced moments in acetophenone is shown in Fig.2.1.b.

The method of taking the polarizable centre to be at the centre of the benzene ring has been found to yield results almost identical with those obtained by regarding the ring as six polarizable centres located at the six carbon atoms.[41]

Knowing the induced moments and the bond moments (μ_{C-H} in the para position of the benzene ring is taken to be 0.4D[41] in the direction H→C) the resultant dipole moment of acetophenone can be determined from a vector diagram. This is found to be 3.07D directed at an angle 51°30' to the projection of the C_1-C_4 axis, away from the ring. The observed dipole moment is 2.82D and in order to obtain this result an additional moment of 0.35D along the C_1-C_4 axis and directed into the ring would have to be introduced. The moment of 2.82D would then make an angle of 57° with the projection of the C_1-C_4 axis. The direction and magnitude of the introduced moment of 0.35D probably has no real physical significance. It certainly could not be attributed to a mesomeric effect as this is known to act away from the ring.[44]

It is probable therefore that the direction of the additional moment comes about due to the error in the assumptions that have accumulated in calculating the resultant moment.

From the values of θ determined the C_1 values may be evaluated from eqns.1.30 and 1.31. If $\theta = 51^{\circ}30'$ then $C_1 = 0.39$ and if $\theta = 57^{\circ}$ then $C_1 = 0.30$.

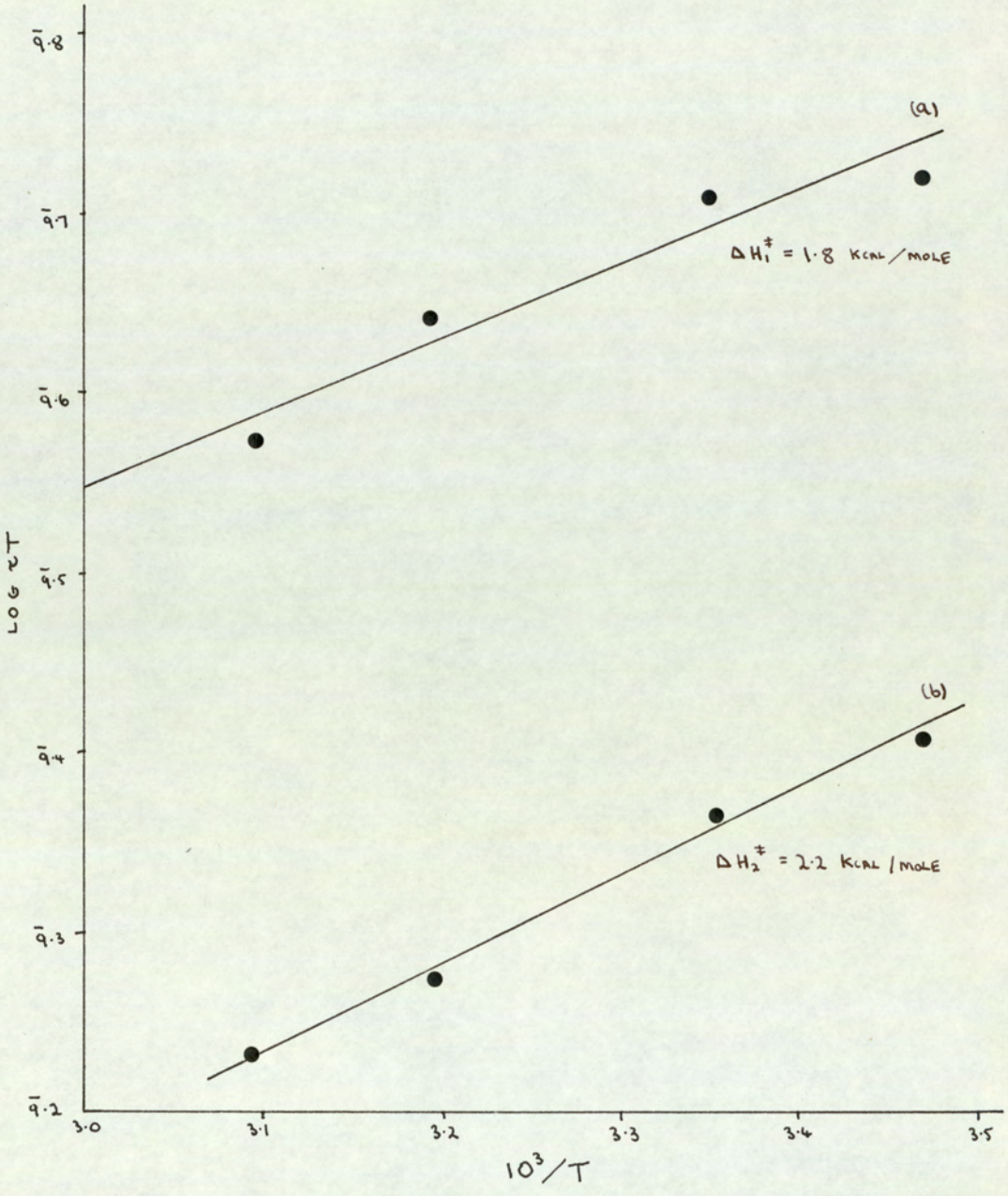
It can be seen that the calculation of C_1 values from bond moment considerations could be subject to considerable error due to the assumptions that are involved in the calculations. A somewhat simpler approach of determining θ is provided from a consideration of group moments. In a para-substituted acetophenone, where the dipole direction of the para-substituent is along the $C_1 - C_4$ axis, the dipole moment may be related to those of the mono-substituted compounds by the equation

$$(\mu_{p\text{-}X\text{acetophenone}})^2 = (\mu_{\text{Acetophenone}})^2 + (\mu_{C_6H_5X})^2 - 2\mu_{\text{Acetophenone}}\mu_{C_6H_5X}\cos\theta \qquad 2.5$$

If there is but little mesomeric interaction between the acetyl group and the para-substitutent then it may be assumed that θ derived from eqn.2.5 will be the same for θ in acetophenone. If X=chlorine then $\mu_{p\text{-chloroacetophenone}} = 2.29D$[29] and $\mu_{\text{chlorobenzene}} = 1.58D$.[41] The dipole moment of acetophenone is 2.82D. From these values θ is calculated to be $54^{\circ}\ 23'$ giving a C_1 value of 0.33. Furthermore $\mu_{4\text{-acetylpyridine}} = 2.29D$ and $\mu_{\text{pyridine}} = 2.2D$[29] giving $\theta = 52^{\circ}\ 32'$ with $C_1 = 0.37$. A similar type of calculation by Baliah and

Aparajithan[45] on p-nitroacetophenone yielded a value of $\Theta=55^{o}$. Little error appears to be introduced therefore in assuming that the dipole moment of acetophenone subtends an angle of 54^{o} with the projection of the C_1-C_4 axis with a corresponding C_1 value of 0.33. It was decided therefore to analyse the data for acetophenone in the various solvents with C_1 fixed at 0.33 in a computer programmed to evalulate τ_1 and τ_2 from eqns.1.28 and 1.29. Since there appears to be very little change in the dipole moment with solvent then C_1 should also be solvent independent. The values of τ_1 and τ_2 obtained are listed in Table 2.1. A molecular relaxation time of 17.2×10^{-12} sec, from the $\epsilon'-\epsilon''$ plot, for acetophenone in cyclohexane at $25^{o}C$ seems reasonable when compared with the value of 16.2×10^{-12} sec for ethylbenzene[27] in the same solvent and at the same temperature. An objection could be raised that the molecular relaxation time for acetophenone is longer than that of o-hydroxyacetophenone ($\tau_o=16.4\times10^{-12}$ sec in cyclohexane at $20^{o}C$)[46] which has been described by Smyth as being a rigid molecule. However, this molecule will remain flat during rotation due to the hydrogen bond between the hydrogen atom of the hydroxyl group and the oxygen atom of the carbonyl group. If acetyl group rotation was occuring in acetophenone, as the molecule rotated, then a larger volume could be swept out during molecular rotation resulting in a correspondingly longer relaxation time. The effect of the size of the hydroxyl group on the molecular relaxation

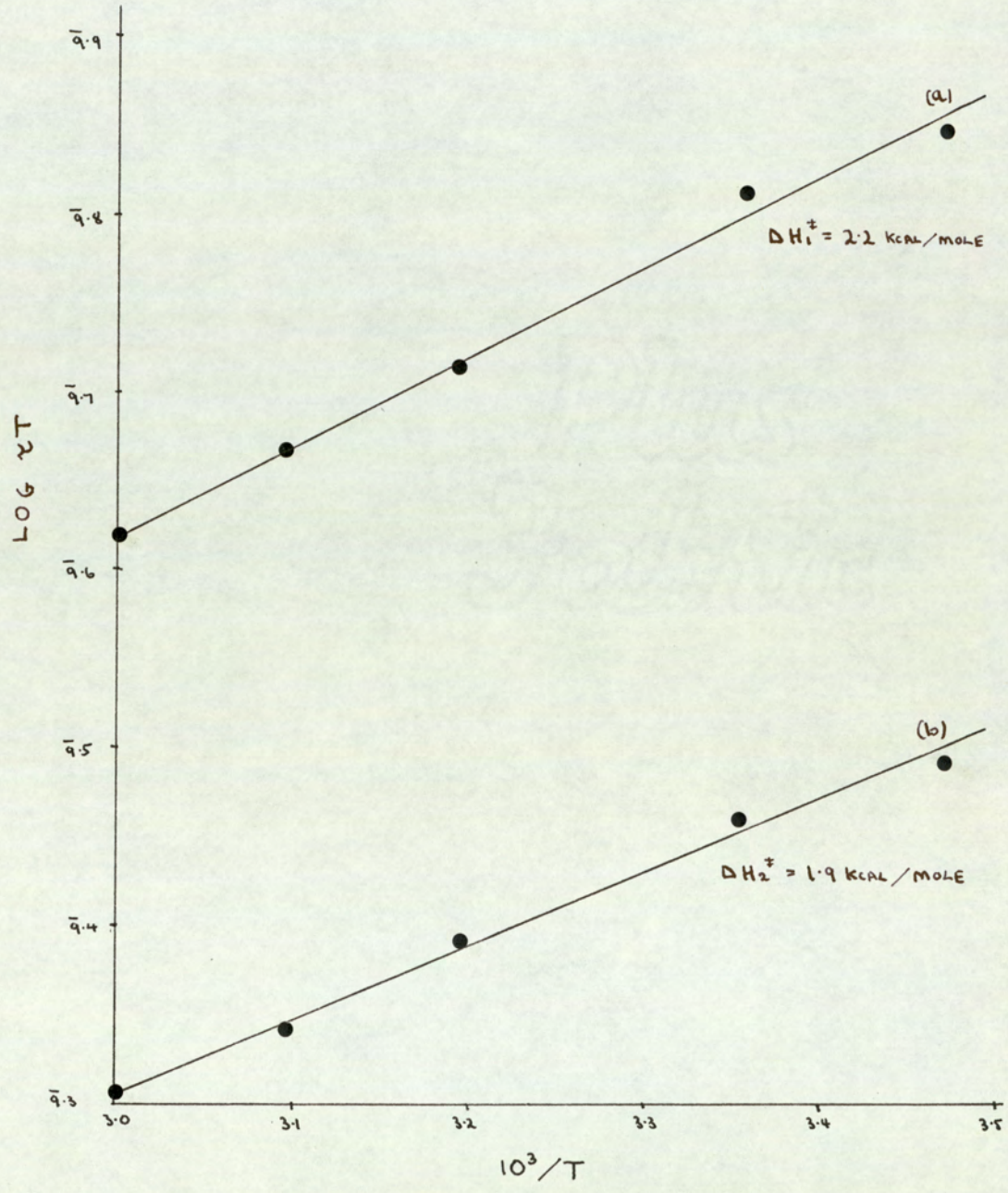
FIG. 2.2 PLOT OF (a) LOG $\tau_1 T$ AND (b) LOG $\tau_2 T$ AGAINST $1/T$ FOR ACETOPHENONE IN CYCLOHEXANE.



time of o-hydroxyacetophenone should not be all that significant since it protrudes less than the acetyl group from the benzene ring. If the presence of the hydroxy group in the ortho position did have an effect on the relaxation time due to its size then it would be hard to explain the molecular relaxation times of chlorobenzene and o-dichlorobenzene which are 10.6 and 10.4×10^{-12} sec respectively in benzene at 23°C.[47] In this case an atom in the ortho position of the same size as that in the 1 position has had no effect upon the relaxation time. The situation of acetophenone having a longer molecular relaxation time than o-hydroxyacetophenone has also been observed by Knobloch who obtained a τ_1 of 13.4×10^{-12} sec for the former molecule and a τ_1 of 13.3×10^{-12} sec for the latter in benzene solution at 20°C.[48] These molecular relaxation times appear short however when compared with that of ethylbenzene in cyclohexane at 20°C.

Acetophenone was measured at four temperatures in cyclohexane and from the relevant $\log \tau T - 1/T$ plot the enthalpy of activation to molecular relaxation ($\Delta H_1^{\ddagger}$) was calculated to be 1.8 ± 0.5 kcal/mole and for group relaxation ($\Delta H_2^{\ddagger}$) to be 2.2 ± 0.4 kcal/mole (Fig.2.2.a ,b). $\Delta H_1^{\ddagger}$ appears to be of the correct order of magnitude when compared with the value of 1.6 ± 0.4 kcal/mole for iodobenzene in p-xylene.[27] The $\Delta H_2^{\ddagger}$ value is higher than any previously determined by Smyth for acetyl group rotation in a number of aromatic compounds since his values for $\Delta H_2^{\ddagger}$ lie between 1.1 and 1.5

FIG. 2.3. PLOT OF (a) LOG $\tau_1 T$ AND (b) LOG $\tau_2 T$ AGAINST $1/T$ FOR ACETOPHENONE IN P-XYLENE.



kcal/mole.[33,34] However, since the measurements in this study incorporate a greater number in the higher frequency region, where the contribution to the total dielectric loss from the group relaxation process should predominate, a greater accuracy ought to be achieved in the derivation of the ΔH_1^* and ΔH_2^* values.

It can be observed from Table 2.1 that the relaxation times of acetophenone in p-xylene have lengthened in comparison to those obtained from measurements in cyclohexane. Such a lengthening of relaxation times has been observed for nearly all the molecules studied in this laboratory and is possibly due to the interaction of the polar group with the π-electrons of the p-xylene. The consequence of this interaction is that a greater free energy of activation has to be acquired before the molecules can rotate and this results in longer relaxation times being observed. From measurements at five temperatures in this solvent ΔH_1^* was calculated to be 2.2 $\pm$ 0.5 kcal/mole and ΔH_2^* 1.9 $\pm$ 0.4 kcal/mole (Fig.2.3.a,b). The difference in the ΔH_2^* values for measurements in cyclohexane and p-xylene may be due to the experimental error.

It may be useful at this juncture to ascertain what effect intermolecular forces[49] between molecules have on the energy barrier to rotation. Three main types of attractive or van der Waals forces exist in solution. Assuming that the solution of the polar molecules in a non-polar

solvent is very dilute then it can be assumed that there is no interaction between the polar solute molecules themselves. If the solvent is completely non-polar then there will be no dipole-dipole interaction between the polar solute molecules and the solvent molecules. p-Xylene however has a very small dipole moment (μ=0.13D)[50] and hence some dipole-dipole interaction is to be expected in this solvent. The equation governing the interaction energy between two permanent dipoles, 1 and 2, was derived by Keesom who, applying Boltzmann statistics, derived the expression for the average potential energy

$$E_K = - \frac{2\mu_1^2\mu_2^2}{3r^6 kT} \qquad 2.6$$

where the dipoles μ_1 and μ_2 are at a distance r from each other, k is Boltzmann's constant and T is the absolute temperature. This equation is however only very approximate in condensed phases where steric and other factors prevent free molecular rotation since simple Boltzmann statistics are then inapplicable.[49] This contribution to the total intermolecular forces by the dipole-dipole interaction may be important in pure liquids with high dipole moments but it should be relatively small in two component solutions if one of the components has a small dipole moment. More important in this case may be the dipole-induced dipole interactions (Debye interactions) caused by the inducing of a dipole in one molecule by the permanent dipole of the other

due to the polarizability γ of the former. The resulting force is always attractive and the mean potential is given by

$$E_D = -\frac{1}{r^6}\left(\gamma_1\mu_2^2 + \gamma_2\mu_1^2\right) \qquad 2.7$$

However, both the Keesom and the Debye forces would not account for interactions between molecules which have no permanent dipoles. It was found by London that attractions present between non-polar molecules were caused by dispersion forces due to the polarizability of each molecule. The value of E_L, the London dispersion force, is given by the equation

$$E_L = -\frac{3}{2}\frac{\gamma_1\gamma_2}{r^6}\frac{I_1 . I_2}{I_1 + I_2} \qquad 2.8$$

where γ is the polarizability of the molecule and I is the ionisation potential. This equation is only very approximate however for polyatomic molecules in which the forces will be non-radial and in which intramolecular dispersion forces could also be present.

The values of E_K, E_D, and E_L for various values of r are listed in Table 2.4 for the system acetophenone (1) in p-xylene (2) where $\mu_1 = 2.82D$, $\mu_2 = 0.13D$, $\gamma_1 = 1.423\times10^{-23}$ cc, $\gamma_2 = 1.417\times10^{-23}$ cc and $I_1 = I_2 = 10eV$. $T = 298.15^{\circ}K$. The values of γ are the average calculated by (i) summing up the individual bond refractions (taken from Ref.41) and dividing by $4/3\,\pi N$ where N is Avogadro's number and (ii) deriving γ from the

equation

$$\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d} = \frac{4}{3} \pi N \gamma \qquad 2.9$$

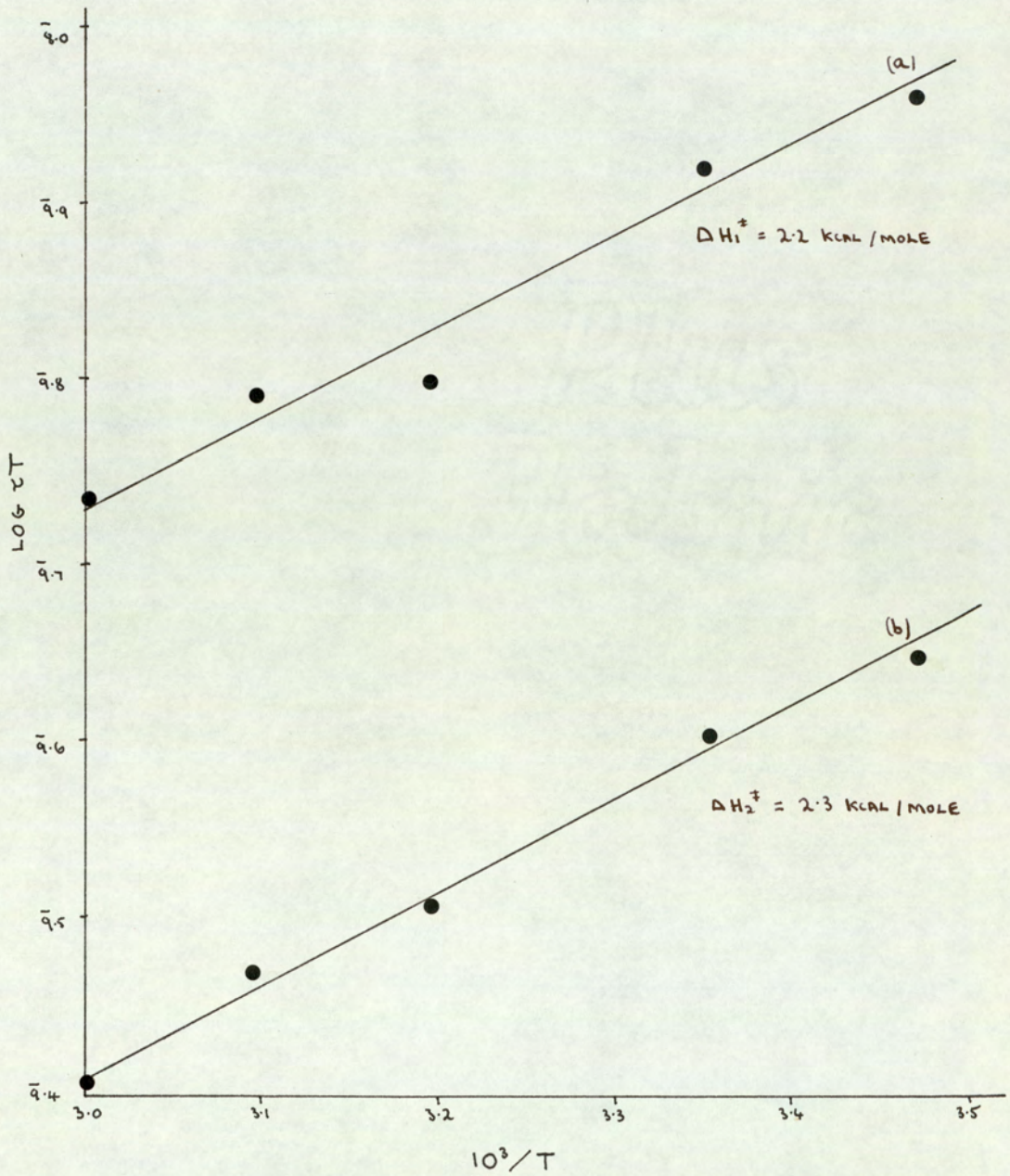
where n_D is the refractive index of the compound in question at the frequency of the sodium D line, M is the molecular weight and d is the density. The ionisation potential values are of typical magnitude for molecules of this type.

Table 2.4. Values of the Dipole-Dipole Interaction Energy (E_K), Dipole-Induced Dipole Interaction Energy (E_D) and London Dispersion Force (E_L) for Acetophenone in p-Xylene at 25°C for various values of r.

r (Å)	E_K	E_D	E_L
	kcal/mole		
3	0.04	2.23	47.84
4	0.007	0.40	8.52
5	0.002	0.10	2.23
6	0.0007	0.03	0.75

It can be seen from Table 2.4 that, within the approximations of the equations, for acetophenone in p-xylene London dispersion forces should provide the largest contribution to the intermolecular forces between solute and solvent molecules. It would also appear that intermolecular forces could provide a significant contribution to the energy barrier to rotation. Pimentel and Mc.Clellan[51] have stated that the van der Waals interaction energy is in general a few tenths of a kcal/mole for solutions of polar solute molecules in a non-polar solvent. However, in addition to intermolecular forces the size and shape of the molecule,

FIG. 2.4. PLOT OF (a) LOG $\tau_1 T$ AND (b) LOG $\tau_2 T$ AGAINST $1/T$ FOR ACETOPHENONE IN DECALIN.



temperature, viscosity of the solvent, steric effects and the resonance energy between an attached group and the benzene nucleus should all influence the resulting $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ values.

The viscosity of decalin is approximately four times that of p-xylene at 25°C and this will explain the longer molecular and intramolecular relaxation times observed in this solvent. Hence at 15°C the τ_1 values are 18.2, 24.5 and 31.4x10^{-12} sec for acetophenone in cyclohexane, p-xylene and decalin respectively. The $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ values determined from measurements of acetophenone in decalin at five temperatures are 2.2 $\pm$0.5 kcal/mole and 2.3$\pm$0.4 kcal/mole respectively (Fig.2.4.a,b). The τ_1 and τ_2 values have increased considerably in passing from measurements in cyclohexane to decalin but no similar ratio of increase is found for the $\Delta H^{\ddagger}$ values. If the τ values were converted into the corresponding $\Delta G^{\ddagger}$ values however (from eqn.1.41) then for acetophenone in cyclohexane at 15°C $\Delta G_1^{\ddagger}$ and $\Delta G_2^{\ddagger}$ are 2.68 and 2.28 kcal/mole respectively while for acetophenone in decalin at 15°C $\Delta G_1^{\ddagger}$ and $\Delta G_2^{\ddagger}$ are 2.99 and 2.59 kcal/mole respectively. Hence the free energy of activation for both the molecular and the intramolecular relaxation processes has increased by only 0.31 kcal/mole in transferring from measurements in cyclohexane to decalin at 15°C. Increases of similar magnitude in $\Delta H_2^{\ddagger}$ compared to $\Delta G_2^{\ddagger}$ appear to be observed but with the increased error on the $\Delta H^{\ddagger}$ values (the

error on the $\Delta G^{\ddagger}$ values is approximately $\pm$ 0.1 Kcal/mole) only tentative conclusions should be drawn from any apparent trend. $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are listed in Table 2.2.

Smyth has examined the molecules 2-acetonaphthone,[33] 4-acetyl-o-terphenyl[33] and p-phenylacetophenone[34] in benzene, the first two molecules at five temperatures and the latter at three temperatures. For p-phenylacetophenone the mean relaxation time is 45.3×10^{-12} sec at 20°C which indicates a contribution from an intramolecular relaxation process since p-bromobiphenyl (a smaller molecule) has a relaxation time of 62×10^{-12} sec in cyclohexane at 20°C.[52] Smyth reports values of $\tau_1 = 51 \times 10^{-12}$ sec, $\tau_2 = 8.0 \times 10^{-12}$ sec and $C_1 = 0.88$ for an analysis in terms of two relaxation times. In view of the similarity of the direction of the bond moments in p-phenylacetophenone to those in acetophenone a similar C_1 value might be expected. Unfortunately Smyth measured p-phenylacetophenone at only three wavelengths and hence analysis of the data in terms of two relaxation times could be subject to considerable error. The τ_0 value should be reasonably accurate however and therefore the shortening of the relaxation time below that expected for just molecular rotation should be genuine. One possible cause of the relatively high τ_0 value could be that, since the length of conjugation is considerable the group relaxation time has lengthened appreciably above that in acetophenone while C_1 could still be approximately 0.33. C_1 should have altered

from that in acetophenone somewhat however since the effect of the increased length of conjugation in p-phenylacetophenone has been to increase the dipole moment to 3.11D[53] (μ=2.82D for acetophenone). Hence the μ_1 and μ_2 values may be different for p-phenylacetophenone leading to different C_1 and C_2 values. However, since no dipole moment data exists for para halogen substituted p-phenylacetophenones then it would be difficult to assess the new C_1 value. If the change is assumed to be only small then fixing C_1 in the computer programme at 0.33 and solving for τ_1 and τ_2 gives $\tau_1 = 80 \times 10^{-12}$ sec and $\tau_2 = 36.8 \times 10^{-12}$ sec. The τ_1 value could be acceptable and since a high group relaxation time appears to have been found in p-diacetylbenzene (Chapter 5) it is feasible that the τ_2 values in these compounds are lengthening due to the increased length of conjugation in the molecule.

2-Acetonaphthone has been measured in this study at 25°C in p-xylene and a mean relaxation time of 32.8×10^{-12} sec was obtained. Analysis of the data in terms of two relaxation times yielded $\tau_1 = 40.9 \times 10^{-12}$ sec, $\tau_2 = 13.0 \times 10^{-12}$ sec and $C_1 = 0.8$. The molecular relaxation time of 40.9×10^{-12} sec compares with a relaxation time for 2-bromonaphthalene of 25.5×10^{-12} sec in cyclohexane at 25°C.[27] This large increase could be explained by (i) an approximately 30% increase in the molecular relaxation time in p-xylene due to interaction with the solvent (ii) the acetyl group is larger than the bromine atom and (iii) an error of $\pm$10% on the τ_1 values.

Smyth does not quote a mean relaxation time for 2-acetonaphthone but analysis of his data at 20°C and 30°C yielded τ_0 values of 33.6 and 29.8×10^{-12} sec respectively, in solution in benzene. Smyth's analysis of data into contributions from two relaxation processes yielded $\tau_1 = 33 \times 10^{-12}$ sec, $\tau_2 = 7.3 \times 10^{-12}$ sec and $C_1 = 0.86$ at 20°C.[33]

It is quite possible that C_1 and τ_2 values in 2-substituted naphthalenes are not the same as in the substituted benzene derivatives. The dipole moments of the former are usually larger than those of the latter due to a flow of charge across the naphthalene nucleus towards the substituent. Thus for 2-acetonaphthone the dipole moment is 3.08D compared with 2.82D in acetophenone while the infrared carbonyl stretching frequency is 1678 cm^{-1} compared with 1691 cm^{-1} in acetophenone[37] again suggesting more conjugation in 2-acetonaphthone. This flow of charge could alter the components μ_1 and μ_2 of the dipole moment along and perpendicular to the group rotational axis respectively, which would in turn alter C_1 and C_2 with respect to the substituted benzene derivative. Furthermore, the double-bond character between the acetyl group and nucleus should increase in 2-acetonaphthone and hence a higher free energy of activation (with a correspondingly higher τ_2 value) would have to be acquired for group rotation to take place. Another factor that could be influential in explaining the different C_1 values in 2-substituted naphthalenes is that the fixed

component of the dipole moment of 2-substituted naphthalene compounds does not lie along a symmetry axis of the molecule. The weight factor for molecular rotation about each individual symmetry axis will depend upon the resolved part of the fixed component of the dipole moment along that axis. Rotation about each individual axis may have its own relaxation time while the effect of having to resolve the fixed component of the dipole moment along each axis would be to alter the C values with respect to the mono-substituted compound. For bromobenzene the direction of the dipole moment is along a symmetry axis and therefore, according to the Perrin[54] theory, only one relaxation time would be observed. Thus Hassell[27] obtained a zero distribution angle on the Cole-Cole plot for bromobenzene in cyclohexane and in p-xylene. A significant distribution parameter however has been observed for 2-bromonaphthalene in cyclohexane at 25°C (α=0.08 radians)[27] and since this molecule is rigid it suggests that molecular rotation about different axes could be giving rise to a distribution of relaxation times. If this were the case then it would not be permissible to interprete the dielectric data of 2-acetonaphthone in terms of only one molecular relaxation time and a group relaxation time.

In order to study acetyl group rotation further it was decided to examine a molecule whose molecular dipole moment was perpendicular to the projection of the C_1-C_4 axis. Under this condition the component of the dipole moment that

FIG. 2.5 LOCATION OF THE BOND MOMENTS AND DIRECTION OF THE RESULTANT DIPOLE MOMENT IN 4-ACETYLPYRIDINE.

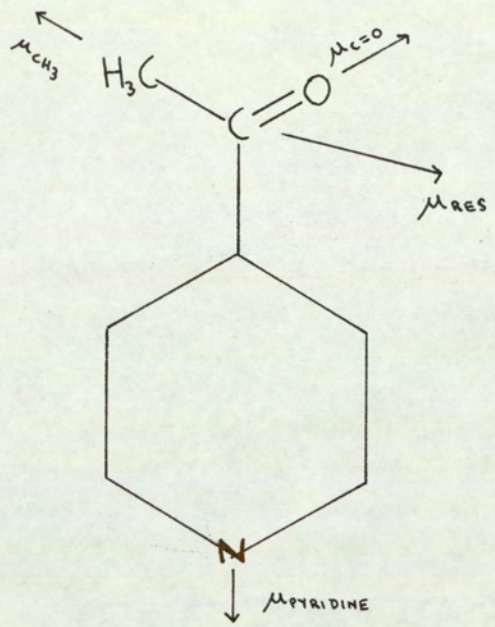
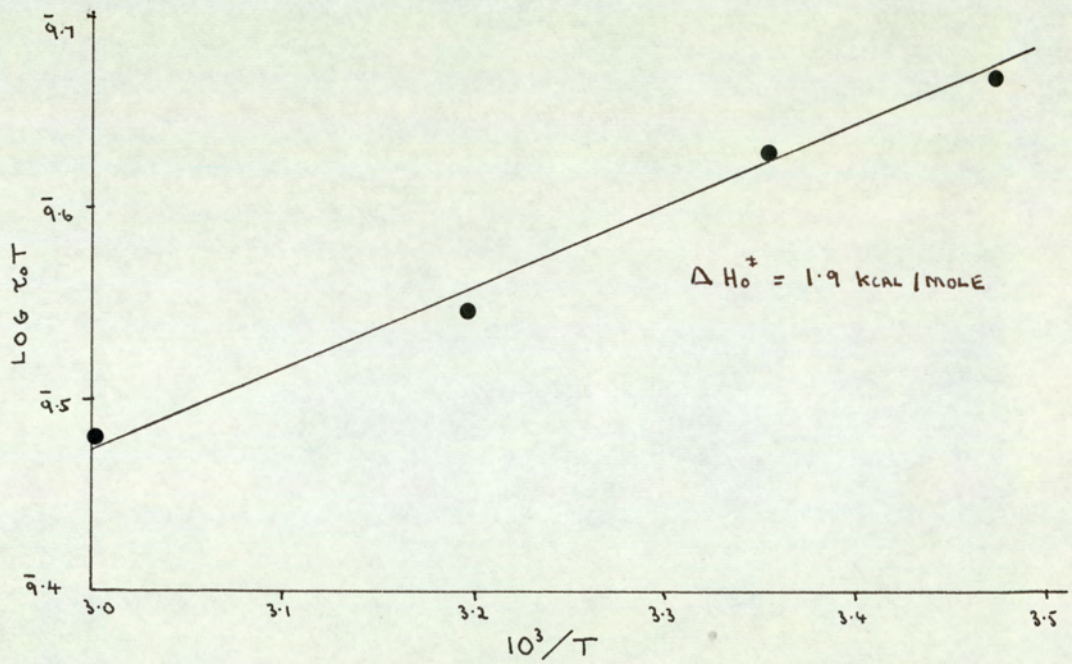


FIG. 2.6 PLOT OF LOG $\tau_0 T$ AGAINST $1/T$ FOR 4-ACETYLPYRIDINE IN P-XYLENE



is normally associated with molecular relaxation is zero and hence group relaxation should be the only relaxation process. Therefore the group relaxation time together with the enthalpy of activation to group relaxation should be determined with a considerably increased accuracy. 4-Acetylpyridine fitted the requirements because calculations involving group moments predicted a C_2 value of 0.95 as the molecular dipole moment makes an angle of only $12^{o}42'$ with the axis perpendicular to the projection of the C_1-C_4 axis (Fig.2.5).

4-Acetylpyridine was examined in p-xylene at four temperatures and in decalin at one temperature. The values of the mean relaxation time are listed in Table 2.1. Since the predicted value of C_2 is so high it is undesirable to analyse the data into contributions from two relaxation times. The mean relaxation times obtained from measurements in p-xylene are longer than those for acetophenone in the same solvent and as 4-acetylpyridine is the smaller molecule this would suggest that either there is a small contribution from a molecular relaxation process which has a high value due to interaction with the solvent or that the nitrogen atom is releasing charge towards the acetyl group therebye increasing the double-bond character in the $C_{aryl}-C_{aliphatic}$ bond which will give rise to a higher energy barrier to rotation. It is generally accepted however that the over-all effect of the nitrogen atom in pyridine

is to withdraw charge from the ring[44,55] and this is further borne out by the higher infrared carbonyl stretching frequency of 1706 cm^{-1} for 4-acetylpyridine[38] compared with that of 1691 cm^{-1} for acetophenone.[37] The former suggestion that the pyridine nucleus is interacting with the π-electron system of the p-xylene solvent molecules and that there is a small contribution from a molecular relaxation process is further supported from a single measurement in decalin at 40°C. In this instance, with the absence of π-electrons in the solvent molecules, a shorter mean relaxation time of 11.6×10^{-12} sec compared with 13.1×10^{-12} sec for acetophenone in decalin at 40°C was observed. In addition, a mean relaxation time of 11.6×10^{-12} sec for 4-acetylpyridine in the viscous solvent decalin would appear to be far too short to be attributed to molecular rotation and would suggest that acetyl group relaxation is the predominant relaxation process in this compound. The enthalpy of activation to group relaxation, calculated from a plot of $\log \tau_0 T - 1/T$, is 1.9 ± 0.3 kcal/mole (Fig.2.6) from the measurements in p-xylene and this compares well with the values previously obtained for acetyl group rotation in acetophenone.

Knobloch has measured 4-acetylpyridine in benzene at 20°C and reports relaxation times of $\tau_1 = 12.8 \times 10^{-12}$ sec $\tau_2 = 1.4 \times 10^{-12}$ sec and $C_1 = 0.88$.[56] It is difficult to visualise the physical significance of such a large C_1 value when group moment calculations and also the relaxation time data

submitted in this study suggests that acetyl group rotation is the predominant relaxation process in this compound. It seems reasonable to suggest that if one process was largely predominating an analysis into two relaxation times, while mathematically possible, might have no physical meaning.

The dipole moment of 4-acetylpyridine in p-xylene at 25°C is 2.30D which compares with values of 2.38D in benzene at 20°C[56] and 2.41D in benzene at 25°C.[44] No atom polarization correction has been applied in these latter two cases and this should explain the higher dipole moments that were reported.

Dielectric studies have been undertaken by Mehrotra and Saxena[57] on 2-acetylpyridine and 2-bromopyridine at a single wavelength in benzene at 20°C. The relaxation times reported are 7.88 and 9.96×10^{-12} sec respectively and the shorter relaxation time of the former compound is attributed to a contribution from intramolecular relaxation of the acetyl group. Knobloch[56] has also measured 2-acetylpyridine in benzene at 20°C and obtained a single relaxation time of 16.8×10^{-12} sec from measurements at five wavelengths and which ought therefore to be the more accurate result. However, if the errors on the measurements for 2-acetylpyridine and 2-bromopyridine were consistent it is possible that the conclusion of Mehrotra and Saxena that acetyl group rotation is taking place in 2-acetylpyridine may not be affected.

In addition to 4-acetylpyridine measurements have

been carried out in this laboratory on para-halogenated acetophenones[58] where again the dipole moment of the molecule will be in a direction approximately perpendicular to the projection of the $C_1 - C_4$ axis. The relaxation times observed for these molecules are definitely much shorter than values which would be predicted for molecular rotation and the shortening is to such an extent that acetyl group rotation must be the predominant relaxation process. For example, p-bromoacetophenone has a mean relaxation time of 12.7×10^{-12} sec in p-xylene at 40°C whereas p-bromoanisole (Chapter 3) and p-bromotoluene[27] have molecular relaxation times of 27.5 and 17.4 $\times 10^{-12}$ sec respectively, under the same conditions, both of which are smaller molecules.

ω,ω,ω-Trifluoroacetophenone has been studied in solution in cyclohexane and p-xylene. No dipole moment data exists for the para-halogenated derivatives of this compound and therefore it is more difficult to assess the angle that the molecular dipole moment subtends with the projection of the $C_1 - C_4$ axis. However, calculations employing bond moments, neglecting inductive effects, suggest that C_1 will be approximately 0.9 and that therefore molecular relaxation will be the principal relaxation mechanism. This is verified by the high τ_0 values obtained compared with those of acetophenone. Analysis into two relaxation times at 25°C in cyclohexane yield $\tau_1 = 21.8 \times 10^{-12}$ sec, $\tau_2 = 7.4 \times 10^{-12}$ sec and $C_1 = 0.91$. In p-xylene at 25°C $\tau_1 = 26.5 \times 10^{-12}$

FIG. 2.7 PLOTS OF LOG $\tau_1 T$ AGAINST $1/T$ FOR ω,ω,ω TRIFLUOROACETOPHENONE IN (a) P-XYLENE AND (b) CYCLOHEXANE.

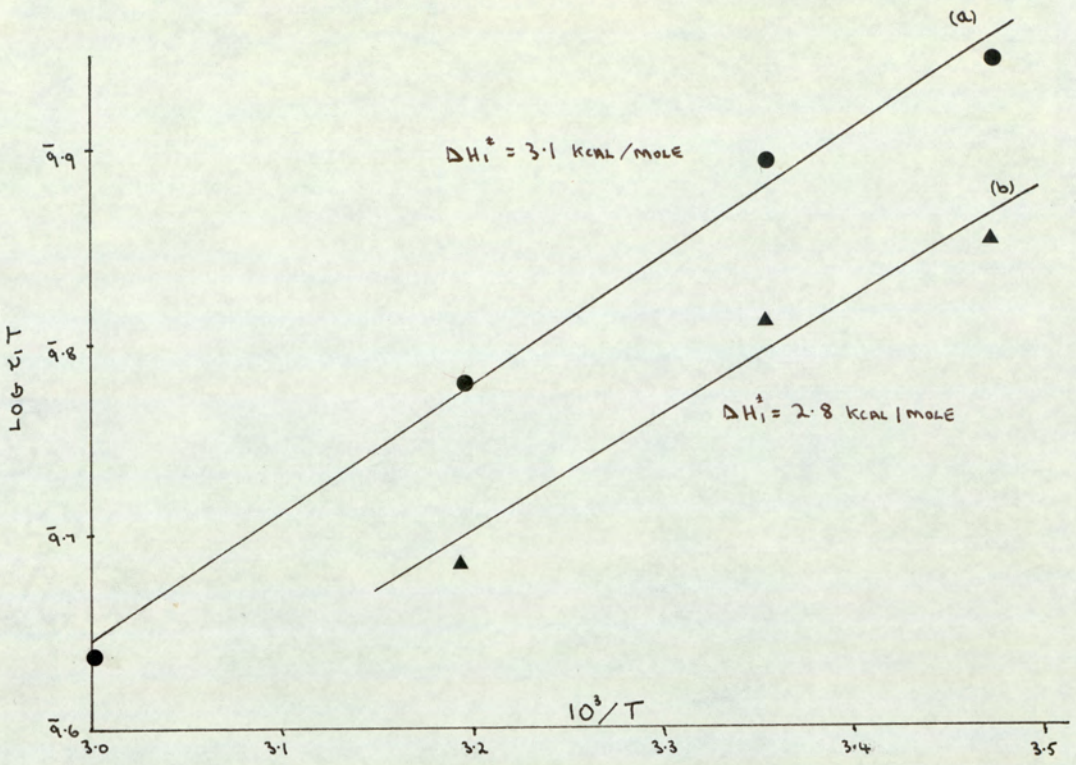
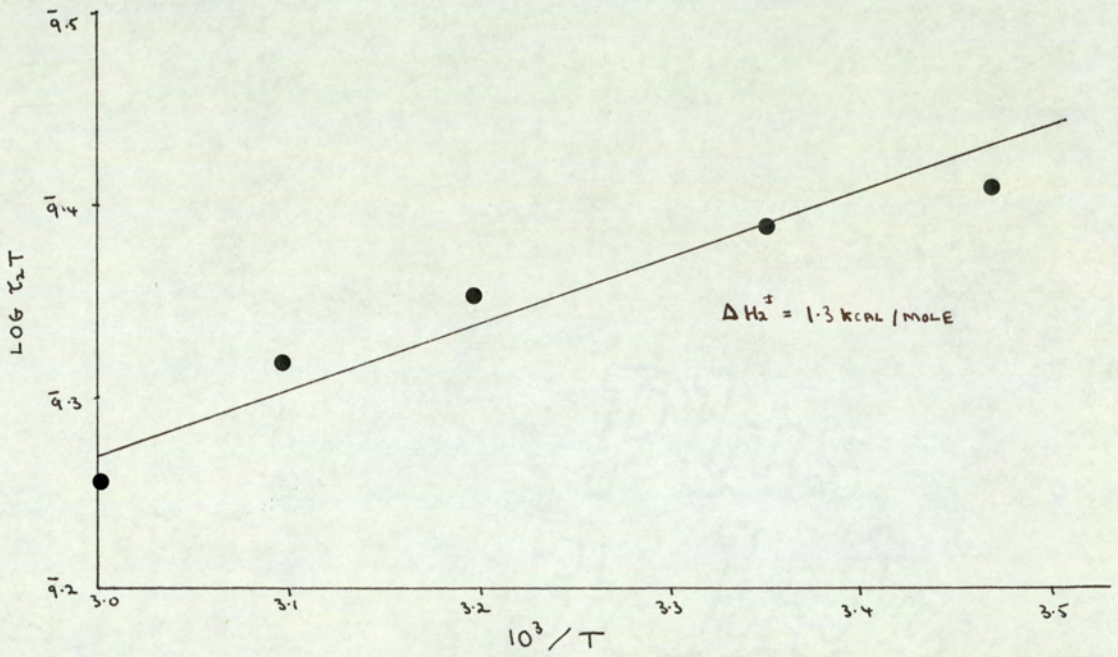


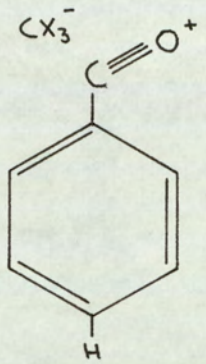
FIG. 2.8 PLOT OF LOG $\tau_2 T$ AGAINST $1/T$ FOR CYCLOHEXYL METHYLKETONE IN P-XYLENE.



sec, $\tau_2 = 11.1 \times 10^{-12}$ sec and $C_1 = 0.78$. The τ_1 values can be determined with a high degree of accuracy ($\sim \pm 6\%$) due to the high C_1 values and therefore they give upper limits for the molecular relaxation times of acetophenone. According to Pauling[36] the van der Waals radius of the hydrogen atom is 1.2 Å while that of fluorine is 1.35 Å. Hence ω,ω,ω-trifluoroacetophenone should not be appreciably larger in size than acetophenone which lends support for the τ_1 values derived for acetophenone being of the correct order. In fact from Courtauld models the ratio of the volume of ω,ω,ω-trifluoroacetophenone to acetophenone is 1.3:1 which is approximately the same as that observed for the ratio of the molecular relaxation times of the two molecules. The ratio of molecular relaxation times of ω,ω,ω-trifluoroacetophenone in p-xylene and cyclohexane gives some indication of the interaction that is taking place in p-xylene. τ_1 has increased by 20 to 30% from measurements in cyclohexane to those in p-xylene and this may be attributed to the interaction of the strongly polar $-C(=O)-CF_3$ group with the π-electrons of the p-xylene. Due to the low weight factor on the intramolecular relaxation process the $\Delta H_2^{\neq}$ values could not be determined but values of $\Delta H_1^{\neq}$ for measurements in cyclohexane and p-xylene are listed in Table 2.2 (see also Fig.2.7)

The infrared carbonyl stretching frequency of ω,ω,ω-trifluoroacetophenone has been determined in carbon

tetrachloride to be 1725 cm^{-1}. This compares with values for ω,ω,ω-trichloroacetophenone of 1717 cm^{-1} [36] and for ω,ω,ω-tribromoacetophenone of 1704 cm^{-1} [38] also both measured in carbon tetrachloride. The carbonyl stretching frequency of acetophenone itself is 1691 cm^{-1} [37] and therefore replacement of the CH_3 group by a CX_3 group (where X=halogen) increases the force constant of the C=O bond possibly due to contributions from a resonance form of the type (II)



(II)

Contributions of this type could be due to the inductive effect of the CX_3 group which appears to decrease in the order $CF_3 > CCl_3 > CBr_3$.

As has been previously stated it has not proved possible to determine the enthalpy of activation to rotation of the $-C(=O)CF_3$ group due to the small weight factor on this relaxation process. It could be postulated that if there was interaction between the p-electrons of the fluorine atoms and the π-electrons of the phenyl ring then the energy barrier to group rotation would be considerably increased above that for acetyl group rotation in acetophenone. However, Sheppard[59] has suggested that p-π interaction is not

significant in trifluoromethoxybenzene and the same conclusion could apply to ω,ω,ω-trifluoroacetophenone. This was verified by the N.M.R. fluorine and proton spectra which showed that the coupling between the fluorine atoms and the ortho protons was extremely weak. Whether this coupling is through bond or through space cannot be ascertained. An investigation of para-halogenated derivatives of ω,ω,ω-trifluoroacetophenone, where C_2 should be considerably increased, could prove very useful in determining the relaxation behaviour and energy barrier to rotation of the $-C(=O)-CF_3$ group.

p-Methoxyacetophenone has been examined in p-xylene at 25°C and the mean relaxation time derived was 26.9×10^{-12} sec. Analysis in terms of two relaxation times gave $\tau_1 = 50.4\times10^{-12}$ sec and $\tau_2 = 15.4\times10^{-12}$ sec with C_1 equal to 0.51. The dipole moment was determined to be 3.48D which compares with a value of 3.51D in benzene at 25°C.[60] The mean relaxation time indicates a contribution from an intramolecular relaxation mechanism when compared with the molecular relaxation time of 31.3×10^{-12} sec for p-bromoanisole in p-xylene at 25°C(Chapter 3), a molecule which is smaller than p-methoxyacetophenone. The molecular dipole moment resulting from rotation of both the methoxy and the acetyl groups will now be calculated. Calculations from group moments have shown that the methoxy group moment subtends an angle of 67°40' with the projection of the C_1-C_4 axis in

anisole, the moment being directed towards the ring (see Chapter 3). The acetyl group moment has been shown to subtend an angle of approximately 54° with the long axis of the molecule the direction being away from the ring. If the groups are freely rotating then the component along the C_1-C_4 axis (μ_1) will remain constant and

$$\mu_1 = \mu_{OCH_3} \cdot \cos 68^\circ + \mu_{-C(=O)-CH_3} \cdot \cos 54^\circ = 0.46D + 1.64D = 2.10D \quad 2.10$$

The components associated with an intramolecular process will be $m_1 = \mu_{OCH_3} \cdot \sin 68^\circ$ and $m_2 = \mu_{-C(=O)-CH_3} \cdot \sin 54^\circ$. At any instant the two components will be separated by an angle ϕ and the resultant dipole moment will be

$$(m_1^2 + m_2^2 + 2m_1 m_2 \cos\phi)^{\frac{1}{2}} \quad 2.11$$

Integrating for all values of ϕ gives the dipolar contribution perpendicular to the C_1-C_4 axis(μ_2).

$$(\mu_2)^2 = \frac{1}{2\pi} \int_0^{2\pi} (m_1^2 + m_2^2 + 2 m_1 m_2 \cos\phi)\, d\phi \quad 2.12$$

$$(\mu_2)^2 = \frac{1}{2\pi}\left[(m_1^2 + m_2^2)\, 2\pi - 0\right] \quad 2.13$$

$$\mu_2 = (m_1^2 + m_2^2)^{\frac{1}{2}} = 2.54\,D \quad 2.14$$

The molecular dipole moment is the resultant of μ_1 and μ_2

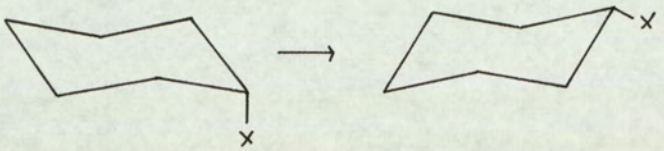
$$\mu = (\mu_1^2 + \mu_2^2)^{\frac{1}{2}} \quad 2.15$$

and μ=3.30D which compares well with the experimental value of 3.48D. Therefore the dipole moment of p-methoxyacetophenone could be explained on the basis of rotation of the polar substituents. From the dipolar contributions μ_1 and μ_2 the weight factor on the molecular relaxation process is calculated to be 0.41 which compares with the experimental value of 0.51. The τ_2 value of 15.4×10^{-12} sec will be a

composite quantity, since both the methoxy and the acetyl group will have a characteristic relaxation time of their own, but with the number of experimental points available it is not desirable to analyse the data in terms of three relaxation times. The τ_2 value of 15.4×10^{-12} sec is long compared with that for methoxy group relaxation in anisole ($\tau_2 = 8.0 \times 10^{-12}$ sec in p-xylene at 25°C) or acetyl group relaxation in acetophenone ($\tau_2 = 9.7 \times 10^{-12}$ sec in p-xylene at 25°C). This lengthening of the intramolecular relaxation time could be explained by the mesomeric effects of the methoxy and acetyl groups reinforcing one another to give more double-bond character in the bonds between the groups and the benzene nucleus. This is further borne out by the negative shift of the infrared carbonyl stretching frequency from 1691 cm^{-1} in acetophenone to 1675 cm^{-1} in p-methoxy-acetophenone.

Finally it was decided to investigate the aliphatic molecule cyclohexylmethylketone to see what effect an absence of conjugation had on the energy barrier to acetyl group rotation compared with the barrier height in the aromatic compounds. The mean relaxation time of 9.1×10^{-12} sec in p-xylene at 25°C compares with that of 12.8×10^{-12} sec for acetophenone. This almost certainly indicates a contribution from an intramolecular relaxation process since molecular relaxation times of cyclohexyl compounds are

usually longer than those of the corresponding phenyl derivatives.e.g. the relaxation time of cyclohexylchloride in benzene at 20°C is 10.4×10^{-12} sec[61] whereas that for chlorobenzene is 8.3×10^{-12} sec.[62] It could be suggested that the intramolecular relaxation process in cyclohexylmethylketone is not acetyl group rotation but the process



involving interconversion between chair forms of the cyclohexane ring, the axial bonds becoming equatorial. An experimental value for this process is however 10.5 kcal/mole[63] while that calculated theoretically is 12.66 kcal/mole.[63] Energy barriers of this magnitude would not be observed in the microwave region and therefore it would be expected that the cyclohexane ring would behave as a rigid unit. Smyth has recently measured bromocyclohexane[64] ($\tau_o = 19.1 \times 10^{-12}$ sec at 25°C in the pure liquid) and found that an attempt to analyse the data in terms of two relaxation times was unsuccessful which suggests that no interconversion between the chair forms is being observed in the microwave region.

Analysing the data for cyclohexylmethylketone in terms of two relaxation times gives a C_1 value of 0.1→0.2. With such small weight factors on the molecular relaxation

process the τ_1 values have no real physical meaning. τ_2 can be determined with an accuracy of ~ $\pm$7%. $\Delta H_2^{\ddagger}$ is calculated from the log τ_2T-1/T plot to be 1.3 $\pm$ 0.6 kcal/mole (Fig.2.8.). This is approximately 0.7 kcal/mole lower than the $\Delta H_2^{\ddagger}$ values obtained for the aromatic compounds and suggests that the additional energy barrier due to conjugation between the acetyl group and the aromatic nucleus is about this value.

Chapter 3

Relaxation Processes of Anisole and Substituted Anisoles.

Introduction

Several studies have been carried out on the relaxation processes in anisole and substituted anisoles. Smyth et al[14,65] have analysed the dielectric data of anisole into contributions from molecular relaxation and re-orientation of the methoxy group and have obtained for the latter process values of 7.2, 7.0 and 6.5×10^{-12} sec at 20°C in nujol, decalin and benzene solutions respectively where the values indicate that the group re-orientation relaxation time is somewhat insensitive to the macroscopic viscosity since the latter values are about 211, 2.61 and 0.65 c.p. respectively. Measurements in the pure liquid state however by Garg and Smyth[64] and by Vaughan, Roeder and Provder[66] yielded a shorter methoxy group relaxation time of 3.2×10^{-12} sec at 20°C. Vaughan et al also examined 1-methoxynaphthalene and 2-methoxynaphthalene in the pure liquid state and, again, these molecules bore shorter methoxy relaxation times than those obtained in dilute solution by Smyth. This is somewhat surprising since relaxation times deduced from measurements on pure polar liquids are almost always longer than those from dilute solution.[67] In addition, some other of the relaxation times quoted by Vaughan et al are not easily explained. For example their value of 2.0×10^{-12} sec for the short relaxation time of anisole at 60°C is to be compared with a value of 1.3×10^{-12} sec for the short relaxation time of 1-methoxynaphthalene. For both these molecules the mesomeric

factors are very similar as is borne out by the close similarity of dipole moments of 1-substituted naphthalenes with the corresponding benzene derivatives whereas in 1-methoxynaphthalene a higher free energy of activation -with a consequent lengthening of the relaxation time-would be anticipated due to steric repulsion between the peri hydrogen and the methoxy group at the 1-position. Another such anomaly is that the extrapolated value of 1.7×10^{-12} sec for the short relaxation time of anisole at 80°C compares with a value of only 1.0×10^{-12} sec for the short relaxation time of 2-methoxynaphthalene although the energy barrier to group rotation in the latter compound should be higher since dipole moments of 2-substituted naphthalenes are usually greater than those of the corresponding benzene derivatives suggesting more conjugation in the molecule. Altogether it would seem that in terms of molecular and intramolecular relaxation processes the actual relaxation time values of Vaughan et al require further consideration.

The investigation of the relaxation processes in anisole has enabled the enthalpy of activation to group rotation to be calculated and the resulting value is compared with existing values quoted in the literature. Studies have also been carried out, in most cases at several temperatures, on p-bromoanisole, p-methylanisole, 2-methoxynaphthalene, trifluoromethoxybenzene, methoxypentafluorobenzene, difluoromethyl phenyl ether and difluoromethyl pentafluoro-

phenyl ether so that a full assessment of methoxy or substituted methoxy group relaxation processes could be made. The relaxation times obtained are listed in Table 3.1. p-Dimethoxybenzene has also been measured but the results for this molecule are discussed in Chapter 5. This study also includes the measurement of molecular dipole moments and these are used to determine the direction of group moments to the rotational axes.

Table 3.1. Relaxation times, distribution parameter(α), static dielectric constant(ϵ_o), dielectric constant at very high frequency(ϵ_∞) and dipole moment(μ) for solutions of weight fraction ω_2 at temperature t°C for molecules containing methoxy groups or substituted methoxy groups.

t (°C)	ω_2	τ_o	τ_1	τ_2	C_1	α	ϵ_o	ϵ_∞	μ (D)
			$\times 10^{-12}$ sec						
				Anisole/p-xylene					
15	0.09125	10.8	78.8	9.6	0.15	0.04	2.4439	2.310	1.19
25	0.10531	9.0	39.6	8.0	0.15	0.03	2.4445	2.298	1.19
40	0.10531	7.7	13.8	6.8	0.15	0.01	2.4047	2.278	1.15
50	0.09502	6.7	11.1	5.8	0.15	0	2.3629	2.258	1.13
60	0.09125	5.8	12.4	4.9	0.15	0	2.3321	2.234	1.14
				Anisole/cyclohexane					
25	0.05967	8.3	38.1	6.5	0.15	0.07	2.1053	2.038	1.20
25	0.07920	8.3	28.0	6.4	0.15	0.06	2.1366	2.048	1.19
				p-Methylanisole/p-xylene					
15	0.09835	9.7				0.03	2.4246	2.311	1.20
25	0.09216	9.0				0.02	2.3924	2.292	1.19
32.5	0.09216	7.8				0	2.3762	2.285	1.16
40	0.09216	6.3				0.02	2.3569	2.264	1.19
50	0.09216	5.9				0	2.3341	2.249	1.17

t (°C)	w_2	τ_0	τ_1	τ_2	c_1	α	ϵ_0	ϵ_∞	μ (D)
		—— $\times 10^{12}$ sec ——							
				p-Methylanisole/p-xylene (cont.)					
60	0.09835	5.2				0	2.3196	2.234	1.16
				p-Bromoanisole/p-xylene					
15	0.04912	32.2	39.2	9.1	0.84	0.09	2.4474	2.291	2.31
25	0.04970	27.1	31.3	7.4	0.88	0.06	2.4235	2.277	2.28
40	0.04970	21.9	27.5	8.9	0.79	0.06	2.3865	2.251	2.28
50	0.04970	19.4	22.6	5.7	0.85	0.05	2.3633	2.236	2.27
60	0.04912	17.4	21.4	6.6	0.80	0.05	2.3362	2.217	2.26
				Trifluoromethoxybenzene/cyclohexane					
10	0.03029	24.1	25.6	2.9	0.94	0.05	2.1291	2.042	2.25
10	0.04001	23.4	25.3	2.7	0.92	0.06	2.1575	2.040	2.27
25	0.02501	18.1	18.9	8.6	0.94	0.02	2.0848	2.021	2.21
25	0.03074	18.5	20.3	3.1	0.90	0.06	2.0997	2.016	2.28
25	0.03517	19.0	22.3	8.2	0.83	0.04	2.1116	2.018	2.25
25	0.03998	18.7	20.1	5.9	0.91	0.03	2.1266	2.020	2.25
25	0.04531	19.0	20.6	7.1	0.91	0.03	2.1405	2.020	2.25
40	0.03074	15.1	16.6	5.7	0.90	0.03	2.0670	1.990	2.28
40	0.03998	15.4	16.6	4.8	0.93	0.05	2.0909	1.991	2.27

t (°C)	w_2	τ_0	τ_1	τ_2	c_1	α	ϵ_0	ϵ_∞	μ (D)
			$\times 10^{12}$ sec						
			Trifluoromethoxybenzene/cyclohexane (cont.)						
60	0.03029	12.8	13.0	2.2	0.95	0.06	2.0279	1.959	2.28
60	0.04001	12.4	13.0	2.7	0.93	0.05	2.0491	1.959	2.27
			Trifluoromethoxybenzene/decalin						
15	0.02118	29.6	32.4	5.8	0.92	0.06	2.2335	2.173	2.07
25	0.02118	25.4	27.0	6.8	0.99	0.04	2.2163	2.160	2.05
40	0.03003	21.2	22.1	4.6	0.95	0.02	2.2124	2.139	2.03
70	0.03003	15.4	15.7	6.2	0.97	0	2.1678	2.100	2.09
			2-Methoxynaphthalene/p-xylene						
25	0.08588	20.3	50.0	10.3	0.5	0.16	2.3757	2.292	1.21
			2-Methoxynaphthalene/cyclohexane						
40	0.09033	13.8	37.1	5.4	0.55	0.22	2.1015	2.033	1.24
			Difluoromethyl phenyl ether/cyclohexane						
25	0.02118	11.7				0.19	2.0838	2.017	2.31
25	0.03456	11.5				0.17	2.1293	2.025	2.26
			Difluoromethyl pentafluorophenyl ether/cyclohexane						
25	0.06362	9.4				0.08	2.0656	2.016	1.47

t (°C)	w_2	τ_0	τ_1	τ_2	c_1	α	ϵ_0	ϵ_∞	μ (D)
			$\times 10^{12}$ sec						
			Methoxypentafluorobenzene/cyclohexane						
15	0.04142	16.9	25.0	5.0	0.70	0.18	2.1284	2.038	2.24
15	0.04782	16.3	25.5	5.4	0.70	0.14	2.1426	2.039	2.19
25	0.03116	15.1	23.9	4.5	0.70	0.16	2.0858	2.020	2.22
25	0.03781	14.9	22.1	4.4	0.73	0.13	2.1009	2.022	2.21
25	0.04908	15.0	25.7	5.7	0.65	0.14	2.1297	2.024	2.22
40	0.03116	13.1	19.0	4.1	0.72	0.15	2.0551	1.995	2.26
40	0.03781	12.9	20.0	4.1	0.70	0.16	2.0703	1.998	2.24
60	0.04066	10.4	15.0	3.3	0.69	0.13	2.0344	1.961	2.25
60	0.04515	10.1	15.0	3.3	0.67	0.12	2.0429	1.964	2.21
			Pentafluorobenzene/cyclohexane						
25	0.04813	7.6				0	2.0623	2.016	1.38
25	0.09456	7.5				0	2.1092	2.016	1.40

Table 3.2. Free Energies ($\Delta G^{\ddagger}$), Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta S^{\ddagger}$) of Activation for Molecular and Intramolecular Relaxation.

t (°C)	$\Delta G_1^{\ddagger}$	$\Delta H_1^{\ddagger}$	$\Delta S_1^{\ddagger}$	$\Delta G_2^{\ddagger}$	$\Delta H_2^{\ddagger}$	$\Delta S_2^{\ddagger}$
	— kcal/mole —		cal/deg/mole	— kcal/mole —		cal/deg/mole
		Anisole/p-xylene				
15				2.32	2.1	-0.73
25				2.31	"	-0.67
40				2.36	"	-0.80
50				2.36	"	-0.77
60				2.32	"	-0.63
		p-Methylanisole/p-xylene				
15				2.28	2.2	-0.24
25				2.38	"	-0.57
32.5				2.37	"	-0.52
40				2.30	"	-0.29
50				2.37	"	-0.50
60				2.37	"	-0.48
		p-Bromoanisole/p-xylene				
15	3.01	1.9	-3.75			
25	3.03	"	-3.69			
40	3.08	"	-3.67			
50	3.12	"	-3.68			
60	3.17	"	-3.72			
		Trifluoromethoxybenzene/cyclohexane				
10	2.82	1.9	-3.25			
25	2.85	"	-3.19			
40	2.91	"	-3.23			
60	2.98	"	-3.24			

t (°C)	$\Delta G_1^{\ddagger}$	$\Delta H_1^{\ddagger}$	$\Delta S_1^{\ddagger}$	$\Delta G_2^{\ddagger}$	$\Delta H_2^{\ddagger}$	$\Delta S_2^{\ddagger}$
	— KCAL/MOLE —		CAL/DEG/MOLE	— KCAL/MOLE —		CAL/DEG/MOLE
			Trifluoromethoxybenzene/decalin			
15	3.02	1.9	-3.78			
25	3.03	"	-3.69			
40	3.09	"	-3.70			
70	3.21	"	-3.73			
			Methoxypentafluorobenzene/cyclohexane			
15	2.89	1.7	-4.1	1.97	1.5	-1.63
25	2.96	"	-4.19	2.02	"	-1.74
40	3.03	"	-4.22	2.04	"	-1.72
60	3.07	"	-4.08	2.08	"	-1.75

Table 3.3. Literature Values of Relaxation Times of Anisole and Substituted Anisoles together with Enthalpies of Activation for Molecular Relaxation ($\Delta H_1^{\ddagger}$) and for Intramolecular Relaxation ($\Delta H_2^{\ddagger}$).

Compound	Solvent	t (°C)	τ_0	τ_1	τ_2	c_1	$\Delta H^{\ddagger}$ KCAL/MOLE	Ref.
			——	$\times 10^{12}$ SEC ——				
Anisole	Benzene	20		20	6.5	0.2		65
		40		15	5.6	0.2		"
		60	6.6					"
Anisole	Benzene	20	7.0	9.6	0.8	0.81		68
Anisole	Benzene	19	5.6					28
Anisole	Benzene	25	7.3					19
Anisole	Decalin	20	10.8	21.9	7.0	0.35	$\Delta H_1^{\ddagger} = 1.3$	14
		40	9.0	18.2	6.0	0.32	$\Delta H_2^{\ddagger} = 0.6$	"
		60	7.6	15.0	5.5	0.38		"
Anisole	Nujol	20	17.8	69	7.2	0.4	$\Delta H_1^{\ddagger} = 2.5$	14
		40		46	6.6	0.4	$\Delta H_2^{\ddagger} = 0.1$	"
		60		36	6.3	0.38		"

Compound	Solvent	t (°C)	τ_0	τ_1	τ_2	c_1	$\Delta H^{\ddagger}$ kcal/mole	Ref.
			—	$\times 10^{12}$ sec	—			
Anisole	Pure Liquid	20		14.8	3.2	0.77	$\Delta H_1^{\ddagger} = 2.7$	66
		40		10.5	2.6	0.76	$\Delta H_2^{\ddagger} = 1.7$	"
		60		7.9	2.0	0.75		"
Anisole	Pure Liquid	20		14.7	3.2	0.78	$\Delta H_1^{\ddagger} = 2.6$	64
		40		10.6	2.7	0.75	$\Delta H_2^{\ddagger} = 1.5$	"
		60		8.5	2.3	0.73		"
p-Chloro-anisole	Nujol	20	374	380	10.5	0.79	$\Delta H_1^{\ddagger} = 6.4$	14
		40		210	10.0	0.77	$\Delta H_2^{\ddagger} = 0$	"
		60		91	10.0	0.73		"
p-Methyl-anisole	Nujol	20	16.6	100	11.5	0.3	$\Delta H_1^{\ddagger} = 4.1$	14
		40		63	10.6	0.22	$\Delta H_2^{\ddagger} = 0.1$	"
		60		38	10.0	0.22		"
p-Phenyl-anisole	Nujol	20	61	345	14.6	0.44	$\Delta H_1^{\ddagger} = 6.1$	14
		40		195	14.2	0.35	$\Delta H_2^{\ddagger} = 0.3$	"
		60		85	12.1	0.38		"
1-Methoxy-naphthalene	Decalin	20	55.2	79.4	27.5	0.61		14
		40	44.7	63.1	25.0	0.59		"
1-Methoxy-naphthalene	Nujol	20	347	640	27.5	0.7	$\Delta H_1^{\ddagger} = 6.1$	14
		40	155	316	24.6	0.68		"
		60	100	159	33.4	0.66		"
1-Methoxy-naphthalene	Pure Liquid	20		136	2.3	0.87	$\Delta H_1^{\ddagger} = 4.2$	66
		40		77.1	1.1	0.88		"
		60		50.4	1.3	0.85		"
2-Methoxy-naphthalene	Decalin	20	33.1	94	15.8	0.49		14
		40	23.3	72	14.4	0.46		"

Compound	Solvent	t (°C)	τ_0	τ_1	τ_2	c_1	$\Delta H^{\neq}$ kcal/mole	Ref.
			— $\times 10^{12}$ sec —					
2-Methoxy-naphthalene	Nujol	20	500	912	20	0.58		14
		40		648	19	0.52	$\Delta H_1^{\neq} = 2.8$	"
		60		450	18.2	0.49	$\Delta H_2^{\neq} = 0$	"
2-Methoxy-naphthalene	Pure Liquid	80		14.9	1.0	0.82		66
3,5-Dimethyl-anisole	Benzene	20	16	18	4.5	0.72	$\Delta H_1^{\neq} = 2.2$	53
		40	13	13	5	0.71	$\Delta H_2^{\neq} = 0$	"
		60	10	10	5	0.69		"
2,6-Dimethyl-anisole	Benzene	20	25	14	40	0.48	$\Delta H_1^{\neq} = 2.1$	53
		40	20	11	25	0.44	$\Delta H_2^{\neq} = 3.9$	"
		60	15.1	8	17	0.39		"
2,4,6-Tri-methylanisole	Benzene	20	15.9	22.7	0.8	0.69		68
2,4,6-Tri-chloroanisole	Benzene	18	20.9					28
"	"	20		27.2	1.5	0.88		79
"	"	20	12					80
2,6-Dichloro-anisole	Benzene	20	19.9					80
2,4,6-Tri-bromoanisole	Benzene	18	23.4					28

Discussion

Previous workers who have examined the dielectric absorption of anisole have all reached the conclusion that the observed mean relaxation time is too short to be attributed solely to a molecular relaxation process and that therefore there is a contribution to the total dielectric absorption from methoxy group rotation. One of the earliest attempts to determine the relaxation time of anisole was made by Fischer who found that the mean relaxation time was 7.3×10^{-12} sec in benzene at 25°C.[19] This result was compared with a relaxation time of 9.6×10^{-12} sec, calculated from eqn. 2.2, for molecular rotation. The shortening of the relaxation time was attributed to methoxy group rotation. Fischer's calculated value for molecular relaxation appears low however since Courtauld models suggest that anisole is larger than bromobenzene which has a relaxation time of 12.0×10^{-12} sec in cyclohexane at 20°C and 14.0×10^{-12} sec in p-xylene at 15°C.[27] In addition, anisole is similar in size and shape to benzyl chloride which has a molecular relaxation time of 15.4×10^{-12} sec in p-xylene at 25°C (Chapter 5). The mean relaxation times for anisole in p-xylene and in cyclohexane at several temperatures, obtained in this study, are listed in Table 3.1. The values of 9.0 and 8.3×10^{-12} sec at 25°C in p-xylene and cyclohexane, respectively, clearly indicate a contribution from an intramolecular process when compared with the above molecular relaxation time values.

Determinations of the mean relaxation time of anisole have also been made in decalin giving a value of 10.8×10^{-12} sec at 20°C.[14] This value, from measurements in a solvent with a viscosity approximately four times that of p-xylene, not only shows that there is a contribution from group rotation but also suggests that this is the predominant relaxation process since, from a consideration of molecular models, the molecular relaxation time of anisole should be approximately 0.87 times that of acetophenone and as the interpolated τ_1 value for acetophenone in decalin at 20°C is 29.7×10^{-12} sec a molecular relaxation time of approximately 25.8×10^{-12} sec would be expected for anisole. Furthermore, measurements on anisole in the highly viscous solvent nujol (η =211 c.p. at 20°C) yielded a calculated mean relaxation time of 19.5×10^{-12} sec at 20°C[14] again suggesting that methoxy group rotation is the predominant relaxation process since any significant contribution from molecular relaxation would have the effect of lengthening the mean relaxation time considerably.

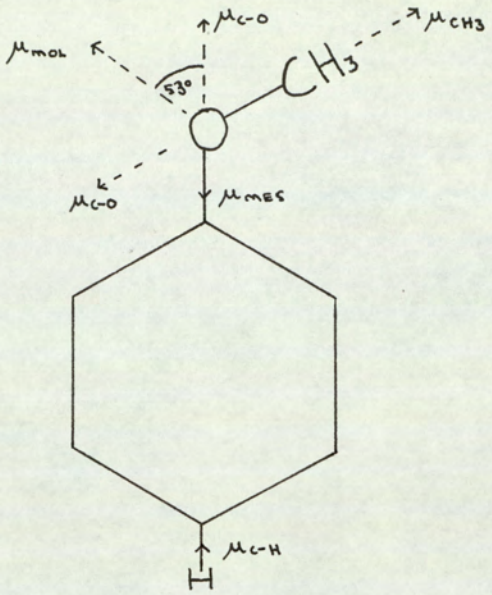
In order to determine the group and molecular relaxation times of a molecule it is useful to have an accurate assessment of C_1, the weight factor on the molecular relaxation process. If this value can be calculated with a sufficient degree of accuracy then its value may be taken as fixed and this in turn will lower the number of variables in the determination of τ_1 and τ_2 and allow a more precise

estimate to be made of the latter parameters. It must be realised of course that if the τ_1 value so calculated does not compare with the relaxation time of any rigid molecule of similar shape and size then it must be accepted that the calculation of C_1 is in error and therefore C_1 should also be treated as a variable parameter. A check on the calculation of C_1 is provided by the determination of the relaxation times of para-substituted derivatives of the parent compound for if C_1 (experimental) is approximately equal to C_1 (calculated) in these compounds then this would support the initial C_1 calculation. It is a general feature of relaxation time data in the literature that the C_1 values are quoted without any reason being given for the change in C_1 from compound to compound. In addition many erroneous results exist which require further investigation. For example, Forest and Smyth[65] find that the C_1 value for anisole in benzene at 20°C is 0.2 i.e. the contribution to the total dielectric absorption by the molecular relaxation process is only 20%. Klages and Zentek[68] however found that from measurements of anisole in the same solvent and at the same temperature the C_1 value was 0.8 i.e. there was an 80% contribution to the total dielectric absorption from the molecular relaxation process. Obviously one of these results must be in considerable error. An attempt has been made in this study to relate the observed relaxation times with C_1 values in the compounds investigated.

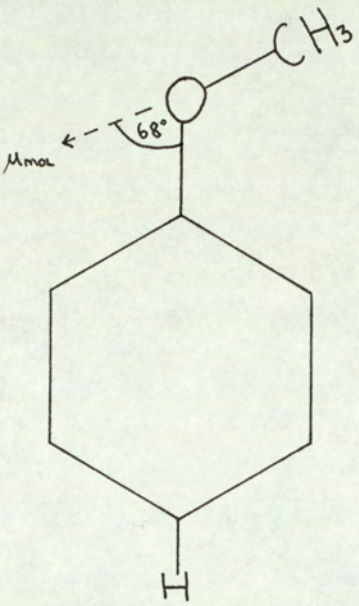
In order to determine C_1 it is necessary to calculate, θ, the angle that the molecular dipole moment (μ) subtends with the projection of the C_1-C_4 axis, from a consideration of either bond or group moments, and then, by resolving the dipole moment into components along and perpendicular to the C_1-C_4 axis of the molecule, C_1 may be evaluated from eqns. 1.27 and 1.32. A derivation of the C_1 value of anisole from bond moments necessitates first of all a calculation of the C-O bond moment. This can be deduced from the moment of dimethylether (μ=1.25D).[29] Neglecting inductive effects and assuming an oxygen valency angle of 111.5°[69] the observed dipole moment (1.25D) is equal to $2\cdot\mu_{O-CH_3}\cdot\cos(111.5^\circ/2)$ resulting in a $O-CH_3$ bond moment of 1.11D. If the methyl group moment is 0.3D[41] directed away from the oxygen atom then the C-O bond moment is 1.41D. The oxygen valency angle in anisole is assumed to be equal to 120°. The molecular dipole moment (μ) of anisole equals 1.2D and is the resultant of the two components μ_1 and μ_2 along and perpendicular to the long axis respectively. Neglecting inductive effects μ_1 is the algebraic sum of the $C_{aryl}-O$ bond moment (=1.41D if equal to the $C_{alkyl}-O$ bond moment), an aromatic C-H bond moment due to the para hydrogen (0.4D), the component of the aliphatic $O-CH_3$ bond moment along the long axis ($\mu_{O-CH_3}\cdot\cos60^\circ$) and a mesomeric moment. The component μ_2 is equal to $\mu_{O-CH_3}\cdot\sin60^\circ$. Since $\mu^2=\mu_1^2+\mu_2^2$ then μ_1 may be determined and hence the mesomeric moment is

FIG. 3.1 DIRECTION OF MOLECULAR DIPOLE MOMENT OF ANISOLE DERIVED FROM

(a) BOND MOMENT CALCULATIONS



(b) GROUP MOMENT CALCULATIONS



evaluated to be 0.54D directed towards the benzene ring. The angle (θ) that the molecular dipole moment subtends with the projection of the C_1-C_4 axis is calculated to be $53^{\circ}26'$ with the moment directed away from the ring. C_1/C_2 is then equal to $(\cos 53^{\circ}26'/\sin 53^{\circ}26')^2$ and as $C_1+C_2=1$ then $C_1=0.36$. The location of the bond moments and the angles that they subtend in anisole are shown in Fig.3.1.a. From bond moment calculations it has been shown that the molecular dipole moment of anisole is directed away from the benzene nucleus. Taking inductive effects into account would not alter this conclusion since it is generally accepted that the methoxy group withdraws charge by the inductive mechanism.[10] If the direction of the molecular dipole moment in anisole was away from the ring then it would be expected that a para-halogenated anisole would have a smaller dipole moment than that of the corresponding halobenzene because the component of the methoxy dipole moment along the long axis would oppose the carbon-halogen dipole moment. However, para-chloroanisole has a dipole moment of 2.32D in benzene at $20^{\circ}C$[29] and therefore this suggests that the dipole moment of the methoxy group must be directed towards the ring and supporting the C-Cl moment.

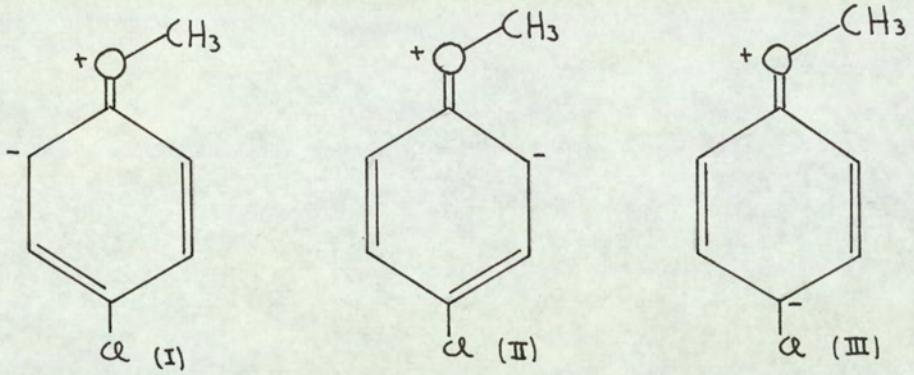
C_1 may be calculated from group moments for anisole in an analogous manner to that employed for calculating C_1 in acetophenone. The dipole moment of a para-substituted anisole, where the moment of the para-substituent is along

the C_1-C_4 axis, may be related to the moments of the mono-substituted compounds by the equation

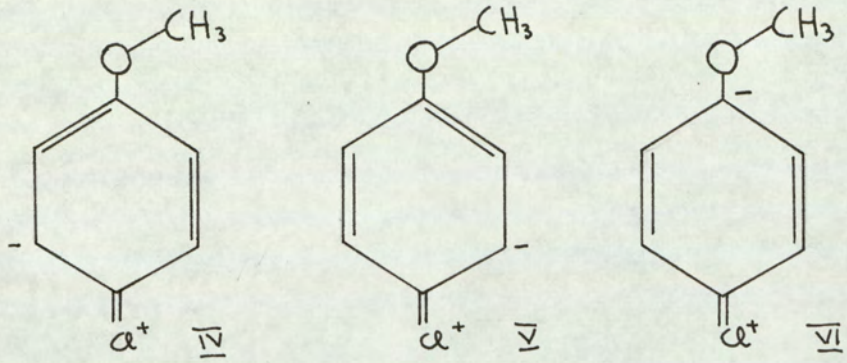
$$(\mu_{p\text{-}Xanisole})^2 = (\mu_{anisole})^2 + (\mu_{C_6H_5X})^2 + 2\mu_{anisole}\cdot\mu_{C_6H_5X}\cos(180^\circ-\theta) \quad 3.1$$

where θ is the angle that the methoxy group dipole subtends with the long axis of the molecule. If X=Cl then $\mu_{p\text{-chloroanisole}}$ =2.32D[29], $\mu_{C_6H_5Cl}$ =1.58D[41] and the methoxy group dipole is calculated to make an angle (θ) of $67^\circ40'$ with the projection of the C_1-C_4 axis, directed towards the ring (Fig.3.1.b). The C_1 value is then determined to be 0.15 which would suggest that methoxy group rotation is the principal relaxation process in anisole. A similar type of calculation to that above incorporating the dipole moments of 4-methoxypyridine (μ=2.94D)[29] and pyridine (μ=2.2D)[29] yielded a θ of $61^\circ46'$ and hence C_1=0.22. The large discrepancy in results obtained between group and bond moment calculations could be due to the assumption that the $C_{aryl}-O$ and the $C_{alkyl}-O$ bond moments are equal. In all probability the dipole moment between oxygen and the sp^2 hybridised carbon atom is less than that between oxygen and the sp^3 hybridised carbon atom since the former carbon atom should be more electronegative. This would result in a tendency for the dipole moment of anisole to be directed towards the ring. The other alternatives to explain the divergence in results from bond and group moment calculations are (i) the mesomeric moment of anisole is not 0.54D but

is approximately 2.0D so that the molecular dipole moment of anisole is still directed at an angle of $53^{o}26'$ with the projection of the C_1-C_4 axis but towards the ring or (ii) a large interaction between the mesomeric effects of the methoxy group and the para-substituted group in para-substituted anisoles is giving rise to a displacement of charge towards the para-substituted group and hence the angle calculated from eqn.3.1 cannot be taken as equal to the angle θ in anisole. With regard to (i) a mesomeric moment of 2.0D seems high. Values of 0.4D[40] and 0.96D[44] are quoted in the literature for the mesomeric moment of anisole but values of this magnitude would not be sufficient to cause the moment of anisole to be directed towards the ring, assuming the rest of the bond moment calculations to be correct. With regard to (ii) there are two o-p- directing groups in opposition and for such a case the interaction moment is usually found to be low.[41] The mesomeric effect of the methoxy group will tend to give contributions to the state of the molecule from structures such as I, II and III in p-chloroanisole



while the mesomeric effect of Cl will lead to contributions from structures such as IV, V and VI.



IV V VI

Interaction between the mesomeric effects of the two groupings will give rise to a difference between observed and calculated values of the dipole moment and this difference is called the interaction moment. Smith calculates the angle that the methoxy group dipole in anisole subtends with the projection of the C_1-C_4 axis to be 76° [41] from a knowledge of the dipole moments of anisole and p-dimethoxybenzene since for free rotation of identical end groups in a para-disubstituted compound

$$\mu_{obs} = \sqrt{2}\ \mu_g \sin\theta \quad [71] \qquad 3.2$$

where μ_g will be the dipole moment of anisole in this particular case. Using this value of 76° for θ the difference between observed and calculated values of the dipole moment of p-chloroanisole was found to be only -0.04D while for p-bromoanisole it was +0.04D.[41] The use of eqn.3.2 in deriving θ is open to objection since completely free rotation of the groups is unlikely to occur. Moreover, the use of eqn.3.2 still does not permit the direction of the

group dipole moment to be assessed. For example, in p-dimethoxybenzene the same dipole moment would be derived if the methoxy group dipoles were directed at 76° away from the ring or at 76° towards the ring. In general however it would appear that when two o-p- directing groups are in opposition the mesomeric interaction between them is small and hence the value of θ calculated from eqn.3.1 should have the same value both in anisole and in p-chloroanisole.

The inductive effect of the halogen atom on the methoxy group will be very small (< 0.02D) since the effect is inversely proportional to the cube of the distance between the primary dipole and the polarizable centre and for p-halogenated anisoles this distance is at least 5Å.

Having assessed the possibility of all the above factors it was decided to use the value of $C_1 = 0.15$, previously determined, in an analysis of the data of anisole for contributions from two relaxation processes. The values of τ_1 and τ_2 obtained from the computer analysis are listed in Table 3.1. With such a small weight factor on the molecular relaxation process the τ_1 values are highly inaccurate and no significance should be attached to them. For low C_1 values τ_1 is extremely sensitive to small changes in C_1. This is borne out by calculating τ_1 for anisole in p-xylene when $C_1 = 0.2$ (see Table 3.3). It is observed that the anomalously high τ_1 values of 78.8 and 39.6×10^{-12} sec that were obtained with $C_1 = 0.15$, at 15°C and 25°C respectively,

have been reduced to 12.3 and 20.5x10^{-12} sec while the τ_2 values have altered only very slightly. Hence it should be concluded that with C_1 values of less than approximately 0.2 no significant accuracy can be attached to the τ_1 values.

Table 3.3. Molecular and Group Relaxation Times for Anisole in p-Xylene with $C_1 = 0.2$

t (°C)	τ_1 — x 10^{12} sec —	τ_2
15	12.3	10.0
25	20.5	7.6
40	13.0	6.5
50	10.7	5.6
60	11.3	4.6

The group relaxation times obtained with $C_1 = 0.15$ are 8.0 and 6.4x10^{-12} sec in p-xylene and cyclohexane respectively at 25°C. These results compare with values of 7.2, 7.0 and 6.5x10^{-12} sec in nujol,[14] decalin[14] and benzene[65] solutions respectively. The C_1 parameters reported in these solvents are 0.39, 0.35 and 0.20 respectively which supports the result of this study that methoxy group rotation is the principal relaxation process in anisole. However, the τ_2 values listed in Table 3.1 are at variance with those deduced from measurements on the pure liquid and also with those of Klages and Zentek[68] from measurements of anisole in benzene. Vaughan et al,[66] from measurements of anisole in the pure liquid state, reported a τ_2 value of 3.2x10^{-12} sec at 20°C with $C_1 = 0.77$ while Smyth et al[64] also reported a τ_2 value of 3.2x10^{-12} sec with $C_1 = 0.78$. Klages and Zentek[68]

obtained similar C_1 values from measurements of anisole in dilute solution in benzene since their analysis gave $\tau_1 = 9.6 \times 10^{-12}$ sec, $\tau_2 = 0.8 \times 10^{-12}$ sec with $C_1 = 0.81$ at $20^{\circ}C$. The τ_1 value appears short however since anisole is larger than bromobenzene which has a relaxation time of 14.0×10^{-12} sec in p-xylene at $15^{\circ}C$[27] and if the τ_1 value was wrong then the whole analysis could be affected. In addition the C_1 value of 0.81 is in complete disagreement with Smyth's value of $C_1 = 0.2$ for measurements in dilute solution in benzene and with the calculated value of $C_1 = 0.15$. Another factor against the high C_1 value of 0.81 is that much larger τ_0 values would then be expected from the measurements of anisole in the viscous solvents decalin and nujol than are actually observed. Certainly the results in these solvents do not suggest any where near an 80% contribution from molecular relaxation.

For measurements in the pure liquid state dipole-dipole forces will be appreciable, especially where $\mu > 1D$, and this should have the effect of raising the relaxation times above those found in dilute solution. Furthermore, the factor $3\epsilon_0/2\epsilon_0 + \epsilon_\infty$, relating the measured relaxation time to the microscopic relaxation time in eqn.1.40, can no longer be taken as unity and this factor should also account for an increase in the measured relaxation time above that found in dilute solution in a non-polar solvent. Taking these points into account it is somewhat surprising that the

τ_2 values found for measurements in the pure liquid state are shorter than for many measurements made in dilute solution. One explanation of the shorter τ_2 value obtained in the pure liquid could be that this is a composite value resulting from intramolecular rotation and one corresponding to some form of relaxation motion relating to the presence of aggregates of polar solute molecules, for example a rate process connected with the dissociation of one molecule from the aggregate or some form of lattice vibration associated with such aggregates. With regard to a rate process it would be expected that C_1 would be more temperature dependent than is actually observed if indeed such a process was present. In addition, rate processes appear to be accompanied by an increase of entropy. Thus a positive entropy of activation was observed for liquid pyrrolidine for the rate process involving breaking of the NH···N bond[72] while a positive entropy of activation has also been observed in a study of the rate process for the dissociation of aliphatic alcohols at radio frequencies.[73] For dipole re-orientation processes a negative entropy of activation normally ensues. Evidence is now emerging for lattice vibrations in pure liquids. Thus Chantry and Gebbie[74] have reported absorption bands with maxima in the 20-50 cm^{-1} region for liquid halobenzenes and state that a normal interpretation of these bands is that they are liquid lattice bands. Nevertheless recent work by Garg and Smyth[75] indicates that for liquid C_6H_5X, where X=

F, Cl and Br , which have been used as examples to support the presence of a further dispersion region involving a very short relaxation time, such a contribution is hardly tenable. This is because the value of ϵ_∞ is very close to that of n_D^2. This however is not the case for anisole where, from the Vaughan et al data,[66] the difference is 0.20 and is of the magnitude considered by Hill[76] to be significant for the existence of a process involving the vibration of a molecule about a temporary equilibrium position which is determined by the arrangement of the neighbouring molecules. Further anisole does not rotate in the solid state[77] which is again a characteristic feature of molecules which might exhibit such a process. Although the data does not establish the presence of the Hill type of mechanism at least the $\epsilon_\infty - n_D^2$ difference is suggestive of an additional relaxation process to that of methoxy and molecular relaxation in the pure liquid state. Such a process would account for the short τ_2 values obtained from measurements in the pure liquid state. Work by Hassell[27] on halobenzenes, nitrobenzene and benzonitrile gives no evidence of the Hill type of mechanism for these solutes in dilute solution in non-polar solvents probably because a lattice system is less likely to be built up than for the case of pure polar liquids.

Dielectric absorption measurements were made on anisole in p-xylene at five temperatures and the enthalpy of activation to group rotation (ΔH_2^*) was calculated from

FIG. 3.2. PLOT OF LOG $\tau_2 T$ AGAINST 1/T FOR ANISOLE IN P-XYLENE.

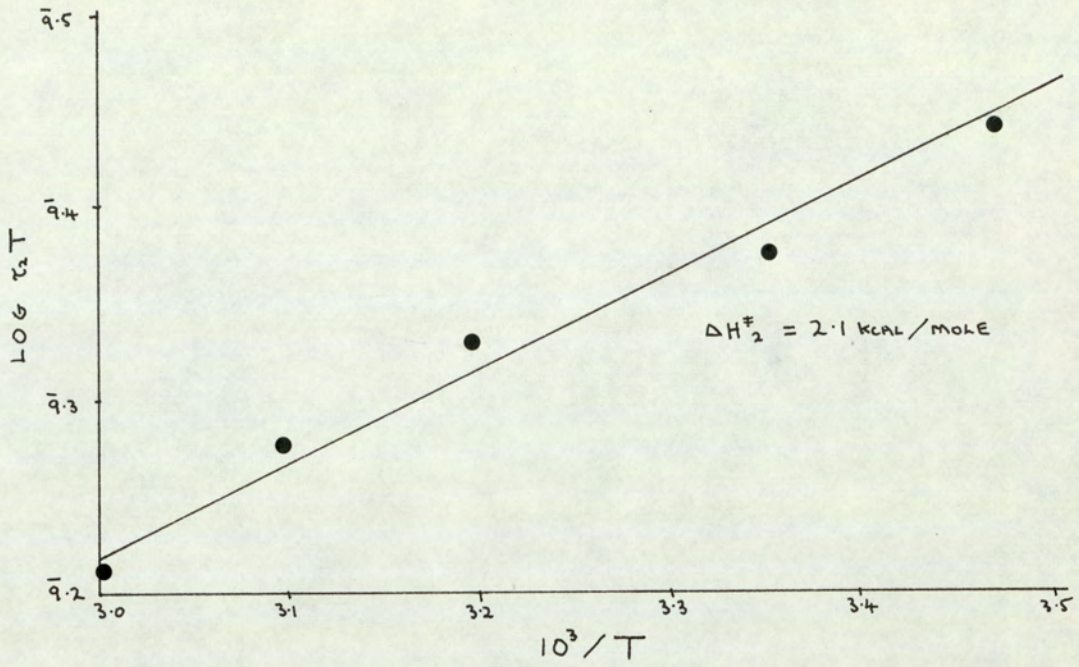
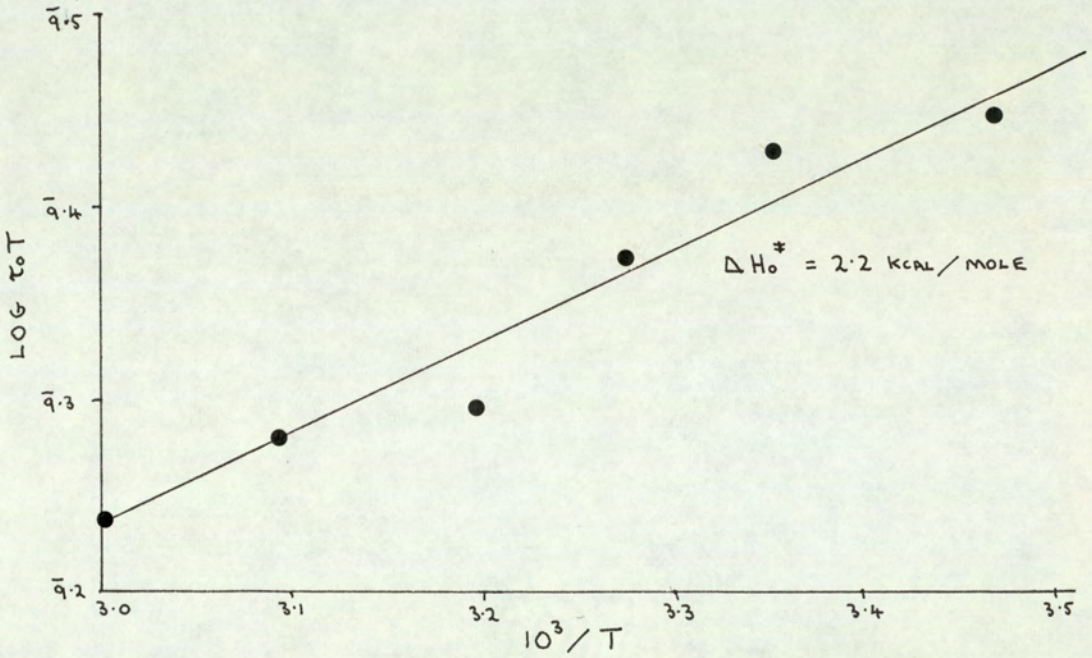


FIG. 3.3. PLOT OF LOG $\tau_0 T$ AGAINST 1/T FOR P-METHYLANISOLE IN P-XYLENE.



the plot of log $\tau_2 T$ -1/T to be 2.1 $\pm$ 0.5 kcal/mole (Fig.3.2). The majority of workers who have examined anisole have obtained lower values for $\Delta H_2^{\ddagger}$. For example, Garg and Smyth[64] have recently reported a $\Delta H_2^{\ddagger}$ value of 1.5 kcal/mole for anisole in the pure liquid state but as has been shown above τ_2 could be a composite value. Smyth has also derived τ_2 from measurements of anisole in decalin and nujol at various temperatures.[14] $\Delta H_2^{\ddagger}$ is not actually quoted but using his data it is evaluated to be 0.6 kcal/mole in decalin and 0.1 kcal/mole in nujol. Moreover the $\Delta H_2^{\ddagger}$ values for p-chloroanisole, p-methylanisole, p-phenylanisole and 2-methoxynaphthalene in nujol are 0, 0.1, 0 and 0 kcal/mole respectively. It is extremely unlikely however that methoxy group rotation should meet a zero energy barrier to rotation for, apart from any resonance contributions causing an energy barrier due to double-bond character in the C_{aryl}-O bond, the group must meet an energy barrier due to the displacement of solvent molecules as it rotates. In addition many of Smyth's τ_1 values from measurements in nujol appear anomalous. For example, the τ_1 value of p-chloroanisole at 20°C is 374×10^{-12} sec while that of p-phenylanisole, a much larger molecule, is 345×10^{-12} sec.[14] p-Phenylanisole is approximately the same size as 2-methoxynaphthalene and this has a molecular relaxation time of 912×10^{-12} sec at 20°C.[14] Furthermore, p-methylanisole is a larger molecule than p-chloroanisole since, according to Pauling,[36] the van

der Waals radius of the methyl group is 2.0Å while that of the chlorine atom is 1.8Å. However, the τ_1 value of p-methylanisole is only 100×10^{-12} sec while that of p-chloroanisole is 345×10^{-12} sec at 20°C. Evidently as some of the τ_1 values could be in error then so also could be the τ_2 values and this of course would have a direct effect upon ΔH_2^*.

In order to examine the position further it was decided to study the molecule p-methylanisole because the methyl group moment is in a direction opposite to the fixed component of the methoxy group so this molecule would be expected to have more internal rotation as the fixed component is reduced whereas the component capable of internal rotation remains essentially constant. Since anisole should only have a 15% contribution from molecular rotation in any case it would be expected that in p-methylanisole only an intramolecular process would be involved. In fact group moment calculations suggest that $C_2=0.98$ and therefore only group relaxation should be observed in this molecule. With such a high weight factor on this process both τ_2 and ΔH_2^* should be obtained with considerable accuracy i.e. $\pm$ 5% on τ_2 and $\pm$ 0.3 kcal/mole on ΔH_2^*. p-Methylanisole was studied at six temperatures in solution in p-xylene. As C_1 is so low it is undesirable to interprete the data in terms of two relaxation times and therefore the mean relaxation time τ_0 will be equivalent to the group relaxation time τ_2. It is evident, from Table 3.1, that the mean

relaxation times of p-methylanisole compare very well with the group relaxation times of anisole, a factor which tends to support the C_1 calculations for anisole. The relaxation time of 9.0×10^{-12} sec for p-methylanisole in p-xylene at 25°C compares with a molecular relaxation time of 23.0×10^{-12} sec for p-bromotoluene,[77] a molecule of similar size. Therefore a large contribution from group relaxation to the total dielectric absorption in p-methylanisole is clearly indicated. The enthalpy of activation to group rotation is calculated to be 2.2 ± 0.5 kcal/mole (Fig.3.3) which compares very favourably with the value obtained for methoxy group rotation in anisole. Hence it would appear that the enthalpies of activation to methoxy group rotation in anisole and p-methylanisole are approximately the same as for acetyl group rotation in acetophenone i.e. ~ 2 kcal/mole.

Smyth has examined p-methylanisole in nujol and the C_1 value was deduced to be approximately 0.25.[14] The τ_0 value is not quoted but a computer analysis of the data at 20°C yielded a value of 16.6×10^{-12} sec. This result could well be attributed to just group rotation since the viscosity of the solvent is ~ 211 c.p. at 20°C and therefore a lengthening of the group relaxation time would be expected.

The dipole moment of 1.18 ± 0.02D obtained for p-methylanisole in p-xylene from this study compares with Vaughan's value of 1.12D for the pure liquid,[78] taking the distortion polarization to be 1.1 times the electron polar-

ization in the latter case. The dipole moment of p-methylanisole in benzene is 1.21→1.24D.[29]

Fong and Smyth[53] have examined the molecules 2,6-dimethylanisole and 3,5-dimethylanisole in solution in benzene and quote mean relaxation times of 25 and 16×10^{-12} sec respectively, at 20°C. The longer relaxation time of the former molecule is attributed to the restriction of rotation of the methoxy group by the ortho-substituted methyl groups. Klages and Zentek[68] have however measured 2,4,6-trimethylanisole in benzene at 20°C and obtained a mean relaxation time of 15.9×10^{-12} sec. Steric repulsion to methoxy group rotation should occur to the same extent in this compound as in 2,6-dimethylanisole but if molecular relaxation were the only process then a longer relaxation time would be expected. It seems reasonable to suppose therefore that methoxy group rotation can take place in these compounds and that the longer relaxation time of 2,6-dimethylanisole, relative to 3,5-dimethylanisole, is due to the direction of the moments of the ortho-substituted methyl groups increasing the fixed component of the dipole moment and therebye increasing the contribution from molecular relaxation. For 2,4,6-trimethylanisole the moments of the methyl groups will cancel out and therefore the C_1 value should be the same as in anisole. A longer mean relaxation time relative to anisole will be expected due to the increase in molecular size of this compound. A number of measurements

have also been made on 2,4,6-trichloroanisole. Le Fèvre et al[28] studied this compound in benzene at 18°C and obtained a mean relaxation time of 20.9×10^{-12} sec. The magnitude of the relaxation time was thought to suggest hindered methoxy group rotation. The relaxation time for this compound is however inconsistent with the value of 15.9×10^{-12} sec for 2,4,6-trimethylanisole in benzene at 20°C[68] since the C_1 values should be similar while methyl groups are larger than chlorine atoms. One possible explanation for the longer relaxation time of the chlorine derivative is that there is a through space interaction between the oxygen and chlorine atoms and that this field effect is more important in giving rise to a high energy barrier to methoxy group rotation than is the steric effect. Klages and Knobloch[79] have also measured 2,4,6-trichloroanisole in benzene at 20°C and obtained relaxation times of $\tau_1 = 27.2 \times 10^{-12}$ sec, $\tau_2 = 1.5 \times 10^{-12}$ sec and $C_1 = 0.88$. The τ_2 value appears extremely small if in fact methoxy group rotation is hindered. Maier[80] has measured the molecules 2,4,6-trichloroanisole and 2,6-dichloroanisole in benzene at 20°C and derived mean relaxation times of 12.0 and 19.0×10^{-12} sec respectively. The former value is certainly short compared with Le Fèvre's value of 20.9×10^{-12} sec[28] and suggests, if correct, that methoxy group rotation is virtually unhindered by steric effects. If 2,4,6-trichloroanisole were a rigid molecule then a longer τ_0 value would be expected compared with that of 2,6-dichloro-

anisole. It is evident that the problem of steric hindrance to methoxy group rotation is far from solved. Certainly the relaxation time values reported by Maier[80] and by Klages and Zentek[68] for 2,4,6-trichloroanisole and for 2,4,6-trimethylanisole respectively would suggest that there is little steric hindrance to methoxy group rotation but further studies are required to clarify the situation.

The study of para-substituted anisoles has been extended by an examination of the molecule p-bromoanisole. Calculations from group moments give a C_1 value of 0.76 suggesting that this molecule will relax predominantly by molecular rotation. This is borne out by the long mean relaxation time values. For example, at 25°C, $\tau_0 = 27.1 \times 10^{-12}$ sec, $\tau_1 = 31.3 \times 10^{-12}$ sec, $\tau_2 = 7.4 \times 10^{-12}$ sec and $C_1 = 0.88$. Analysis of the data in terms of two relaxation times gave an average C_1 value of 0.83 which compares well with the calculated value and again suggests that the C_1 calculations from group moments are adequate. The τ_2 values, while not very accurate due to the small weight factor on this process, are of the same order of magnitude for group rotation in anisole and p-methylanisole. The molecular relaxation times can be determined with an accuracy of $\sim \pm 7\%$ and results for this compound have proved useful in assessing the molecular relaxation times of molecules of similar size. p-Bromoanisole was studied at five temperatures in p-xylene and an enthalpy of activation to molecular rotation of 1.9 ± 0.5

FIG. 3.4 PLOT OF LOG $\tau_1 T$ AGAINST $1/T$ FOR P-BROMOANISOLE IN P-XYLENE.

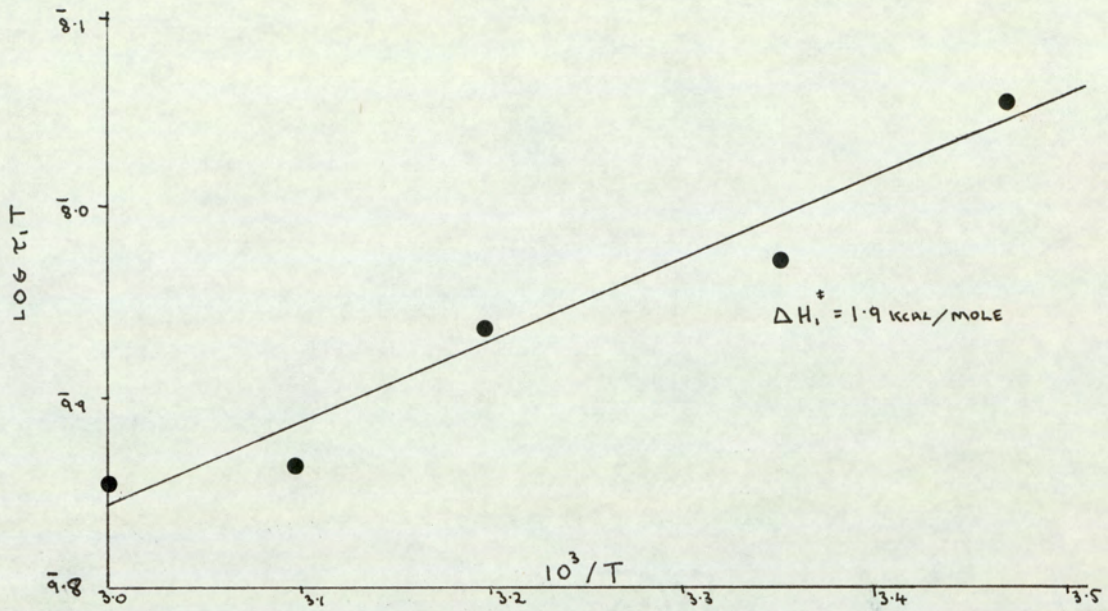
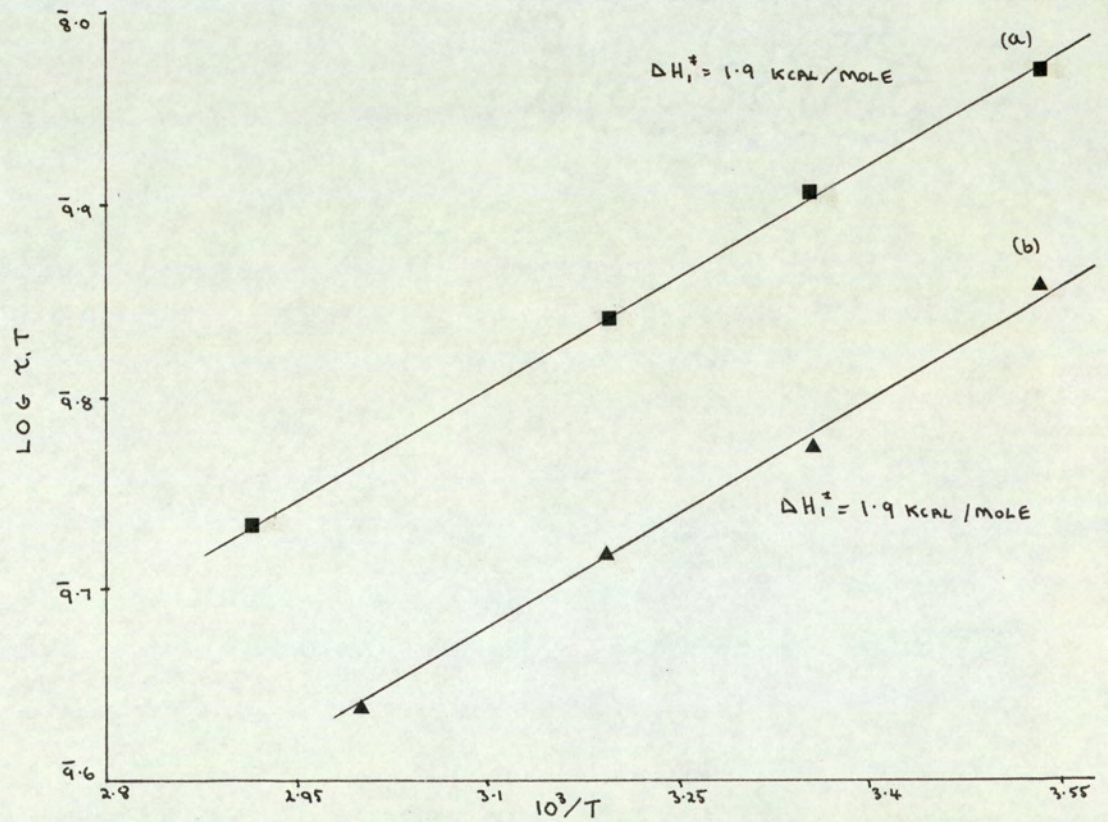


FIG. 3.5 PLOTS OF LOG $\tau_1 T$ AGAINST $1/T$ FOR TRIFLUOROMETHOXY-BENZENE IN (a) DECALIN AND (b) CYCLOHEXANE



kcal/mole was obtained (Fig.3.4).

2-Methoxynaphthalene has been studied at 25°C in solution in p-xylene yielding a mean relaxation time of 20.3×10^{-12} sec. The molecular relaxation time for this molecule should be in excess of 25.5×10^{-12} sec which was the relaxation time obtained for 2-bromonaphthalene in cyclohexane at 25°C;[27] probably a value of 30 to 35×10^{-12} sec is of the right order for τ_1. The mean relaxation time therefore appears to indicate either an increase in C_1 or in τ_2 relative to anisole for if C_1 was 0.15 and τ_2 was 8.0×10^{-12} sec as in anisole in p-xylene at 25°C then a much shorter τ_0 value would be expected. It seems probable therefore that the factors discussed in Chapter 2 which influence the mean relaxation time of 2-acetonaphthone are also effective in raising the mean relaxation time of 2-methoxynaphthalene above that which would be expected. In addition, the considerable distribution parameters observed for 2-methoxynaphthalene in p-xylene at 25°C and in cyclohexane at 40°C of 0.16 and 0.22 respectively could suggest contributions from more than two relaxation processes which would then be consistent with the distribution parameter observed for the rigid molecule 2-bromonaphthalene.[27] Vaughan et al[66] have examined 2-methoxynaphthalene in the pure liquid state at 80°C and obtained relaxation time values of $\tau_1 = 14.9 \times 10^{-12}$ sec and $\tau_2 = 1.0 \times 10^{-12}$ sec with $C_1 = 0.82$. Their analysis appears faulty when the molecular relaxation time is compared

with that of 1-methoxynaphalene. For this molecule the extrapolated value of τ_1 is 30.6×10^{-12} sec at 80°C but 2-substituted naphthalenes usually have longer relaxation times than the corresponding 1-substituted derivatives.[33]

A molecule whose dielectric relaxation properties have been extensively examined in this study is trifluoromethoxybenzene (phenyl trifluoromethyl ether). This compound was measured in solution in cyclohexane at four temperatures and at a number of different weight fractions. The average value of the molecular dipole moment is 2.26D which compares with 2.36D reported by Sheppard[70] from measurements in solution in benzene at 25°C. The divergence in moments is probably due to the fact that the atom polarization has not been subtracted from the total polarization in Sheppard's determinations and hence a higher dipole moment would be observed.

For free rotation in a para-disubstituted compound, where the end groups are identical, the observed dipole moment is related to the dipole moments of the substituted groups by eqn.3.2. The dipole moment of 1,4-bis(trifluoromethoxy)-benzene is 0.81D[70] and that of trifluoromethoxybenzene is 2.26D hence Θ is 14°41' and C_1 is calculated to be 0.94. C_1 in trifluoromethoxybenzene may also be calculated from the moment of p-bromophenyl trifluoromethyl ether (μ=1.0D).[70] Using equations analogous to 2.5 and 3.1 the value of Θ in trifluoromethoxybenzene is calculated to be 21°55', with the

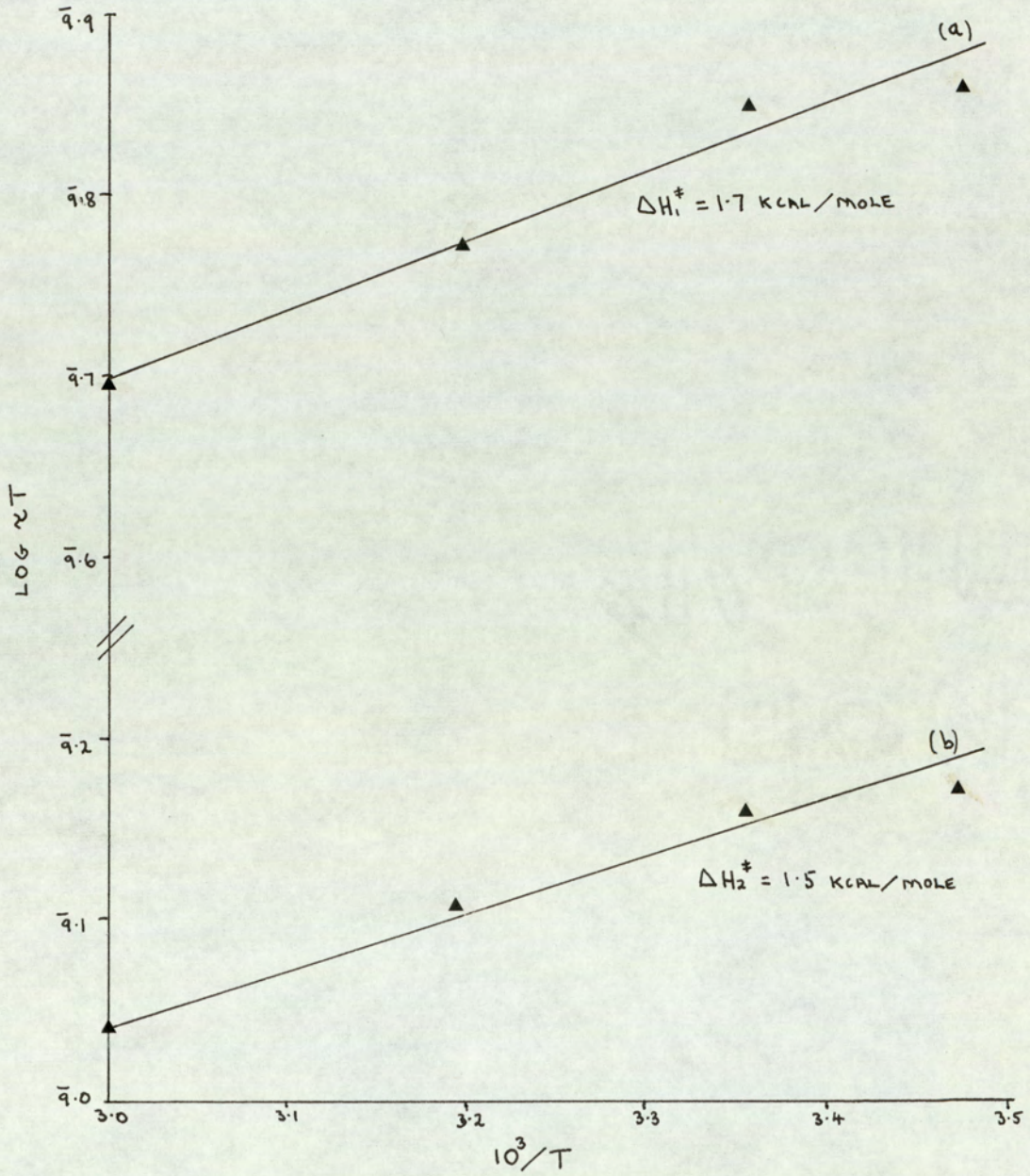
moment directed away from the ring, and hence $C_1 = 0.87$. Thus the principal relaxation process should be molecular relaxation and this is borne out by the high τ_0 values that are observed. Analysis of the dielectric data in terms of two relaxation times gave an average C_1 value of 0.92 and since the weight factor on τ_2 is therefore only 0.08 the group relaxation time cannot be determined with any degree of accuracy. The enthalpy of activation for the molecular relaxation process was calculated to be 1.9 ± 0.4 kcal/mole (Fig.3.5.a) which is of the correct order of magnitude expected for a molecule of this size. The group relaxation times are listed but no trend in temperature was observed.

Measurements were also carried out on trifluoromethoxybenzene in solution in decalin. As would be expected the mean relaxation times have lengthened in this solvent because the higher viscosity will give rise to a larger hindering barrier to rotation. The mean relaxation time at 25°C is 25.4×10^{-12} sec in this solvent. Similar C_1 values are obtained as from the measurements in cyclohexane so again no accurate assessment of the group relaxation time can be made. Studies were carried out at four temperatures in solution in decalin and the enthalpy of activation was calculated to be 1.9 ± 0.4 kcal/mole(Fig.3.5.b). Thus although the free energy of activation to molecular rotation has increased in the more viscous solvent the enthalpy of activation has, within the experimental error, remained

constant. A study of para-halogenated derivatives of trifluoromethoxybenzene, where C_2 would be considerably increased, should prove very useful since the trifluoromethoxy group has many interesting characteristics. Sheppard[70] has calculated the Taft σ-parameters for trifluoromethoxybenzene and concluded that the OCF_3 group should enhance the inductive withdrawal of electrons by oxygen to the extent that deactivation of the aromatic system occurs to the same, or greater, extent than for halogens. In addition, electron release by the resonance mechanism is diminished below that for an alkoxy group. A study of OCF_3 group rotation in para-halogenated derivatives of trifluoromethoxybenzene should show how these effects influence the energy barrier to group rotation compared with that of OCH_3 group rotation in anisole.

Another fluorinated compound that has been examined is methoxypentafluorobenzene ($C_6F_5OCH_3$). In order to calculate the C_1 value for this compound from group moments it was first of all necessary to determine the dipole moment of pentafluorobenzene. It did not necessarily follow that the dipole moment of pentafluorobenzene would be the same as that of fluorobenzene because the dipole moment of pentachlorobenzene is reported in the literature to be 0.89D[29] while that of chlorobenzene is 1.58D.[41] However, for pentafluorobenzene the dipole moment was determined to be 1.39D in cyclohexane at 25°C which compares with 1.39D for fluoro-

FIG. 3.6. PLOT OF (a) LOG $\tau_1 T$ AND (b) LOG $\tau_2 T$ AGAINST $1/T$ FOR METHOXYPENTAFLUOROBENZENE IN CYCLOHEXANE.



benzene in p-xylene at 15°C.[27] It is possible that steric and dipolar repulsive effects in pentachlorobenzene will force the atoms out of the plane of the ring and this could result in a smaller dipole moment. The relaxation time derived for pentafluorobenzene was 7.4×10^{-12} sec at 25°C in cyclohexane. Knowing the dipole moment of this compound the C_1 value for methoxypentafluorobenzene was determined to be 0.78. This compares with an observed average C_1 value for all the concentrations examined of 0.70. The τ_0 value of 15.0×10^{-12} sec also suggests a significant contribution from a molecular relaxation process. The enthalpy of activation for molecular relaxation is 1.7 ± 0.5 kcal/mole and is therefore of the same order found for other molecules of this size (Fig.3.6) The methoxy group relaxation times are somewhat shorter in this molecule than in others that have been studied and also the enthalpy of activation to group rotation is only 1.5 ± 0.7 kcal/mole which compares with a value of 2.1 ± 0.5 kcal/mole in anisole. Whether these differences are real or simply arise due to the small weight factor on the group relaxation process leading to a greater error on τ_2 is difficult to say. Certainly a fairly considerable mesomeric interaction is indicated in methoxy-pentafluorobenzene by its dipole moment of 2.23D relative to that of p-fluoroanisole (μ=2.04D in benzene at 25°C)[81] and as the dipole moment is increased a greater flow of charge should occur from the methoxy group which should contribute

to the raising of the group relaxation time.

The molecules difluoromethyl phenyl ether and difluoromethyl pentafluorophenyl ether have been examined in cyclohexane at 25°C. For both of these compounds there will be three relaxation times; one due to molecular rotation, one due to O-CF_2H group rotation and the other due to CF_2H group rotation. Analysis of the data into contributions from three relaxation processes is complicated by the fact that measurements are only normally made at five or six microwave frequencies and therefore the number of parameters that require determination compared with the number of experimental points available does not permit an accurate analysis. The τ_o value of difluoromethyl pentafluorophenyl ether is 9.4×10^{-12} sec while that of difluoromethyl phenyl ether is 11.6×10^{-12} sec. The former is the larger molecule but the effect of the C_6F_5 group is to lower the contribution from molecular rotation producing a shorter mean relaxation time. This shows that the direction of the O-CF_2H group moment must be away from the benzene ring with the C_6F_5 group moment in opposition, resulting in both a smaller molecular dipole moment and dipole component associated with molecular rotation.

Chapter 4

Mesomeric and Coupled Ring Rotation Mechanisms.

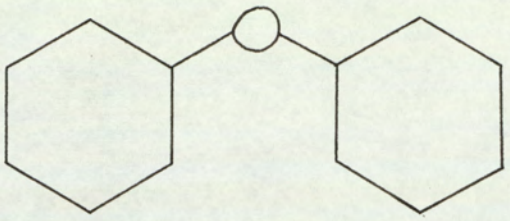
Introduction

Diphenylether and many of its 4,4'-substituted derivatives have relaxation times which are short in comparison with those estimated for relaxation of a rigid molecule.[82-4] Thus diphenylether has a relaxation time of 3.7×10^{-12} sec in benzene at 20°C[80] whereas the estimated value for molecular rotation is 15.4×10^{-12} sec.[80] Several mechanisms have been suggested to account for these short relaxation times and they are now discussed in some detail.

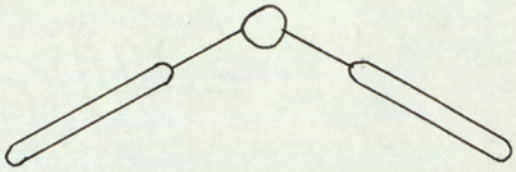
One of the first mechanisms proposed to account for the short relaxation time of diphenylether was in-plane inversion of the oxygen atom. However, ammonia and its isotopic forms appears to be unique in exhibiting an inversion frequency in the microwave region.[85] Thus ammonia has an inversion frequency at 24 Gc/sec and ND_3 at 16 Gc/sec but for heavier molecules the inversion frequency is lowered considerably. For example, for PH_3 the inversion frequency is a fraction of a Megacycle while it is a year for AsH_3 and centuries for SbH_3.[85] As diphenylether and its substituted derivatives are comparitively heavy molecules and since inversion does not appear to have been observed even in the most simplest ether, water, it would be expected that in-plane inversion would occur outside the microwave region.

Another mechanism that has been considered is that of phenoxy group rotation[86] but this also would not explain the short relaxation time of diphenylether since the relaxation

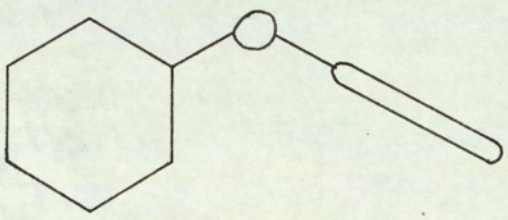
Fig. 4.1. Possible structures of the diphenylether molecule.



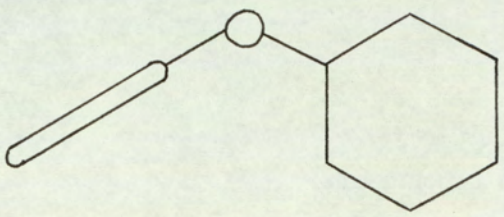
A



B



C

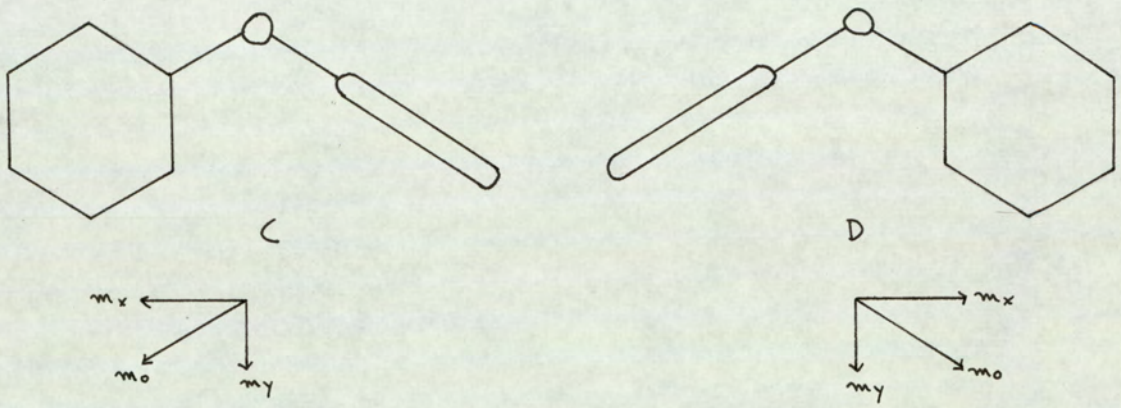


D

time expected for phenoxy group rotation should be approximately that of fluorobenzene ($\tau = 6.8 \times 10^{-12}$ sec in p-xylene at 15°C).[27] Furthermore phenoxy group rotation would lead to a movement of the centre of gravity of the molecule consequently involving translational motion. This would not be acceptable but could be remedied by coupled motions of the other phenyl group as the phenoxy group rotates.

In view of the ineffective explanation of the short relaxation times of diphenylether and its 4,4'-substituted derivatives by the above mechanisms, Higasi and Smyth[87] proposed another mechanism based on the mesomeric moments that are present in these molecules. Four structures (Fig. 4.1) were considered for the diphenylether molecule and the equivalent structures C and D were regarded as the most probable because (i) structure A should be sterically hindered (ii) structure B does not have any additional binding resulting from the resonance energy of the molecule (iii) structures C and D are the most consistent with electron diffraction measurements[88] and with the dipole moments of 2,2'-substituted diphenylethers.[86] Structures C and D were used as the basis for calculations involving the mesomeric shift of charge mechanism. In these structures one ring is planar with the C-O-C plane and, due to orbital overlap, a mesomeric effect is created along the O-C bond from the oxygen atom towards the phenyl ring. The other ring is perpendicular to the C-O-C plane and hence no mesomeric

release of charge is possible. If ring rotation occurs so that there is a change from structure C to structure D then the component of the mesomeric moment perpendicular to the plane bisecting the C-O-C angle (m_x) will have changed direction by 180°. This situation is represented diagrammatically below.

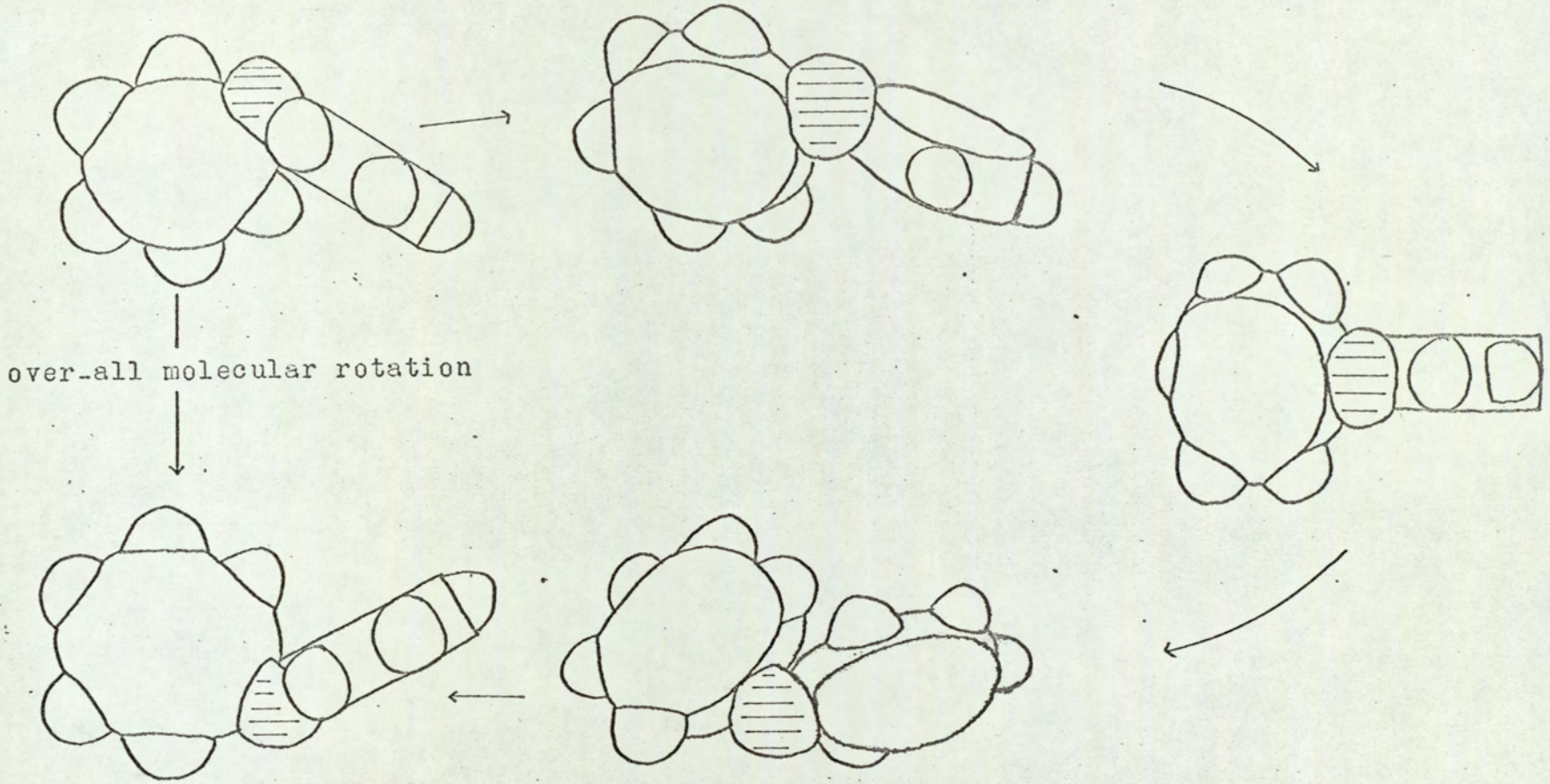


m_o is the mesomeric moment along the O-C bond and m_x and m_y are its two components perpendicular and parallel to the plane bisecting the C-O-C angle respectively. Hence the short relaxation process would be associated with phenyl group rotation causing a change in the magnitude and direction of m_x. This mechanism is hereafter called mechanism A. If the two rings rotated simultaneously in such a way that ϕ_2 is kept equal to $180-(90+\phi_1)$, where ϕ_1 and ϕ_2 are the angles that the phenyl groups subtend with the C-O-C plane then, under these conditions, Higasi and Smyth[87] showed that phenyl group rotation would meet a minimum hindering potential

barrier. They employed calculations which quantitatively accounted for the short relaxation time of diphenylether when a mesomeric moment of 1.2D was taken. This mechanism appears to be very similar to that proposed by Fischer[89] who proposed that the short relaxation time of diphenylether could be attributed to a fluctuation of the atomic dipole moment of the oxygen atom due to mesomeric interactions with the π-electrons of the phenyl ring, the effect altering with ring displacement. Hence a change in direction and magnitude of the atomic dipole as a function of ring rotation would be possible and should have a particularly short relaxation time associated with it. However, this mechanism would predict short relaxation times for all ethers while there are abundant examples to the contrary (e.g.p-bromo-anisole). The main difference between the mechanism proposed by Fischer and that of Higasi and Smyth is that in the former the oscillating charge is considered to be localised on the lone pair orbitals of the oxygen atom while in the latter mechanism the oscillating charge extends throughout the conjugated system.

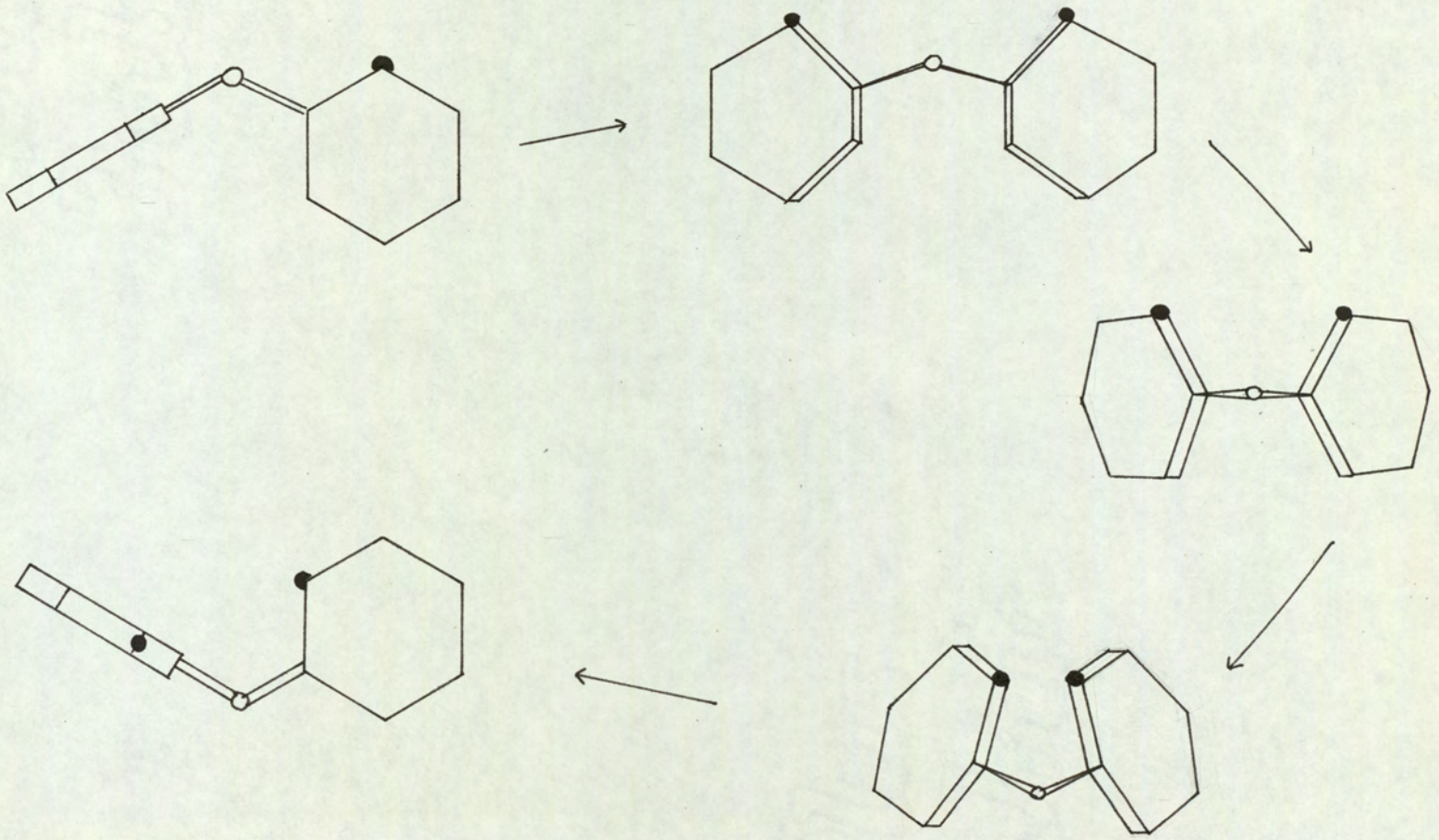
It has been suggested by Fong[90] that 'mesomeric effects play little or no part in the lowering of relaxation times of these molecules' as the values of the mesomeric moments that have to be assumed are higher than can be reasonably justified. Taking diphenylether as a specific example he proposes that phenoxy group rotation coupled by

Fig. 4.2. Molecular dipole orientation by coordinated rotation around the C-O bonds.



suitable motions of the other phenyl ring could lead to a short relaxation process. Two such coupled internal rotation mechanisms were discussed. . The first of these is a combination of rotational motions of the C_6H_5O groups around the C-O bond producing a 180° change in molecular orientation by passage through a continuous series of successive configurations illustrated by the five shown in Fig.4.2. The molecular dipole moment has reversed its direction by a process that should have a shorter relaxation time than that associated with molecular rotation since less volume is swept out during relaxation. If each C_6H_5 group is considered relative to the other C_6H_5-O bond then the motion is rotatory but relative to an external framework the resultant movement would appear oscillatory. This relaxation process is similar to that described by Maier[80] who suggested that the oxygen atom could describe an arc of 180°, due to an intramolecular process, without changing appreciably its valency angle, whereas the orientation of the two phenyl groups varies only within 20° to 30°. It was further suggested by Maier[80] that there would be no essential intramolecular barrier to rotation since decreasing resonance with one ring would be compensated by increasing resonance with the other ring. The second mechanism proposed by Fong[90] is an edgewise rotation of the C_6H_5O groups coupled with tilting of the other phenyl ring as the direction of the O-C bond changes, so that motion of the centre of mass

Fig 4.3. Molecular dipole orientation by edgewise ring rotation coupled by tilting of the other ring. Ortho hydrogens are shown to indicate the relative positions of the two rings.



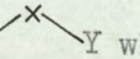
is minimised (Fig.4.3). Fong considers that both of these coupled rotation mechanisms will have a relaxation time slightly longer than that which would be associated with the rotation of a benzene molecule. He therefore compares the relaxation time for these processes with that of molecular rotation for fluorobenzene ($\tau = 6.8 \times 10^{-12}$ sec in p-xylene at 15°C).[27] The relaxation time of fluorobenzene is probably an upper limit for the relaxation time of the benzene molecule. A lower limit could be that of pyridine which has a relaxation time of 3.0×10^{-12} sec in cyclohexane at 25°C.[27] Fong's examples of coupled rotations will henceforth be taken collectively and known as mechanism B.

Although the over-all relaxation process and the intramolecular coupled rotations in mechanism B follow different paths between the same initial and final states both lead to a reversal of the direction of the molecular dipole moment. Fong[90] suggested that if the alternate paths have equal probabilities then the observed relaxation time τ_o is a composite value given by the equation

$$\frac{1}{\tau_o} = \frac{1}{\tau_m} + \frac{1}{\tau_i} \qquad 4.1$$

where τ_m and τ_i are molecular and intramolecular relaxation times respectively. This leads to the anomalous result however that τ_o, the observed relaxation time, could be shorter than both τ_m and τ_i i.e. the energy barrier relating to the relaxation time observed is less than either of the

two actual energy barriers. In Fong's description of the relaxation processes in diphenylether it is suggested that the molecule can reverse its direction by a process involving a small energy barrier (intramolecular coupled rotations) and by a process involving a large energy barrier (molecular rotation) and that these two types of rotation will be taking place simultaneously. However this is extremely unlikely for if molecular rotation is to take place then the intramolecular rotations as described by Fong would have to cease otherwise there would be no fixed component of the dipole moment. In addition, if there is a high and a low energy barrier between two equilibrium positions then the path involving the process with the smaller energy barrier is bound to be preferred. Maier[40], unlike Fong, suggests that in diphenylether short coupled ring rotations alone will account for the short relaxation time. Molecular rotation is only likely to occur if the molecule becomes locked during the intramolecular rotation process and this may be possible if steric effects play an important role. In mechanism A, where the intramolecular process is phenyl group rotation, there should always be a fixed component of the dipole moment and hence a contribution from molecular rotation.

Although the specific example of diphenylether has been cited for mechanism B it will, unlike mechanism A, apply for any molecule of the type  whether it be

aromatic or aliphatic.

Smyth and co-workers[82-3] have recently made further studies of aromatic ethers and have concluded that while mechanism A may have some effect in shortening the relaxation time mechanism B is the more important and general phenomena. One of their major criticisms of mechanism A was that in order to account for the short relaxation times of several ethers mesomeric moments far larger than normally expected would have to be assumed. Anderson and Smyth[82] carried out a number of calculations of dipole moments of substituted aromatic ethers assuming a zero mesomeric moment and concluded that a comparison of calculated and observed moments 'gives no evidence of the large mesomeric moments seemingly necessary to make the mesomeric charge shift a generally important factor in lowering the relaxation times of these molecules'.

Higasi[91] states that the mesomeric moment of diphenylether is the result of an averaging out of all the possible positions of the phenyl groups in the molecule. The quoted values do not therefore represent the maximum values. He estimated the maximum mesomeric moment in diphenylether to be approximately 1.32D and with a mesomeric moment of this magnitude mechanism A could give an appreciable contribution to the observed relaxation time. For this and reasons indicated later, it was considered that a further study of the intramolecular processes in such molecules might be worth while. Consequently, work was directed at studying solutes

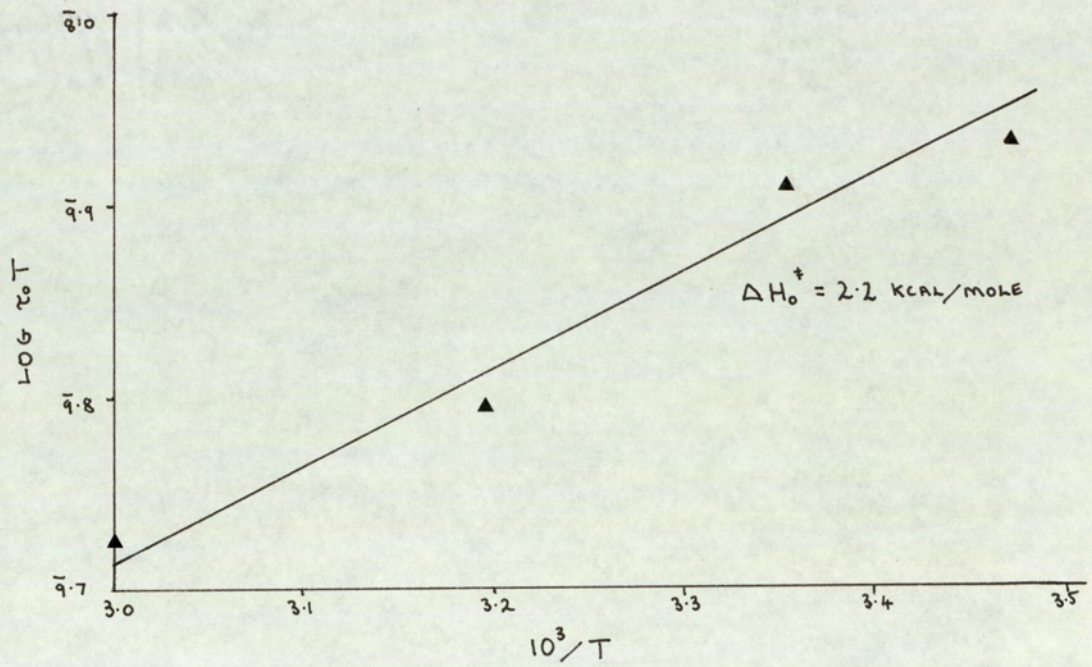
of the type Y–X–Y where both X and Y are varied. A study of both aliphatic and aromatic substances seemed a potential route for distinguishing between contributions from mechanisms A and B.

Table 4.1. Relaxation times, distribution parameter (α), static dielectric constant(ϵ_o), dielectric constant at very high frequency(ϵ_∞) and dipole moment(μ) for solutions of weight fraction w_2 at temperature t°C for molecules which may exhibit mesomeric or coupled ring rotation mechanisms.

t (°C)	w_2	τ_o ($\times 10^{12}$ sec)	α	ϵ_o	ϵ_∞	μ (D)
		Benzophenone/cyclohexane				
25	0.03168	19.0	0.04	2.1603	2.033	2.93
40	0.03168	15.2	0.03	2.1273	2.011	2.92
		Decafluorobenzophenone/p-xylene				
15	0.13612	30.0	0	2.3642	2.292	1.31
25	0.13612	27.4	0	2.3484	2.282	1.30
40	0.10404	20.0	0	2.2925	2.245	1.30
60	0.10404	16.0	0	2.2543	2.211	1.30
		Dicyclohexylketone/cyclohexane				
25	0.03620	14.8	0.08	2.1430	2.028	2.69
40	0.03620	11.2	0.04	2.1097	2.004	2.69
		Diethylether/cyclohexane				
15	0.06519	2.7	0.07	2.1508	2.035	1.22
		Diethylketone/cyclohexane				
15	0.01457	2.9	0.11	2.1459	2.033	2.74
15	0.03580	3.4	0.10	2.3258	2.047	2.74
		4-Benzoylpyridine/p-xylene				
25	0.03901	38.0	0.07	2.4946	2.292	2.99
40	0.03758	30.4	0.06	2.4415	2.256	3.01

t (°C)	ω_2	τ_0 ($\times 10^{-12}$ sec)	α	ϵ_0	ϵ_∞	μ (D)
			m-Dibenzoylbenzene/p-xylene			
25	0.03045	43.6	0	2.4313	2.292	3.52
60	0.03045	27.7	0	2.3305	2.227	3.50

FIG. 4.4. PLOT OF LOG $\tau_0 T$ AGAINST $1/T$ FOR DECAFLUOROBENZOPHENONE IN P-XYLENE.



Discussion

The observed relaxation time for a dilute solution of benzophenone in the non-interacting solvent cyclohexane is of the correct order for molecular relaxation but a non-zero distribution coefficient may suggest more than one relaxation process. The distribution coefficient is fairly small and could be a result of experimental error but it could also be explained by the existence of the mesomeric shift of charge mechanism A. This would fit in with the almost normal relaxation time since, as the fixed dipole component of the molecule is large, the mesomeric contribution should be small. This is because the weight on a particular relaxation process depends upon the square of the associated dipole moment component and since the dipole moment of benzophenone is 2.92D then, even with a mesomeric moment of about -0.5D , the molecular relaxation process would predominate and the mean relaxation time would be of the order of that for relaxation of the rigid molecule. Sutton[92] obtained a mesomeric moment of -0.28D for benzophenone. Fong[90] considers that the conjugation in the benzophenone molecule makes the energy barrier to group rotation so high that it largely inhibits mechanism B. Such a high energy barrier would seem by no means certain since the conjugation between the keto group and the π-electron system in molecules containing acetyl groups does not appear to prevent acetyl[33-4] group relaxation as energy barriers of only $\sim$ 1.5 kcal/mole and $\sim$ 2 kcal/mole (Chapter 2) have been observed. Since

the mesomeric moment of benzophenone is not appreciably different from acetophenone[92], then the resonance effects in the two systems might be expected to be similar and the benzophenone molecule not necessarily rigid. In addition, benzoyl group rotation is indicated in p-dibenzoylbenzene by the relaxation time of 21.8×10^{-12} sec in p-xylene at $60^{\circ}C$, a value which is far too short for molecular rotation (Chapter 5). Group rotation is not so immediately evident in m-dibenzoylbenzene however which has a relaxation time of 43.6×10^{-12} sec in p-xylene at $25^{\circ}C$. For a meta-disubstituted compound with rotating polar groups the fixed components of the group moments do not cancel out and hence there will be a contribution from a molecular relaxation process. The dipole moment of m-dibenzoylbenzene can be calculated for 'free rotation' of the groups from the equation

$$\mu^2 = 2\left(\mu_{C(=O)C_6H_5}\right)^2 + \left(\mu_{C(=O)C_6H_5}\right)^2 \cos^2\theta \cos\psi \qquad 4.2$$

where θ is the angle that the benzoyl group moment subtends with the rotational axis and ψ is the angle separating the two rotational axes. For the case of a meta-substituted compound $\psi = 120^{\circ}$ and taking $\mu_{C(=O)C_6H_5} = 2.92D$ and $\theta = 65^{\circ}$ the dipole moment of this molecule is calculated to be 3.94D which compares with the observed value of 3.51D. However, if m-dibenzoylbenzene existed in only planar forms the calculated dipole moment would be 3.99D and therefore the observed dipole moment cannot be used in support of group rotation. Group rotation

in this compound could be suggested by the mean relaxation time of 27.7×10^{-12} sec in p-xylene at 60°C, a value which compares with that for benzoyl group rotation in p-dibenzoylbenzene of 21.8×10^{-12} sec, the lengthening of the relaxation time in the meta-substituted compound being attributed to a contribution from molecular relaxation. A similar increment in mean relaxation times from the para- to the meta-disubstituted compound is observed for p-dimethoxybenzene ($\tau_o = 6.9 \times 10^{-12}$ sec)[19] and m-dimethoxybenzene ($\tau_o = 10.9 \times 10^{-12}$ sec)[19], in solution in benzene at 25°C, in which compounds methoxy group rotation is almost definitely present. If molecular relaxation was the only relaxation process in the benzoyl compounds then it would be expected that the para-derivative would have the longer relaxation time due to its greater length. This is borne out by the molecular relaxation times of p-chlorotoluene ($\tau_1 = 17.5 \times 10^{-12}$ sec)[52] and m-chlorotoluene ($\tau_1 = 14.1 \times 10^{-12}$ sec)[52] in cyclohexane at 20°C. Since p-dibenzoylbenzene has a shorter relaxation time than m-dibenzoylbenzene then benzoyl group rotation would be indicated in these compounds. Resonance effects should be less in benzophenone due to its smaller length in which case the relaxation time for phenyl group rotation could be short.

For decafluorobenzophenone molecular models indicate that rotation of the C_6F_5 groups about the aromatic to aliphatic carbon bond is appreciably sterically hindered, and since the distribution is zero, then there is no detectable intramolecular

process. The relaxation time of 27.4×10^{-12} sec at 25°C in p-xylene is, therefore, characteristic only of molecular rotation and the fact that $\alpha = 0$ suggests that the non-zero distribution coefficient of benzophenone, which is of similar shape and size, has significance and may be related to an intramolecular process. The relaxation times of decafluorobenzophenone were determined at four temperatures and, from a plot of $\log \tau_0 T - 1/T$, $\Delta H_1^{\ddagger}$ was calculated to be 2.2 ± 0.4 kcal/mole (Fig.4.4). The molecular dipole moment determined by the Guggenheim[26] method for decafluorobenzophenone was 1.51D, while the moment determined from eqn. 1.48, involving the infinite frequency intercept on the Cole-Cole plot was 1.30D. The Guggenheim approach involves n_D^2 (where n_D is the refractive index for the sodium D lines) in place of ϵ_∞ and when ϵ_∞ is significantly greater than n_D^2, too low a moment results from eqn. 1.48. The difference $\epsilon_\infty - n_D^2$ may then sometimes indicate some form of intramolecular motion, such as libration of a group since the ϵ_∞ value would contain an additional polarization contribution over that included in n_D^2. Thus the cause of the low moment of decafluorobenzophenone could be due to such a contribution through libration of the C_6F_5 groups. The dipole moment of decafluorobenzophenone, even as determined from the Guggenheim approach ($\mu = 1.51$D), is less than that of 4,4'-difluorobenzophenone ($\mu = 1.78$D). As has been seen in Chapter 3, the moments of pentafluorobenzene and fluorobenzene are the same while if the $C_6F_5-C-C_6F_5$ angle was larger than

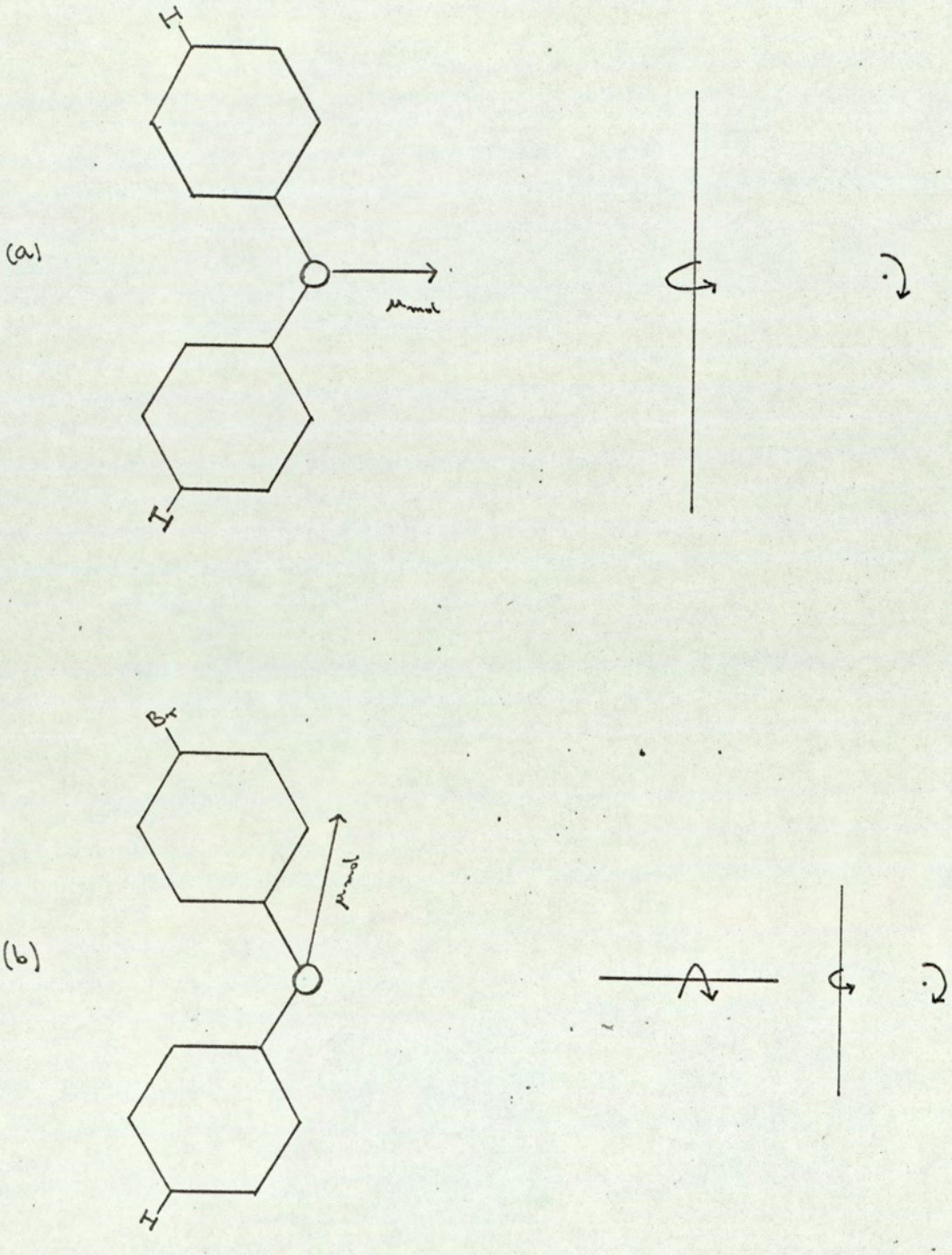
the C_6H_4F-C-C_6H_4F angle, as might be expected from steric considerations, then a larger dipole moment in decafluorobenzophenone would be expected. Models indicate that structures of the type A, C and D of Fig.4.1 are sterically improbable for decafluorobenzophenone but structure B may be more easily achieved. For this structure there will be no stabilisation by resonance, i.e. no mesomeric flow of charge towards the carbonyl group, and hence this could account for the lower dipole moment of decafluorobenzophenone relative to 4,4'-difluorobenzophenone.. The dipole moment of benzophenone as determined by the Guggenheim and microwave methods is in good agreement[91] suggesting that in this case the ring rotation is less restricted. Vaughan and Smyth[93] obtained convincing evidence of a contribution from a molecular and a short relaxation process in liquid benzophenone. The latter process was attributed to phenyl group rotation but it is possible that additional effects are present in the pure liquid which would give rise to an additional dispersion region.

The relaxation time of 14.8×10^{-12} sec for dicyclohexylketone in cyclohexane at 25°C is shorter than would be expected for molecular rotation since cyclohexyl compounds have longer relaxation times than the corresponding phenyl derivatives (Chapter 2). It would be expected therefore that the relaxation time of dicyclohexylketone would be longer than that of 19.0×10^{-12} sec for benzophenone in cyclohexane at 25°C. The fact that it is shorter, together with a significant

distribution coefficient, suggests more than one relaxation process. Since dicyclohexylketone is an aliphatic compound then mechanism A can be rejected and a small contribution from mechanism B would seem likely. The distribution of relaxation times could be due to the molecules being temporarily 'locked' in a rigid position for which over-all molecular rotation could occur independently of the coupled internal rotations. Dicyclohexylether has been studied by Smyth[82] and relaxation times of 17.0×10^{-12} sec and 13.0×10^{-12} sec, in benzene at $20^{\circ}C$ and $40^{\circ}C$ respectively, were reported. Steric effects should be greater in this compound than in dicyclohexylketone and hence it is possible that in dicyclohexylether no intramolecular rotation can take place. This would account for the relaxation time of 17.0×10^{-12} sec in benzene at $20^{\circ}C$ being longer than Maier's[80] estimated value of 15.4×10^{-12} sec for diphenylether while as the observed relaxation time of dicyclohexylketone is shorter than that of benzophenone some intramolecular rotation is indicated.

Purcell and Smyth[94] examined cyclohexylphenylether in benzene solution at $20^{\circ}C$ and analysed the results into contributions from two relaxation times. However, owing to the lack of data on such compounds they did not correlate the longer relaxation time with the molecular process involved. A plot of ϵ'' against ϵ' reveals separation into two semi-circular contributions characteristic of two relaxation times of different magnitude and a rough estimate of these relaxation times from

Fig. 4.5. Directions of the Molecular Dipole Moments in (a) Diphenyl ether (b) p-Bromophenylphenylether, together with the possible axes of Molecular Rotation.



the wavelength maxima values gave 53 and 6.7×10^{-12} sec which are in good agreement with those of 66 and 6.6×10^{-12} sec by the chord method.[12,13] The value of 6.6×10^{-12} sec is far too short to be attributed to molecular relaxation and most likely contains at least some contribution from an intramolecular process. The moment of 1.55D for cyclohexylphenylether is greater than that of diphenylether and simple aliphatic ethers and therefore suggests an additional dipole moment component. For diphenylether and its 4,4'-substituted derivatives the permanent dipole components on the long axis (the one perpendicular to the two-fold axis and which lies in the C-O-C plane) of the molecule will cancel out, but in cyclohexylphenylether there will be a fixed component along this axis owing to the effects of the H-C bond moment of +0.4D in the para-position of the phenyl ring and the aliphatic C-H moments of -0.3D on the cyclohexyl group since the components of both types of C-H moment will support each other along the long axis. The presence of a fixed moment along this axis implies that the molecular dipole moment no longer bisects the molecule as in the Y⟋X⟍Y type and relaxation about an additional axis becomes feasible. Relaxation about this axis would involve an appreciably greater volume being swept out than about the other two axes with a consequent lengthening of the relaxation time (Fig.4.5). Thus the long relaxation time may be correlated with such a molecular process. This is borne out by values of a similar magnitude for 4-pyridylphenylether,[84] 4-bromophenyl-

phenylether[82] and 3-nitrophenylphenylether[84] where τ_o=52.2, 72 and 41x10^{-12} sec respectively, in benzene at 20°C. In addition measurements in this study on 4-benzoylpyridine, a molecule of similar size to benzophenone, produced a mean relaxation time of 38.0x10^{-12} sec in p-xylene at 25°C and therefore rotation about an additional axis has had the effect of doubling the mean relaxation time of that observed for benzophenone. n-Butylphenylether,[83] which possesses similar features with respect to C-H moments as cyclohexylphenylether, has a τ_o of 25x10^{-12} sec in benzene at 20°C and this shorter value may reflect additional relaxation motions related to the various internal rotations possible for alkyl-X compounds. The relaxation time of 10.1x10^{-12} sec for diphenylphenylether[84] in benzene at 20°C is not anomalous when compared with the relaxation times of the previous molecules since the fixed component along the long axis is zero. The short relaxation time could be accounted for by a contribution from mechanism B, although as with diphenylether a significant contribution from mechanism A remains feasible if the mesomeric moment is appreciable since the molecular dipole moment is only 1.07D.

Diethylether and diethylketone were chosen for examination since their lack of any significant mesomerism excluded a contribution from mechanism A. The relaxation times observed were 2.4x10^{-12} sec for diethylether and 3.1x 10^{-12} sec for diethylketone in cyclohexane solution at 15°C and these compare with values of 3.2 and 4.1x10^{-12} sec for

n-butylalcohol and n-pentylalcohol,[95] respectively, in benzene at 20°C, and indicates that, although diethylether and diethylketone are of the type Y^XY, there is no appreciable shortening of the relaxation time below that expected from normal internal rotation in alkyl-Z compounds. This is supported by the work on diethylether and n-butylbromide in the pure liquid state[96] for which the ratio of the mean relaxation times is similar to the ratio of their macroscopic viscosities suggesting similar relaxation mechanisms in the two compounds.

Anderson and Smyth[92] compared experimental and calculated values of the dipole moments of substituted phenylethers where the calculated values were based on neglect of any mesomeric contributions. Comparison of these values shows that the deviations are by far the most substantial for nitro and halogeno groups with the substituent in the 4-position. These are molecules in which the resonance effects should be the most pronounced and their deviations bear out that the mesomeric moment is not negligible as in e.g. 4-nitrophenylphenylether where the experimental moment is 0.69D higher than the calculated value. The 4,4'-nitro- and the 4,4'-halogenophenylethers have been key compounds in the study of the relaxation time data with respect to the establishing of mechanism B. The existence of significant mesomeric effects in aromatic ethers is also supported by its significance in anisole and its substituted derivatives. Values range between 0.4D[40] and 0.96D[44] in anisole, while for bis(4-nitrophenyl)ether

and bis(4-bromophenyl)ether Sutton and Hampson[97] obtained mesomeric interaction moments of 0.75D and 0.3D respectively i.e. increases in mesomeric moment over that in diphenylether itself. Further, Higasi's[91] work on the mesomeric moment in diphenylether indicates that its value may be substantial. Values for the dipole moment of bis(4-nitrophenyl)ether are 2.22D[93] and 2.79D[94] while that of bis(4-bromophenyl)ether is 0.60D.[94] Both of these molecules must have significant contributions from an intramolecular relaxation process since the relaxation times are 12.5[93] and 14.0×10^{-12}[94] sec for bis(4-nitrophenyl)ether in benzene at 20°C and 8.7×10^{-12}[94] sec for bis(4-bromophenyl)ether in nujol at 20°C and for the latter molecule at least, due to its low dipole moment, a significant contribution from mechanism A would be expected.

Anomalies arise when mechanism B is solely used to explain the short relaxation time of some compounds. For example, liquid diphenylmethane has a reduced relaxation time at 60°C ($\tau_o = 4.6\times10^{-12}$ sec)[98] which is only about one third of liquid benzophenone[99] whereas bis(4-nitrophenyl)methane[94] has a relaxation time of 22.8×10^{-12} sec at 20°C which is not appreciably shorter than the value of the rigid molecule since, on Maier's[80] estimate of 15.4×10^{-12} sec for the relaxation time of rigid diphenylether in benzene at 20°C and scaling up the ratio of the molecular volumes from Courtauld models, the estimated time is $\sim 25\times10^{-12}$ sec. The τ_i values calculated from eqn. 4.1 are 7.5×10^{-12} sec for diphenylmethane ($\tau_m = 11.9\times$

10^{-12}sec) and 260×10^{-12} sec for bis(4-nitrophenyl)methane. The large τ_1 value calculated for the latter compound is probably due to the inadequacy of eqn.4.1 for it is difficult to visualise how a contribution from such a long relaxation time could possibly have the effect of shortening the observed relaxation time below that estimated for molecular rotation. There is no reason why there should be such little shortening of the relaxation time below that estimated for molecular rotation in bis(4-nitrophenyl)methane, while there is appreciable shortening in diphenylmethane, if solely mechanism B is considered, as the steric effects in the two molecules should be similar. The mean relaxation time of diphenylmethane could be explained if a substantial movement of charge occurred from the methylene group into the π-electron system through hyperconjugation since the molecular dipole moment is only 0.36D. When the molecular moment is increased to 4.32D in bis(4-nitrophenyl)methane any contribution from mechanism A would be relatively small and hence the observed relaxation time would be similar to that of the rigid molecule which is in fact the case. The shorter relaxation time of bis (4-bromophenyl)sulphide ($\tau_o = 8.2\times10^{-12}$sec, μ=0.68D)[84] relative to that of diphenylsulphide($\tau_o = 9.2\times10^{-12}$sec, μ=1.55D)[84], in benzene at 20°C, could again be accounted for by some contribution from mechanism A since, although bis(4-bromophenyl)sulphide is the larger molecule, its dipole moment is less than half of that of diphenylsulphide leading to relatively a much smaller

contribution from the molecular relaxation process. Diphenylsulphide with a higher dipole moment would have a smaller contribution from mechanism A and therefore its longer relaxation time could be explained. However, these arguments do not exclude some intramolecular contribution from mechanism B.

Another apparent anomaly in explaining the observed relaxation time as resulting from molecular relaxation and mechanism B is that the value for bis(4-bromophenyl)sulphide is shorter than that for bis(4-nitrophenyl)ether although the former is the larger molecule, and in addition, the C-O-C angle is larger than that for C-S-C[100] which ought to facilitate mechanism B. Again, a contribution from mechanism A could explain this anomaly since the much smaller moment of the sulphide could lead to a much smaller contribution from molecular relaxation resulting in a shorter observed relaxation time.

Diphenylether[99] and diphenylsulphide[98] have both been examined in nujol ($\eta \sim 211$c.p. at 20°C) yielding relaxation times of 6.2 and 28.8×10^{-12} sec at 20°C. For liquid diphenylether Vaughan and Smyth[93] analysed the dielectric data to yield a τ_2 value of 3.4×10^{-12} sec with $C_1 = 0.28$ while Higasi and Smyth[87] have calculated C_1 to be 0.15. If only mechanism A and molecular relaxation operate when in the solvent nujol, then although τ_2 and C_1 ought to exhibit little alteration with variation of medium, τ_1 will be increased appreciably. Its value in nujol may be estimated by scaling up Maier's[80] value of 15.4x

10^{-12} sec for the molecular relaxation time of benzophenone in nujol to benzene which gives a $\tau_1 = 175 \times 10^{-12}$ sec. Since $C_1 = 0.15 \rightarrow 0.28$ then there should be a significant contribution from molecular relaxation in diphenylether and therefore a mean relaxation time appreciably in excess of the observed value of 6.2×10^{-12} sec would be expected. Clearly a model based solely on molecular relaxation plus mechanism A is inadequate and it becomes necessary to invoke mechanism B. The latter mechanism would also be expected to operate for diphenylsulphide in solution in nujol although its longer mean relaxation time would suggest a greater contribution from molecular relaxation. This could be explained in two ways:- (i) mechanism A would offer a smaller contribution in diphenylsulphide because its molecular dipole moment is larger and also its mesomeric moment is smaller.[96] Both these factors should lead to a smaller effect on relaxation time shortening than is the case for diphenylether: (ii) the C-S-C valency angle ($109^{\circ}30'$ in bis(4-bromophenyl)sulphide)[69] is $13\frac{1}{2}^{\circ}$ smaller than the C-O-C angle in the corresponding ether and steric hindrance may cause the former molecule to be more rigid giving a greater contribution from molecular relaxation. However, the shorter relaxation time for bis(4-bromophenyl)sulphide (8.2×10^{-12} sec) relative to bis(4-nitrophenyl)ether (12.5×10^{-12} sec) would suggest that (ii) does not provide an adequate solution.

In the absence of more precise mesomeric moments, no

clear-cut decision can be made in most cases as to the relative contributions from mechanisms A and B in aromatic ethers and sulphides. When the molecular dipole moment is large, mechanism A would be unimportant in determining the magnitude of the observed relaxation time. However, for molecules with a low moment (e.g. $\mu < 1D$), mechanism A could offer a significant contribution and seems necessary to explain the observed relaxation times of certain molecules. Thus, the tendency of aromatic ethers and sulphides of the type  with a low moment to have a short observed relaxation time. This is also the case for diphenylmethane. For dicyclohexylketone, mechanism B appears essential to account for the relaxation time shortening. In fact, both intramolecular mechanisms seem necessary to explain the literature relaxation time data and there seems no reason why both should not operate in aromatic ethers and sulphides.

Chapter 5

Relaxation Processes in para-Disubstituted Benzenes and Related Compounds

Introduction

A study of molecules of the type X-C_6H_4-X and X-X, where X is a rotating polar group, is useful because the fixed components along the long axis of the molecule will cancel out and hence the only relaxation mechanism that should be observed is group rotation. The mean relaxation time, τ_o, will therefore be associated with the group relaxation process and since τ_o can be determined with an accuracy of approximately $\pm 5\%$ a study of these compounds will permit an accurate evaluation of the enthalpy of activation to group rotation to be made.

Dipole moment studies alone may give some indication as to whether the end groups are freely rotating but they do not provide an absolute test. The problem of calculating the dipole moments associated with such free rotation was first discussed by Williams.[71] If the group dipoles (μ_g) subtend an angle θ with the long axis of the molecule then the components along this axis, $\mu_g \cos\theta$, will cancel out and the dipole moment of the molecule will be only associated with the relative dispositions of the two components, $\mu_g \sin\theta$, perpendicular to this axis. For the case of free rotation of the groups, i.e. all positions of the two components equally probable, then the dipole moment of the molecule (μ) is given by $\mu = \sqrt{2}.\mu_g \sin\theta$ (eqn.3.2). By comparing calculated and observed values of the dipole moment some indication may be gained as to whether free rotation of the groups is taking place. The problem is complicated by several factors however. Completely

free rotation of groups is unlikely to be an actuality and therefore some deviation between the calculated dipole moment and that observed must be expected. Among the factors that could account for the absence of free rotation are (i)mesomerism present in the molecule which will cause planar cis and trans configurations to be energetically favoured (ii)hindrance to rotation by the solvent molecules and (iii)intra- and inter-molecular forces. Another factor that has to be taken into account is that the same dipole moment would be calculated as for free rotation of the end groups if (i)the molecule was fixed in equal amounts of cis and trans forms (ii)the groups in these cis and trans forms rotated freely within the limits $\pm\phi$ or (iii)the oscillations, not being free, were such that the probability of any angle of swing was some function of that angle, the same function applying to each group. It can be realised therefore that dipole moment studies alone do not provide a very absolute indication of group rotation in these molecules.

A better approach is to study the dielectric relaxation times of these molecules for if only group rotation is occurring then a short relaxation time, approximately the same as that observed for group rotation in the mono-substituted compound, would be anticipated while if the molecule existed in only cis and trans forms molecular rotation of the cis form would be observed with a correspondingly long relaxation time. Group oscillations, as outlined above, should lead to a

resonance absorption with a characteristic frequency in the far infrared region and would not be observed in the microwave region.

Compounds of the type X-C_6H_4-X have been investigated, where X=OCH_3, $-C(=O)-CH_3$, $-CH_2Cl$, $-C(=O)-C_6H_5$, $-NH_2$ and of the type X-X where X= $-C(=O)-CH_3$ and $-C(=O)-C_6H_5$. Studies have also been made on tetrafluorohydroquinone and benzyl chloride. The latter compound was investigated in order to compare the $-CH_2Cl$ group relaxation time in the mono-substituted compound with that in α,α'-dichloro-p-xylene. Determinations of the enthalpy of activation to group rotation have been made in a number of cases.

Table 5.1. Relaxation times, distribution parameter (α), static dielectric constant (ϵ_o), dielectric constant at very high frequency (ϵ_∞) and dipole moment (μ) for solutions of weight fraction ω_2 at temperature t °C for p-disubstituted benzenes and related compounds.

t (°C)	ω_2	τ_o	τ_1 $\times 10^{12}$ SEC	τ_2	C_1	α	ϵ_o	ϵ_∞	μ (D)
			p-Dimethoxybenzene/cyclohexane						
15	0.05818	8.3				0.04	2.1683	2.061	1.69
25	0.06586	6.9				0.04	2.1634	2.048	1.69
40	0.06751	5.7				0	2.1345	2.032	1.67
50	0.05818	4.9				0	2.0886	2.005	1.67
			p-Diacetylbenzene/p-xylene						
15	0.02688	23.5				0.07	2.4394	2.299	2.75
25	0.02074	21.9				0.07	2.3862	2.281	2.79
25	0.02886	21.4				0.06	2.4333	2.287	2.78
40	0.02688	16.0				0.02	2.3822	2.261	2.73
60	0.02688	13.1				0	2.3394	2.228	2.75
			α,α'-Dichloro-p-xylene/p-xylene						
15	0.03981	7.0				0.10	2.4052	2.300	2.03
25	0.03321	5.7				0.08	2.3638	2.280	2.04
40	0.03321	5.2				0.05	2.3285	2.259	1.93
50	0.04513	4.6				0	2.3405	2.254	1.90
60	0.03981	3.9				0	2.3030	2.227	1.94

t (°C)	ω_2	τ_0	τ_1	τ_2	c_1	α	ϵ_0	ϵ_∞	μ (D)
		—— $\times 10^{-12}$ sec ——							
α,α'-Dichloro-p-xylene/cyclohexane									
25	0.01496	3.9				0.02	2.0548	2.023	2.09
Benzyl chloride/p-xylene									
15	0.05589	13.0	15.8	2.6	0.81	0.09	2.4595	2.315	1.71
25	0.05171	11.2	15.4	4.7	0.70	0.09	2.4209	2.296	1.70
40	0.05171	9.3	12.6	4.9	0.61	0.05	2.3828	2.269	1.68
50	0.05589	8.5	11.4	3.6	0.71	0.04	2.3686	2.254	1.67
60	0.05171	8.3	8.9	5.9	0.81	0	2.3354	2.236	1.65
Benzyl chloride/cyclohexane									
25	0.05955	7.5	14.4	2.9	0.58	0.14	2.1728	2.046	1.78
p-Dibenzoylbenzene/p-xylene									
60	0.00914	21.8				0	2.2394	2.204	3.53
p-Phenylenediamine/1,4-dioxan									
25	0.03600	5.3				0.29	2.4759	2.338	1.80
Tetrafluorohydroquinone/1,4-dioxan									
25	0.05932	27.7				0.11	2.6462	2.344	2.69
Diacetyl/cyclohexane									
25	0.19775	1.4				0.14	2.2558	2.160	0.65
25	0.30089	1.4				0.17	2.4294	2.240	0.71

t (°C)	w_2	τ_0	τ_1	τ_2	c_1	α	ϵ_0	ϵ_∞	μ (D)
			$\times 10^{12}$ sec						
			Diacetyl/carbon tetrachloride						
15	0.21649	2.2				0.15	2.7547	2.510	0.68
15	0.29946	2.0				0.15	2.9543	2.570	0.72
			Dibenzoyl/cyclohexane						
40	0.01427	24.3				0.08	2.0616	1.997	3.48
			Dibenzoyl/carbon tetrachloride						
15	0.01005	48.0				0.09	2.3778	2.260	3.47
15	0.01860	48.9				0.08	2.4903	2.275	3.45
40	0.01888	35.3				0.06	2.4224	2.225	3.52

Table 5.2. Free Energies (ΔG^*), Enthalpies (ΔH^*) and Entropies (ΔS^*) of Activation for Molecular and Intramolecular Relaxation.

t (°C)	ΔG_1^* — kcal/mole —	ΔH_1^* —	ΔS_1^* cal/deg/mole	ΔG_2^* — kcal/mole —	ΔH_2^* —	ΔS_2^* cal/deg/mole
			p-Dimethoxybenzene/cyclohexane			
15				2.24	2.1	-0.5
25				2.23	"	-0.4
40				2.24	"	-0.4
50				2.24	"	-0.4
			p-Diacetylbenzene/p-xylene			
15				2.83	2.0	-3.0
25				2.90	"	-3.0
40				2.89	"	-2.8
60				2.98	"	-2.9
			Benzyl chloride/p-xylene			
15	2.61	1.7	-3.2			
25	2.69	"	-3.3			
40	2.74	"	-3.3			
50	2.78	"	-3.3			
60	2.74	"	-3.1			
			α,α'-Dichloro-p-xylene/p-xylene			
15				2.13	1.6	-1.8
25				2.10	"	-1.7
40				2.18	"	-1.9
50				2.20	"	-1.9
60				2.18	"	-1.7

Table 5.3. Literature Values of Relaxation Times of p-Dimethoxybenzene and p-Diacetylbenzene together with Enthalpies of Activation for Molecular Relaxation ($\Delta H_1^{\ddagger}$) and for Intramolecular Relaxation ($\Delta H_2^{\ddagger}$).

Compound	Solvent	t (°C)	τ_0	τ_1	τ_2	C_1	$\Delta H^{\ddagger}$ KCAL/MOLE	Ref.
			——	$\times 10^{12}$ SEC	——			
p-Dimethoxy-benzene	Benzene	20	6.2					65
		40	5.2				$\Delta H_2^{\ddagger} = 0.88$	"
		60	4.6					"
"	"	20	9.7					101
		40	6.4				$\Delta H_2^{\ddagger} = 2.9$	"
		60	4.6					"
"	"	20		8.5	0.75	0.73		79
"	"	25	6.9					19
"	Xylene	15	6.3					18
"	Decalin	20	17.5	31.6	13.8	0.19		14
		40	13.5	27.5	11.0	0.17	$\Delta H_0^{\ddagger} = 2.2$	"
		60	9.8	21.9	9.6	0.16		"
"	Nujol	20	20.0	112	14.0	0.22		14
		40	14.8	97	10.5	0.18	$\Delta H_0^{\ddagger} = 2.1$	"
		60	11.6	40	7.2	0.15		"
"	Pure Liquid	60		8.5	0.7	0.87		66
		80		6.2	0.9	0.88		"
p-Diacetyl-benzene	Benzene	20	24.6	27	7.7	0.85	$\Delta H_1^{\ddagger} = 1.3$	14
		40	19.0	22	6.2	0.84	$\Delta H_2^{\ddagger} = 1.5$	"
		60	16.2	18	4.9	0.82		"
"	"	20		18.8	1.1	0.87		79

FIG. 5.1 PLOT OF LOG $\tau_0 T$ AGAINST 1/T FOR P-DIMETHOXYBENZENE IN CYCLOHEXANE.

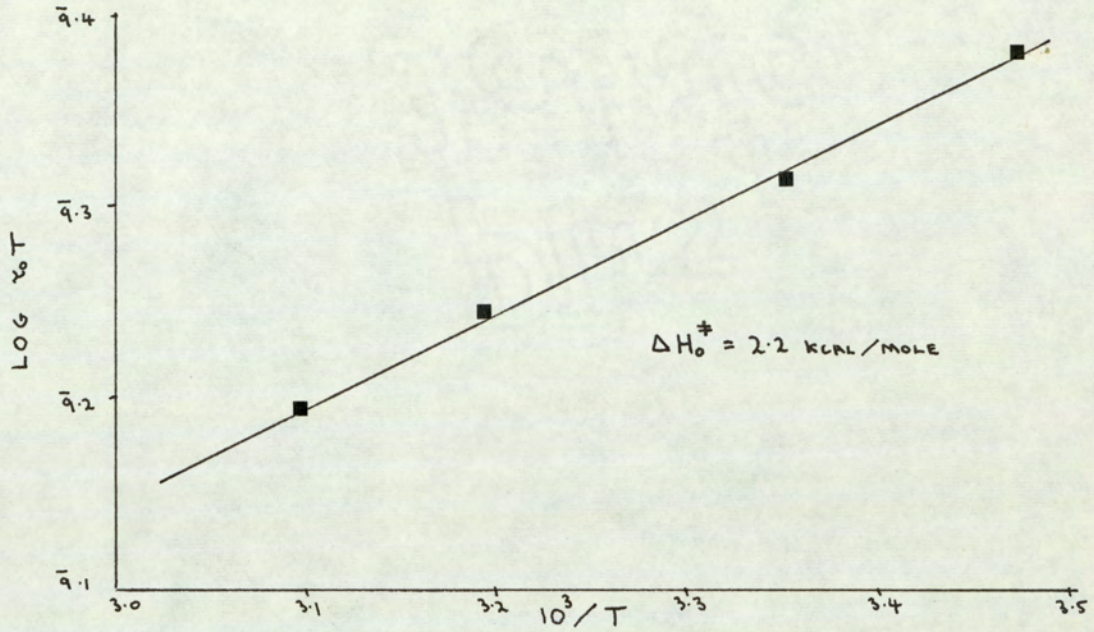
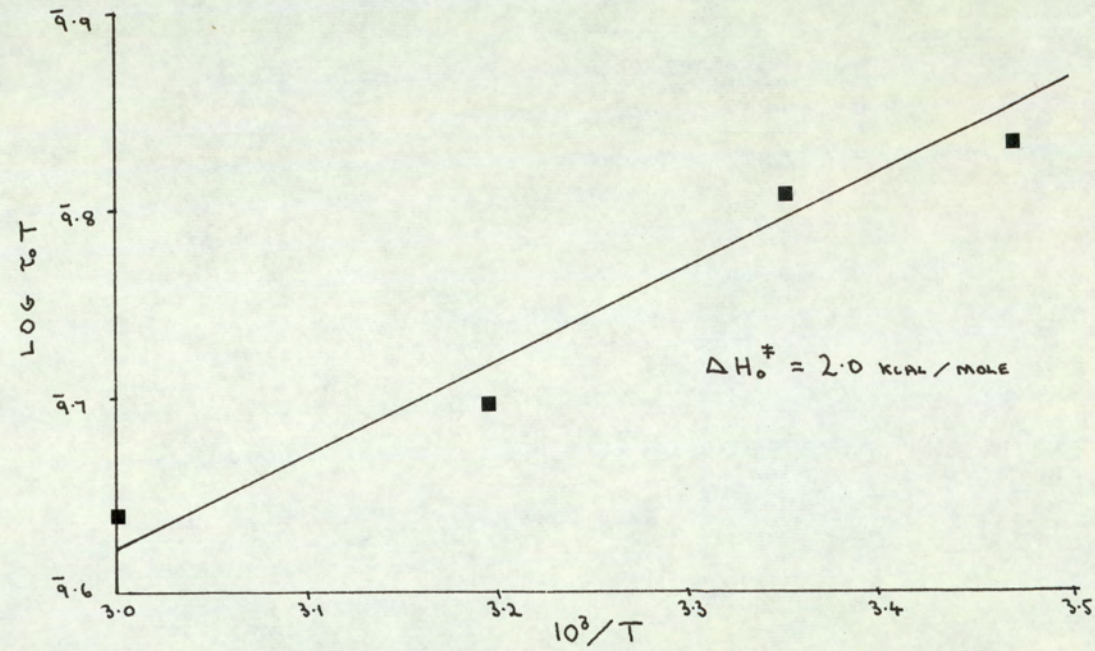


FIG. 5.2. PLOT OF LOG $\tau_0 T$ AGAINST 1/T FOR P-DIACETYLBENZENE IN P-XYLENE.



Discussion

In Chapter 3 the predominant relaxation process in anisole was concluded to be methoxy group rotation and the enthalpy of activation, ΔH_2^*, was evaluated. It was decided to study p-dimethoxybenzene in order to see if the relaxation times and energy barriers to methoxy group rotation had altered due to the presence of two substituted groups. p-Dimethoxybenzene was examined in cyclohexane at four temperatures and a mean relaxation time of 6.9×10^{-12} sec at 25°C was obtained which compares with a τ_2 value of 6.4×10^{-12} sec for anisole in cyclohexane at 25°C. This result clearly suggests that group rotation is the only relaxation process present in p-dimethoxybenzene since τ_0 is almost equal to τ_2 in anisole. p-Bromoanisole, a molecule of similar size to p-dimethoxybenzene, has a molecular relaxation time of 31.3×10^{-12} sec, in p-xylene at 25°C, and hence the short observed relaxation time of p-dimethoxybenzene would suggest that group relaxation is the principal one in this compound. In addition, the dipole moment calculated on the basis of 'free rotation' of the groups, from eqn.3.2 where $\mu_g = 1.2D$ and θ, derived from the group moment calculations in anisole, is 68°, gives $\mu = 1.57D$ which is in good agreement with the observed value of 1.68D. If group rotation is the sole relaxation process then its enthalpy of activation can be derived from the plot of $\log \tau_0 T - 1/T$ and is equal to 2.2 ± 0.3 kcal/mole (Fig.5.1). This compares with a value of 2.1 ± 0.5 kcal/mole

for group rotation in anisole showing that the energy barrier to methoxy group rotation in both these compounds is virtually the same.

Other workers have measured the dielectric absorption of p-dimethoxybenzene and have reached the conclusion that methoxy group rotation is the principal relaxation process in this molecule. Forest and Smyth[65] have recently studied this compound in solution in benzene and reported an enthalpy of activation to group rotation of only 0.88 kcal/mole. Their measurements were carried out at only two microwave frequencies and three temperatures however and therefore a considerable error in their results is possible. In fact Roberti and Smyth[101] also examined p-dimethoxybenzene in benzene at two microwave frequencies and three temperatures and obtained a mean relaxation time of 9.7×10^{-12} sec at $20^{\circ}C$ which compares with Forest's and Smyth's value[65] of 6.2×10^{-12} sec at the same temperature. In addition, the $\Delta H_2^{\ddagger}$ value calculated from the results of Roberti and Smyth is 2.9 kcal/mole. These large deviations in results indicate the inadequacy of measuring the dielectric absorption at such a small number of frequencies. In general, measurements in this study have been made at five or six microwave frequencies and therefore a greater accuracy on the results would be expected.

A good test to see whether group relaxation is the principal relaxation process in a compound is to make studies in viscous solvents such as decalin or nujol (η =2.61 and 211

c.p. respectively at 20°C). If there is a significant contribution from molecular relaxation then the mean relaxation time would be expected to lengthen considerably over that observed in benzene or cyclohexane since molecular rotation would meet a large hindering potential barrier due to the viscosity of the solvent. For example, benzophenone, which appears to relax predominantly by molecular rotation, has a mean relaxation time of 20.5×10^{-12} sec in benzene at 25°C but it is increased to 230×10^{-12} sec in nujol at 25°C.[102] If group rotation is the important process, however, then the relaxation time should not increase appreciably in the more viscous solvent since the groups do not sweep out such a large volume during rotation while the contribution to the energy barrier caused by resonance should remain the same. Smyth has examined p-dimethoxybenzene in decalin and nujol at five microwave frequencies and reported mean relaxation times of 17.5 and 20×10^{-12} sec respectively, at 20°C.[14] Certainly the τ_o value in nujol clearly suggests that methoxy group relaxation is the principal process in this compound. Smyth analyses his results for measurements in these solvents in terms of two relaxation times suggesting that there may be a contribution from molecular rotation either due to the molecule existing in unstable cis and trans forms, the cis form contributing to dielectric relaxation by molecular rotation, or there may be a mesomeric moment along the long axis of the molecule which would give rise to a contribution

from molecular relaxation by end-over-end rotation. However, the results from this study and of later work by Smyth[65] suggests that the dielectric absorption of p-dimethoxybenzene can be characterized quite adequately in terms of one relaxation time. Furthermore if molecular relaxation of a cis form was to occur then it would be expected that the group relaxation time would have to be longer than the molecular relaxation time otherwise before rotation of the cis form could take place the groups would have rotated and altered the direction of the dipole moment. It is also unlikely that the presence of a mesomeric moment in p-dimethoxybenzene would cause end-over-end rotation of the molecule since the mesomeric moment of one group should be cancelled by that of the other group but even if the methoxy groups were rotating in planes at 90° to each other the frequency of reversal of direction of the mesomeric moment would be associated with the group relaxation time and would be too fast for end-over-end rotation to take place. If only group rotation is present in p-dimethoxybenzene then the enthalpy of activation for the measurements in decalin and nujol can be calculated from Smyth's τ_0 results to be 2.2 and 2.1 kcal/mole respectively.

Studies on the pure liquid state of p-dimethoxybenzene by Vaughan, Roeder and Provder[66] have yielded values of $\tau_1 = 8.5 \times 10^{-12}$ sec, $\tau_2 = 0.7 \times 10^{-12}$ sec and $C_1 = 0.87$ at $60^{\circ}C$. The τ_1 value was attributed to group rotation but was thought to be long in comparison with the methoxy relaxation times

that they obtained in other compounds. This they said could have been explained by an incomplete cancelling out of the moment along the rotation axis due to a fluctuating mesomeric moment as the groups rotate and thus there would be a small amount of dispersion associated with end-over-end rotation. However, they further showed that a decomposition of the data into a superposition of terms of the Debye type yielded an additional dispersion that was at a higher rather than a lower frequency. Hence the problem of the long group relaxation time and the additional short relaxation time of 0.7×10^{-12} sec, at 20°C, remained. One possible cause of the short relaxation time is that there is an additional dispersion region in the pure liquid state such as some form of lattice vibration. Fong[17] has discussed the results of Vaughan et al in a review and has suggested that the apparently long group relaxation time in p-dimethoxybenzene may be due to a movement of the benzene nucleus as the methoxy groups rotate. This movement, he says, should take place since it is not acceptable for the benzene nucleus to remain stationary while methoxy group rotation occurs since such a mechanism involves displacement of the centre of gravity of the molecule. Thus simultaneous rotation of the methoxy groups must necessarily be coupled with suitable motions of the benzene nucleus so that the centre of gravity of the molecule may remain stationary during the transitions. The results from this study on p-dimethoxybenzene do not

show an appreciable increase in the τ_0 value above the τ_2 value in anisole but the small distribution parameters observed in a number of the Cole-Cole plots of p-disubstituted benzenes could perhaps be explained by an additional motion such as that described by Fong above.

In marked contrast to p-dimethoxybenzene and anisole the mean relaxation times of p-diacetylbenzene were found to lengthen appreciably beyond the corresponding group relaxation times of acetophenone. Thus the mean relaxation time of p-diacetylbenzene in p-xylene at 25°C is 21.4×10^{-12} sec while the corresponding τ_2 value of acetophenone is 9.7×10^{-12} sec, a difference in terms of $\Delta G^{\ddagger}$ of 0.47 kcal/mole. Fong and Smyth[34] have also reported long relaxation times for τ_0 and have suggested that this is due to a contribution from molecular relaxation. The reason that they put forward for this molecular relaxation contribution is that the potential energy barriers hindering rotation of the acetyl groups could cause the molecule to exist in unstable cis and trans forms, the cis form contributing to dielectric relaxation by molecular rotation. They analyse the results at 20°C in terms of two relaxation times to give $\tau_1 = 27 \times 10^{-12}$ sec, $\tau_2 = 7.7 \times 10^{-12}$ sec and $C_1 = 0.85$. However, it is highly improbable that both molecular and intramolecular relaxation processes could occur about the same axis if the group relaxation time was less than the molecular relaxation time. If $\tau_2 < \tau_1$ then the group will have rotated, altering the

direction of the molecular dipole moment, before the molecule in its cis configuration has been able to rotate from one equilibrium position to another. In a later paper Fong and Smyth[53] reported determinations of the dipole moment of p-diacetylbenzene where the moment increased from 2.86D at 20°C to 2.91D at 60°C. The moment that they calculated for free rotation of the acetyl groups was 3.43D and they suggested that the lower dipole moment observed indicated that the molecule existed in unstable cis and trans forms with the trans form predominating while the change in moment with temperature indicated that the percentage of cis form increased with increase in temperature. The cis form was thought to be less stable due to the greater dipole-dipole repulsion in this configuration. However, dipole-dipole repulsive forces are generally considered to be short range in nature since they arise from overlap of the electron clouds. The carbonyl groups in the cis form of p-diacetylbenzene will be approximately 6 to 7Å apart and therefore the repulsive forces between them should be extremely weak. In addition, no trend of dipole moment over a similar temperature range was observed in this study. This still does not rule out the possibility that a trans form of p-diacetylbenzene may be energetically more favoured since if the carbonyl groups were approximately in line a greater freedom of resonance may be achieved.

If molecular and intramolecular rotations are not occurring about the same axis in p-diacetylbenzene then it

must be considered that either the molecule is rigid or only group relaxation is taking place. The τ_o value of 21.4x 10^{-12} sec in p-xylene at 25°C would appear to be low for molecular relaxation as p-bromoanisole, a molecule smaller than p-diacetylbenzene, has a τ_1 value of 31.3×10^{-12} sec. p-Phenylacetophenone from molecular models is approximately 1.2 times larger than p-diacetylbenzene and has a reported molecular relaxation time of 51×10^{-12} sec in benzene at 20°C.[34] If the molecular relaxation times were directly proportional to their volumes then p-diacetylbenzene would have a molecular relaxation time of 42.3×10^{-12} sec in benzene at 20°C. Smyth, however, only observed a mean relaxation time of 24.6×10^{-12} [34] sec and therefore it would appear that molecular relaxation alone is improbable in p-diacetylbenzene. It was not possible to examine p-diacetylbenzene in the viscous solvents decalin and nujol, and to note the effect on the mean relaxation times, due to problems of solubility.

If 'free rotation' of the acetyl groups was taking place then, from eqn.3.2 where $\mu_g = 2.82D$ and $\theta = 54°$ (from the group moment calculations on p-substituted acetophenones, Chapter 2), the calculated dipole moment of p-diacetylbenzene is 3.23D which compares with the observed value of 2.76D. The deviation could be explained in terms of errors in group moments and θ but it is just as likely to be due to the inadequacy of eqn.3.2. The mean relaxation times of p-diacetylbenzene if interpreted solely in terms of group

relaxation might appear long but this could be explained by the greater length of conjugation in the molecule, relative to acetophenone, giving rise to more double-bond character between the acetyl groups and the phenyl ring resulting in a higher free energy of activation to group rotation. A similar increase was not observed in the group relaxation time of anisole to p-dimethoxybenzene but Klages and Zentek[68] have measured the methoxy disubstituted biphenyl compound, 4,4'-dianisyl, and reported a mean relaxation time of 15.9x 10^{-12} sec, in benzene at 20°C, which compares with their value of 7.3x10^{-12} sec for p-dimethoxybenzene.[68] Rotation about the central pivot bond would most likely require an energy outside the microwave region[103] and therefore in 4,4'-dianisyl only methoxy group rotation should be observed. It appears therefore that, due to the greater length of conjugation in this molecule relative to p-dimethoxybenzene, an increase in the methoxy group relaxation time results. In addition, longer group relaxation times than those observed in acetophenone appear to be indicated in p-phenyl-acetophenone and 2-acetonaphthone where again the length of conjugation is increased.

The suggestion that only acetyl group relaxation may be taking place in p-diacetylbenzene meets further support from Le Fèvre's value of 21.2x10^{-12} sec for the relaxation time of 1,4-diacetyldurene in carbon tetrachloride at 17.5°C.[28] If both this molecule and p-diacetylbenzene were relaxing

predominantly by molecular relaxation then 1,4-diacetyldurene should have a much longer relaxation time than is actually observed due to the increased size of the molecule. In fact, bis(chloromethyl)durene, which is considered by Smyth to be a rigid molecule, has a relaxation time of 43.5×10^{-12} sec in benzene at 20°C[16] and a value greater than this would be expected for 1,4-diacetyldurene if it was rigid. Molecular models suggest that while $-CH_2Cl$ group rotation is sterically hindered by the methyl groups, rotation of the acetyl groups is not so affected. However, the lowering of the dipole moment of 2,4,6-trimethylacetophenone below that of acetophenone[104] and the lengthening of the infrared carbonyl stretching frequency of 2,3,5,6-tetramethylacetophenone above that of acetophenone[37] have been used as evidence for a restriction of acetyl group rotation by the methyl groups for if the acetyl groups cannot achieve coplanarity with the benzene ring then there will be less mesomerism in the methyl substituted molecules causing both a decrease in dipole moment and a carbonyl stretching frequency closer to that in an aliphatic ketone. However, the relaxation time of 1,4-diacetyldurene would definitely indicate some non-rigidity when compared with the relaxation time of bis(chloromethyl)durene. Furthermore, restriction to rotation by ortho-substituted groups, such as methyl or chlorine, of the methoxy group has not been proved despite suggestions that there is steric hindrance. The fact that 1,4-diacetyldurene

has a relaxation time approximately the same as that of p-diacetylbenzene would suggest that group relaxation and not molecular relaxation is the important process in these compounds, the methyl groups in 1,4-diacetyldurene not offering as much resistance to acetyl group rotation as might have been expected. Le Fèvre[28] has also measured 2,4,6-trimethylacetophenone and obtained a mean relaxation time of 22.9×10^{-12} sec in carbon tetrachloride at 22°C. As this compound has a longer mean relaxation time than that of 1,4-diacetyldurene it again suggests that acetyl group rotation is taking place for if the molecules were both rigid the latter molecule would be expected to have the longer relaxation time since it is the larger molecule.

Assuming group relaxation to be the only relaxation process in p-diacetylbenzene the enthalpy of activation is calculated from the plot of $\log \tau \cdot T - 1/T$ to be 2.0 ± 0.6 kcal/mole (fig.5.2). Thus although the free energy of activation for acetyl group rotation in p-diacetylbenzene has increased above that in acetophenone, the enthalpy of activation appears to be approximately the same.

A compound of similar size and shape to p-dimethoxybenzene is α,α'-dichloro-p-xylene. It was decided to compare the $-CH_2Cl$ relaxation process in α,α'-dichloro-p-xylene with that in the mono-substituted compound by measuring first of all the dielectric properties of benzyl chloride. An upper limit for the molecular relaxation time of this compound is

that of ethylbenzene ($\tau_1 = 16.2 \times 10^{-12}$ sec in cyclohexane at 25°C)[27] since the van der Waals radius of the methyl group is 2.0Å while that of chlorine is 1.8Å. The τ_1 value of 14.4×10^{-12} sec therefore appears satisfactory for benzyl chloride in cyclohexane at 25°C. The average C_1 value obtained from measurements at five temperatures in p-xylene and one in cyclohexane is 0.70 which is considerably greater than the value which would be derived from a consideration of group moments. For example, Le Fèvre[105] reports a dipole moment of 1.67D for p-chlorobenzyl chloride and 1.80D for benzyl chloride, in carbon tetrachloride at 25°C, and, using a procedure analogous to that employed in calculating C_1 in acetophenone and anisole, θ , the angle that the $-CH_2Cl$ group moment subtends with the projection of the C_1-C_4 axis in benzyl chloride, is 58°26' with the moment directed away from the ring and hence $C_1 = 0.27$. Moreover the average dipole moment of α,α'-dichloro-p-xylene in p-xylene obtained from this study is 1.97D and from eqn.3.2, where $\mu_g = 1.68$D, an angle of θ = 55°2' is derived which results in a C_1 value of 0.33 in benzyl chloride. Thus either the results for benzyl chloride are erroneous or the use of eqn.3.2 in deriving θ is not valid while for p-chlorobenzyl chloride large mesomeric interactions between the chlorine atom and the methylene chloride group could be leading to calculated C_1 values which are in error. In any event it would seem preferable to postpone a decision as to the exact C_1 value of benzyl chloride

FIG. 5.3 PLOT OF LOG $\tau_1 T$ AGAINST $1/T$ FOR BENZYL CHLORIDE IN P-XYLENE.

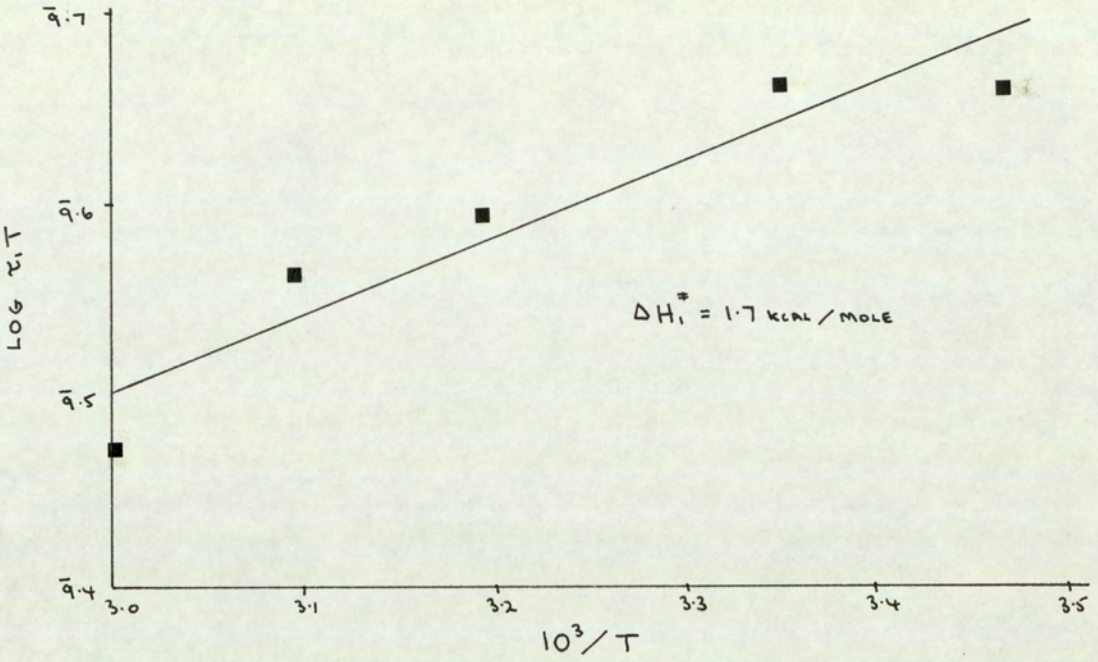
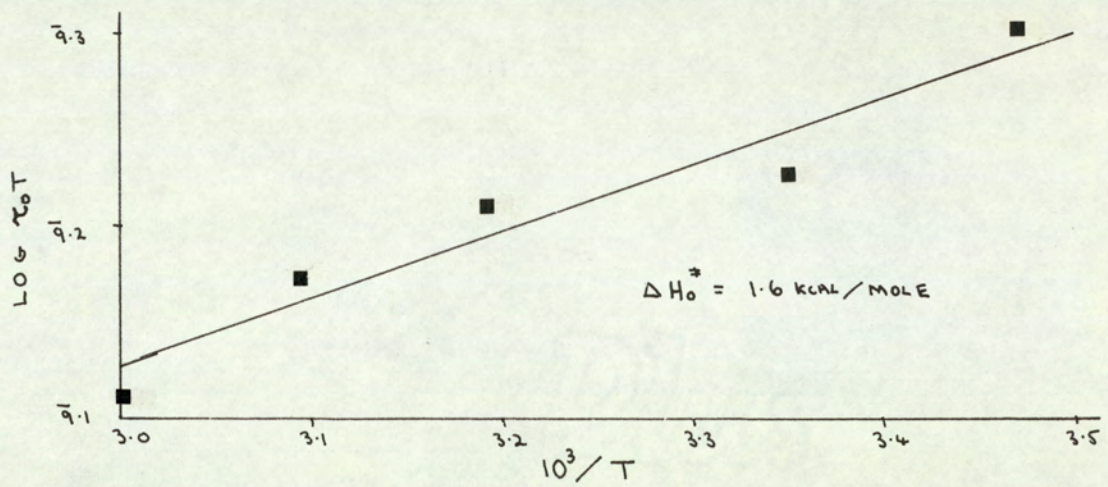


FIG. 5.4 PLOT OF LOG $\tau_0 T$ AGAINST $1/T$ FOR α, α'- DICHLORO-P-XYLENE IN P-XYLENE.



until the relaxation times and dipole moments of a number of para-substituted benzyl chlorides have been measured.

Benzyl chloride was studied at five temperatures in p-xylene and the enthalpy of activation to molecular relaxation was determined to be 1.7 ± 0.6 kcal/mole (Fig.5.3). The τ_2 values did not show any definite trend with temperature probably due to the small weight factor on this process but it can be observed from Table 5.1 that the values obtained for $-CH_2Cl$ group rotation are lower than those for methoxy and acetyl group rotation.

α,α'-dichloro-p-xylene was found to have the very short mean relaxation time of 5.7×10^{-12} sec in p-xylene at 25°C clearly indicating rotation of the $-CH_2Cl$ groups. If group rotation is taking place in α,α'-dichloro-p-xylene then it should also be present in benzyl chloride since in the former compound the length of conjugation is greater and a longer group relaxation time would be expected. Hence the larger τ_0 values of α,α'-dichloro-p-xylene relative to the τ_2 values of benzyl chloride. The larger τ_0 value and the significant distribution angle in α,α'-dichloro-p-xylene could also be explained however by movement of the benzene nucleus as the groups rotate such as was described by Fong.[17]

From measurements of α,α'-dichloro-p-xylene at five temperatures the enthalpy of activation to group rotation was calculated to be 1.6 ± 0.5 kcal/mole (Fig.5.4). Hence it would appear that both the free energy and enthalpy of

activation for rotation of the methylene chloride group is less than that for methoxy and acetyl group rotation. A single determination of the relaxation time of α,α'-dichloro-p-xylene in cyclohexane at 25°C yielded a mean relaxation time of 3.9×10^{-12} sec. This decrease below that observed in p-xylene could be ascribed to less interaction between the $-CH_2Cl$ groups and cyclohexane.

The relaxation processes of p-dibenzoylbenzene have also been investigated but since this compound is very sparingly soluble it could only be studied at 60°C in p-xylene. The mean relaxation time of 21.8×10^{-12} sec almost certainly indicates intramolecular rotation of the benzoyl groups when compared with p-phenylacetophenone, a smaller molecule, which has a molecular relaxation time of 30×10^{-12} sec in solution in benzene.[34] In addition, the mean relaxation time of p-dibenzoylbenzene is less than that of m-dibenzoylbenzene and this, as discussed in Chapter 4, suggests that group rotation is taking place in these compounds for if they were both rigid then the para-substituted compound would be expected to have the longer relaxation time. The dipole moment of 3.53D also compares well with that of 3.74D calculated for 'free rotation' of the benzoyl groups from eqn.3.2 where μ_g=2.92D and θ=65° (from the moment of benzophenone), although this agreement alone would not rule out the possibility of an equal number of cis and trans configurations. As p-dibenzoylbenzene has a large dipole moment phenyl group

rotation alone would not be expected to provide a significant contribution to the shortening of the relaxation time.

p-Phenylenediamine was found to be only very sparingly soluble in most common non-polar solvents with the exception of 1,4-dioxan and it was therefore examined in this. 1,4-Dioxan has a very small dielectric loss and it was therefore measured separately so that this loss could be subtracted from the total. The mean relaxation time of 5.2×10^{-12} sec at 25°C compares with a value of 1.5×10^{-12} sec in benzene at 23°C.[39] The short relaxation time observed could be attributed to an intramolecular process. The extremely high distribution parameter of 0.29 radians on the Cole-Cole plot is appreciably greater than any observed from measurements of other para-disubstituted compounds in p-xylene or cyclohexane, in this study, and could perhaps be attributed to interaction between the protons of the amino group and the lone pair electrons of the oxygen atoms of dioxan. Furthermore the dipole moment of p-phenylenediamine in dioxan is calculated to be 1.80D which compares with a value of 1.51D in benzene.[29] This large increase could be attributed to hydrogen bond formation between the solute and solvent molecules causing an appreciable redistribution of charge. Thus a rate process may be possible involving the breaking of this hydrogen bond, the magnitude of the rate constant for the dissociation process possibly leading to a relaxation time detectable in the microwave region. The position

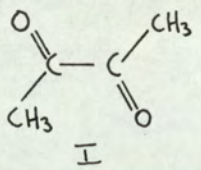
could be further complicated by nitrogen inversion taking place in the amino group at a frequency in the microwave region. This problem however is hardly relevant to this thesis but has been discussed extensively elsewhere.[106]

Tetrafluorohydroquinone had also to be studied in 1,4-dioxan due to problems of solubility. The long mean relaxation time of 27.7×10^{-12} sec suggests that molecular relaxation is the principal relaxation mechanism in this compound which is not altogether surprising since there should be some intramolecular hydrogen bonding between the phenolic hydrogen and the fluorine atoms which would restrict hydroxy group rotation. In addition there is the strong possibility of hydrogen bond formation between the phenolic hydrogen and the lone pair electrons of the oxygen atoms of the dioxan solvent molecules, causing a complex to be formed. The dipole moment of 2.69D in no way indicates free rotation of the hydroxy groups since if this were the case a dipole moment approximately the same as that of hydroquinone (μ = 1.40D in benzene at 44°C)[29] might be expected.

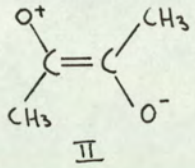
To study the problem of acetyl and benzoyl group rotation further it was decided to examine molecules of the type X-X where X= $-C(=O)-CH_3$ and $-C(=O)-C_6H_5$ i.e. diacetyl and dibenzoyl, and to see if there was any shortening of the relaxation times below that expected for molecular rotation. Unlike p-diacetylbenzene and p-dibenzoylbenzene, intramolecular forces between the carbonyl groups should be more evident in

these compounds since the groups are in close proximity. Hence both dipole-dipole repulsive forces and also steric effects may have to be taken into account to explain the dipole moments and relaxation times of these compounds.

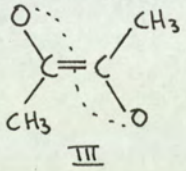
If 'free rotation' of the acetyl groups was present in diacetyl then the calculated moment from eqn.3.2 would be 3.20D since , from a consideration of the dipole moment of acetone, μ_g=2.94D and $\theta = 50^{o}14'$. In fact, the molecular dipole moment is only observed to be 0.68D in cyclohexane at 25°C. This low moment could suggest that (i) the molecule exists in planar cis and trans forms with the trans form predominating (ii) the groups oscillate about a trans configuration (iii) the molecule exists in neither cis nor trans configurations but the effective configuration is a skew structure. Bloom and Sutton[107] have discussed the temperature dependence of the dipole moment of diacetyl and have left undecided whether there be an equilibrium of cis and trans forms or an unusually rigid fixation in the trans configuration. They concluded, however, that there is a very strong tendency for the molecule to be planar which can be attributed to resonance between the structure I and others (II and III) in which the central carbon-carbon bond is double because these would confer a certain degree of the stereochemical character of ethylene upon the molecule.



I



II



III

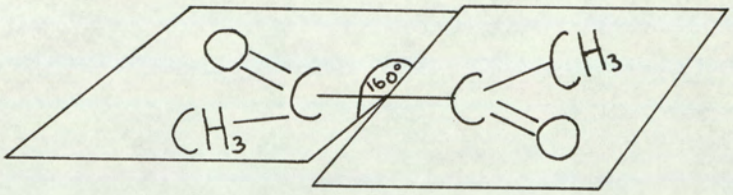
Assuming that diacetyl did exist solely in planar cis and trans forms the percentage of the cis form is $(\mu_{obs} / \mu_{cis})^2 \times 100\%$. In solution in cyclohexane at 25°C $\mu_{obs} = 0.68D$ while $\mu_{cis} = 2\mu_{C{=}O}^{CH_3} \sin\theta$, where θ is the angle that the acetyl group dipole subtends with the projection of the central C-C bond. If $\mu_{C{=}O}^{CH_3} = 2.94D$ and $\theta = 50°14'$ then $\mu_{cis} = 4.52D$ and hence the percentage of cis form is 2.3%. The predominance of the trans form could be explained by the greater dipole-dipole repulsive forces present in the cis configuration making the latter energetically less stable.

Rasmussen et al[108] have recorded the infrared spectra of diacetyl and dibenzoyl. In each case a single strong band attributable to the carbonyl stretching frequency was obtained, at 1718 cm^{-1} and 1681 cm^{-1} respectively. They suggested that since these positions are the ones expected for unconjugated and phenyl conjugated C=O respectively then it would appear that little or no conjugation between the adjacent carbonyl groups was present. Raman studies substantiated the conclusion that there was a weak central C-C bond and a low degree of conjugation and it was concluded by Rasmussen et al[108] that diacetyl and dibenzoyl were likely to be trans. Freeman[38] has also discussed the possibility of cis and trans configurations of diacetyl suggesting that if there was any cis configuration there could be a certain degree of interaction between the two dipoles possibly resulting in increased carbonyl character. Freeman[38] reported

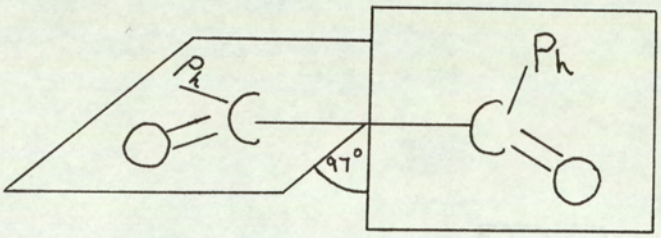
an infrared carbonyl stretching frequency of 1724 cm^{-1} for diacetyl and since this was exactly the same as for the normal monoketone he concluded that diacetyl should exist in the energetically more favourable trans configuration in which the dipole interactions are essentially nullified. However, both diacetyl and dibenzoyl have definite dipole moments and therefore these molecules cannot be fixed in rigid trans conformations for if they were the dipole moment should be zero. Le Fèvre et al[109] have studied diacetyl in solution in benzene and carbon tetrachloride and reported dipole moments of 1.08D and 1.04D respectively, at 25°C. These results compare with those from this study of 0.68D in cyclohexane at 25°C and 0.70D in carbon tetrachloride at 15°C. As the measurements in this study will effectively eliminate any contribution from an unknown amount of atom polarization then the dipole moments calculated ought to be more accurate. The contribution from atom polarization could be particularly large in diacetyl if, due to the considerable dipole-dipole repulsive forces present in the cis form, complete rotation of the groups was not possible allowing only libration to take place. The large difference between the dipole moments calculated in this work and those reported by Le Fèvre, which involve an atom polarization contribution, substantiates the prediction that this contribution is large.

Le Fèvre[109] has evaluated the molar Kerr constant of

FIG. 5.5 CONFIGURATIONS PROPOSED BY R.J.W LE FÈVRE FOR (a) DIACETYL



(b) DIBENZOYL



diacetyl and claims that as this is negative it is qualitatively incompatible that diacetyl exists as a mixture of planar cis and trans isomers since each of these should have a positive molar Kerr constant. This is because the cis form of diacetyl has the axis of maximum polarizability in the same direction as the resultant dipole moment leading to a large positive Kerr constant while for the non-polar trans form a small positive Kerr constant would be expected. Since however a negative Kerr constant was obtained a skew structure was proposed for diacetyl, the azimuthal angle between the planes containing the acetyl groups being estimated to be approximately 160° (Fig.5.5.a).

The relaxation time results obtained for diacetyl would tend to suggest that no intramolecular relaxation is being observed since 1,2-dichloroethane, a molecule of similar size, has a molecular relaxation time of 2.9×10^{-12} sec[110] in cyclohexane at 25°C and it is unlikely that the relaxation time for acetyl group rotation in diacetyl would be shorter than this. The distribution angle of 0.14 → 0.17 for diacetyl in cyclohexane at 25°C is significant but not unusual for a solution of small rigid solute molecules in a non-polar solvent. Thus Hassell[27] obtained significant values for pyridine, furan and thiophen, molecules in which no intramolecular relaxation process could be occurring, and suggested that the solute molecules might experience varying local environments. This would result in a variation of

the energy barriers to molecular re-orientation and give rise to a distribution of relaxation times.

Taking the relaxation time data from this study and also the evidence obtained by Le Fèvre, together with the large atom polarization, it would appear that the most reasonable conclusion is that the mean equilibrium position of diacetyl is a skew structure and no intramolecular rotation is being observed. Presumably the amplitude of the oscillations about this mean position would increase at elevated temperatures and this would account for the higher dipole moments at the higher temperatures as observed by Bloom and Sutton.

The mean relaxation time of 24.3×10^{-12} sec for dibenzoyl in cyclohexane at $40^{\circ}C$ clearly suggests that molecular relaxation is the principal relaxation process when compared with the value for the rigid molecule phenanthraquinone, which is of similar shape and size to dibenzoyl, of 22.2×10^{-12} sec in benzene at $40^{\circ}C$.''' The reasons for the apparent rigidity of dibenzoyl could be (a) high dipole-dipole repulsive forces between the carbonyl groups and (b) steric hindrance to benzoyl group rotation, as indicated by Courtauld models. The dipole moment of 3.48D in cyclohexane at $40^{\circ}C$ could be taken as indicating 'free rotation' of the benzoyl groups when compared with the calculated value from eqn.3.2 of 3.74D but this can be ruled out by the considerations above. Other possibilities are (i) the two halves of the dibenzoyl

molecule are in hindered or restricted rotation (ii) that they are fixed in or making rotational oscillations of low amplitude about planes making an angle ϕ with each other or (iii) that dibenzoyl consists of equal amounts of planar cis and trans forms. Situation (i) can perhaps be eliminated since Le Fèvre[112] found that the dipole moment of dibenzoyl was insensitive to a 25°C rise of temperature in carbon tetrachloride and benzene solutions and to a 65°C change of temperature in decalin. In addition measurements by Higasi[113] on dibenzoyl in benzene over a 25°C range produced no change in moment with temperature (μ=3.62D). If hindered rotation took place then, at elevated temperatures, a greater freedom of rotation would be expected with a corresponding rise in the dipole moment. However, a considerable temperature range for measurements of the dipole moment is really required to draw any firm conclusions. The relaxation time data from this study further suggests that dibenzoyl relaxes only by molecular re-orientation. Situation (iii) is also eliminated since Le Fèvre[109] found that dibenzoyl had a negative Kerr constant. A cis form of dibenzoyl would resemble phenanthraquinone in the disposition of its resultant moment along a direction of high polarizability and therefore also in the algebraic sign of its Kerr constant (large, positive); a trans form, being non-polar, would also have a small positive value. A mixture of cis and trans forms would also have a positive Kerr constant but the fact that the observed Kerr

constant is negative would eliminate this possibility. Case (ii) remains and Le Fèvre[109] found that an azimuthal angle of 97° fitted predicted and measured values of the molar Kerr constants satisfactorily (fig.5.5.b). Dipole moments reported in the literature for dibenzoyl in carbon tetrachloride are 3.60D at 20°C,[109] 3.64D at 25°C,[102] 3.52D at 25°C[113] and 3.46D at 50°C.[113] The moments obtained in this study in carbon tetrachloride are 3.46D at 15°C and 3.52D at 40°C. Hence the difference in dipole moment obtained by the microwave and conventional approaches is small and would suggest that the atom polarization is not appreciable in dibenzoyl, probably due to the increased steric effects in this molecule.

Chapter 6

Conclusions

Discussion

In Chapter 1 the experimental technique and basic theory for the dielectric absorption of a solution of a polar solute in a non-polar solvent was discussed. The technique has been applied to numerous systems so that both the relaxation times and the energy barrier to rotation could be determined. In the majority of cases the measurements have been made at five or six microwave frequencies, which is in excess of the number of frequencies used by most workers, and therefore a greater accuracy is claimed on the results.

The mean relaxation times of acetophenone have been determined in several solvents and, by comparison with the molecular relaxation times of several molecules of similar size, a contribution from acetyl group relaxation is indicated. The weight factor on the molecular relaxation process (C_1) was calculated by two methods and a value of $C_1 = 0.33$ was taken. τ_1 and τ_2 were then calculated with C_1 fixed at this value. The τ_1 values were considered to be of the correct order for a molecule of this size. The $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ values were then determined; the $\Delta H_1^{\ddagger}$ value from measurements in p-xylene being consistent with the value for iodobenzene in p-xylene. The $\Delta H_2^{\ddagger}$ values were 2.2, 1.9 and 2.3 kcal/mole in cyclohexane, p-xylene and decalin respectively, with an error of $\pm$ 0.4 kcal/mole. Acetyl group rotation was also indicated in 4-acetylpyridine, with an energy barrier of 1.9 $\pm$ 0.3 kcal/mole.

A longer mean relaxation time than initially would have been expected was found for 2-acetonaphthone. This could be attributed to both the increased flow of charge across the naphthalene nucleus and the fact that the fixed component of the dipole moment does not lie along a symmetry axis. The study of ω,ω,ω-trifluoroacetophenone proved useful in that, as an accurate evaluation of τ_1 was possible, extra weight was given to the τ_1 values of acetophenone being correct since the ratio of the τ_1 values for the two compounds was found to be approximately in the same proportion as the molecular size.

The mean relaxation time of p-methoxyacetophenone indicated a contribution from a group relaxation process while the dipole moment could also be interpreted in terms of rotation of the acetyl and methoxy groups. A smaller $\Delta H_2^{\neq}$ value was found for cyclohexylmethylketone than for the aromatic compounds examined which was attributed to an absence of conjugation in the system. The decrease in the energy barrier to acetyl group rotation below that found in the aromatic compounds was ~ 0.7 kcal/mole.

The mean relaxation times of anisole definitely indicated a contribution from group relaxation. The small calculated weight factor on τ_1 did not permit an evaluation of $\Delta H_1^{\neq}$ but $\Delta H_2^{\neq}$ was calculated to be 2.1 ± 0.5 kcal/mole. However, the τ_2 values obtained, while of the same order as those found by other workers from measurements in dilute

solution, were larger than those obtained in the pure liquid state. This is somewhat surprising since relaxation times resulting from measurements in the pure liquid state are usually longer. The possibility of an additional dispersion region in the pure liquid state, resulting from the presence of aggregates of molecules, was discussed and it was suggested that there might be a shortening of the observed intramolecular relaxation time due to the presence of this additional process.

p-Methylanisole was studied because calculations suggested that only group relaxation ought to be present in this molecule. The τ_0 values were in good agreement with the τ_2 values in anisole which tended to confirm this prediction. As only group relaxation appears to be present in p-methylanisole then a maximum accuracy ought to be achieved on the energy barrier to rotation. This was determined to be 2.2 $\pm$ 0.5 kcal/mole which is in good agreement with the $\Delta H_2^{\ddagger}$ value found for anisole.

p-Bromoanisole was found to relax predominantly by molecular rotation. Although the τ_2 values cannot be determined so accurately as the τ_1 values they appear to be of the same order found for group relaxation in anisole and p-methylanisole. The accurate evaluation of τ_1 in p-bromoanisole proved useful in assessing τ_1 for molecules of similar size.

Molecular relaxation was also found to be the principal relaxation mechanism in trifluoromethoxybenzene.

This molecule was examined in the solvents cyclohexane and decalin and ΔH_1^* was determined to be 1.9 $\pm$ 0.4 kcal/mole in both these solvents. In order to determine the group relaxation time accurately it would be necessary to examine the para-halogenated derivatives of trifluoromethoxybenzene where C_2 would be considerably increased.

A dipole moment evaluation of pentafluorobenzene was made and this was found to be the same as that of fluorobenzene. This is unlike pentachlorobenzene which has a much smaller dipole moment than that of chlorobenzene.

The possible causes of the short relaxation times of diphenylether and its 4,4'-substituted derivatives were discussed. The two mechanisms considered to be the most important, that proposed by Higasi and Smyth (mechanism A) and that proposed by Fong (mechanism B), were applied to the interpretation of the relaxation time data of several compounds of the type Y–X–Y. The presence of a distribution angle on the Cole-Cole plots of benzophenone indicates a contribution from an intramolecular relaxation process but the relaxation time is about that expected solely for molecular rotation. However, since benzophenone has a comparitively high dipole moment the contribution to the total dielectric absorption from mechanism A would be extremely small. The absence of a distribution angle on the Cole-Cole plots of decafluorobenzophenone indicates a complete absence of intramolecular rotation. The large difference in dipole moments calculated

by the Guggenheim and microwave approaches would suggest libration of the C_6F_5 groups. In addition, the low dipole moment compared with that of 4,4'-difluorobenzophenone indicates that decafluorobenzophenone exists in a 'roof' type of structure (Fig.4.1.b) in which the mesomeric flow of charge is minimised.

It would appear that mechanism B is necessary to explain the shorter relaxation time of dicyclohexylketone relative to benzophenone but many anomalies arise when solely mechanism B is used to explain the short relaxation times of several aromatic ethers and sulphides. Certainly the trend of an increasing mean relaxation time with increase in dipole moment would tend to favour mechanism A.

Molecules of the type $X-C_6H_4-X$, where X is a rotating polar group, were examined since these should have relaxation times which are only characteristic of group relaxation and hence their study should permit an accurate evaluation of both the group relaxation time and the energy barrier to group rotation. For p-dimethoxybenzene mean relaxation time values were obtained which were in good agreement with τ_2 values obtained for anisole. In addition the energy barrier to group rotation in both of these compounds was very similar. Thus the presence of two groups attached in para-positions to the benzene ring did not appear to change the τ_2 and $\Delta H_2^{\ddagger}$ values from those obtained for the mono-substituted compound i.e. the greater length of conjugation in p-dimethoxy-

benzene above that in anisole has not resulted in an increase in the energy barrier to group rotation. A different situation was observed for p-diacetylbenzene, however, where the mean relaxation time has increased considerably above the τ_2 value of acetophenone. Group relaxation still appears to be indicated in p-diacetylbenzene since the τ_0 value is small for molecular rotation while 1,4-diacetyldurene has a relaxation time which is shorter than that of p-diacetylbenzene. If molecular relaxation was the only relaxation process present in the latter compound then it should also be the only one in 1,4-diacetyldurene which should then have a longer relaxation time since it is the larger compound. It would appear that group relaxation is therefore present in both these compounds and that the methyl groups in 1,4-diacetyldurene may not be offering a significant hindrance to acetyl group rotation. Presumably increasing the length of conjugation in p-diacetylbenzene relative to acetophenone has a greater effect on the group relaxation time than for p-dimethoxybenzene and anisole.

α,α'-Dichloro-p-xylene was found to possess a mean relaxation time that suggested that group relaxation was the sole process. Smaller relaxation time values were obtained for $-CH_2Cl$ group rotation than for methoxy or acetyl group rotation and, furthermore, the $\Delta H_2^{\ddagger}$ value was smaller. This may be a result of the smaller size of the $-CH_2Cl$ group.

Group relaxation is also indicated in p-dibenzoyl-

benzene since it has a shorter relaxation time than that of m-dibenzoylbenzene whereas, if molecular relaxation was present in both of these compounds, then the para-derivative should have the longer relaxation time due to its greater length.

Compounds of the type X-X were also investigated where X= $-C(=O)CH_3$ and $-C(=O)C_6H_5$. A large atom polarization is indicated in diacetyl due to the considerable difference in the dipole moments obtained from the conventional and microwave approaches. A high energy barrier to group rotation would be expected in this compound due to the close proximity of the two groups but the short relaxation time suggests that only molecular relaxation is observed. Dibenzoyl is also thought to exhibit only molecular relaxation.

In general enthalpies of activation of ~2 kcal/mole have been observed for both molecular and group relaxation processes in the majority of compounds. This is not altogether surprising since measurements have been carried out in the frequency range 6.7 to 70 Gc/s which, for maximum absorption, corresponds to τ values of 23.8 and 2.3×10^{-12} sec or $\Delta G^{\ddagger}$ values of 2.96 and 1.57 kcal/mole, at 25°C. The τ values observed in this study usually lie between 3 and 40×10^{-12} sec at 25°C i.e. $\Delta G^{\ddagger}$ values of 1.73 and 3.27 kcal/mole and as $\Delta S^{\ddagger}$ always appears to be small and negative for dielectric relaxation processes then $\Delta H^{\ddagger}$ is always less than $\Delta G^{\ddagger}$ and would be expected to lie between 1 and 3 kcal/mole in the frequency range employed. Higher energy barriers might escape detection as they could

require a frequency lower than that in the microwave region while very low energy barriers (e.g. < 0.5 kcal/mole) could have a characteristic frequency in the far infrared region and so again escape detection.

In conclusion it can be said that for the study of relaxation processes that have energy barriers of ~1 to 3 kcal/mole the measurement of the dielectric absorption by the microwave bridge method provides a very powerful means of investigating these processes.

Suggestions for Further Work

The compounds ω,ω,ω-trifluoroacetophenone and trifluoromethoxybenzene have been extensively examined in this thesis but, since the weight factor on the group relaxation process was so small, it was not possible to obtain a precise estimate of the free energies and enthalpies of activation for group rotation. A study therefore of the para-halogenated derivatives would permit these values to be determined since the direction of the carbon-halogen dipole moment is such as to reduce the fixed molecular dipole moment component thus giving rise to a higher weight factor on the group re-orientation process. The way in which the relaxation processes for the $-C(=O)CF_3$ and $-OCF_3$ groups are modified relative to $-C(=O)CH_3$ and $-OCH_3$ due to the presence of the CF_3 unit would make an interesting study.

Two cyclohexyl compounds have been studied in this work; cyclohexylmethylketone and dicyclohexylketone. Comparitively little data exists in the literature for the relaxation times of cyclohexyl compounds. An initial study of the mono-halogenated cyclohexyl compounds would be useful in assessing the molecular relaxation times for further cyclohexyl compounds containing such groups as $-OCH_3$, $-CH_2Cl$, $-OH$, $-SH$ and $-NH_2$. A full investigation of the differences in group relaxation times when the group is attached to an aliphatic nucleus and then to an aromatic nucleus could be made and the additional energy barrier that results due to

conjugation of the group with the aromatic nucleus could be determined.

In the discussion of Chapters 3 and 5 it was considered that methoxy and acetyl group rotation in substituted anisoles and acetophenones might be possible even when there are methyl groups in the two ortho positions. An intensive study could be carried out on the affect of the group relaxation time when there are groups in the ortho positions by examining 2,6-di- fluoro-, chloro-, bromo-, iodo- and methyl- anisoles and acetophenones. In addition the 2,4,6-trisubstituted compounds would be examined. If the latter had shorter relaxation times than the corresponding disubstituted compounds then this would indicate some non-rigidity in the compounds. The shortening would have been caused by the dipole moment of the group in the 4-position in the trisubstituted anisole or acetophenone decreasing the molecular dipole moment component associated with molecular rotation.

An examination of 1,4- and 2,6-disubstituted naphthalenes, where the substituents are identical groups, e.g. methoxy or acetyl, should be of interest. In both of these compounds group rotation should be the principal relaxation process and it would be useful to see (i) how in the 1,4-substituted compound the energy barrier to group rotation is modified by the presence of hydrogen atoms in the 5- and 8-positions, relative to group rotation in the para-disubstituted benzene and (ii) how the energy barrier is altered in the 2,6-

substituted compound where there is a comparitively long length of conjugation between the substituents.

The effect of long lengths of conjugation between groups on their relaxation time could be further investigated by studying the para-disubstituted biphenyls. Group relaxation should be the only relaxation mechanism in these compounds and the relaxation times for such groups as $-OCH_3$, $-C(=O)CH_3$ and $-CH_2Cl$ could then be compared with those obtained in the para-disubstituted benzenes and the mono-substituted benzenes. In all probability the increased length of conjugation should result in higher energy barriers to group rotation being obtained.

A study is also required of para-halogenated benzyl chlorides. A higher C_1 value than estimated from group moment calculations was obtained for benzyl chloride and it is necessary to examine the para-halogenated derivatives so that from both the dipole moment and relaxation time data the $-CH_2Cl$ relaxation time and charge distribution in these compounds can be determined.

4-Acetylpyridine and 4-benzoylpyridine have both been studied in this work but a complete investigation of 4-substituted pyridines containing for example $-OCH_3$, $-CH_2Cl$, $-C(=O)H$, $-OH$ or $-NH_2$ groups could well prove useful in finding out how the resonance effects in the pyridine nucleus affect the group relaxation times relative to those obtained when the group is attached to a benzene nucleus.

Appendix

(1) Tables of Experimental Results

Tables 1 to 4 of the Appendix contain the experimental data of the systems discussed in Chapters 2 to 5 respectively.

The dielectric constants and loss factors determined by the microwave bridge method are tabulated as ϵ'_{meas} and ϵ''_{meas}. Whenever an analysis of the dielectric data into two discrete relaxation times has been carried out ϵ'_{calc} and ϵ''_{calc} are given which are the dielectric parameters calculated from eqns. 1.28 and 1.29 (see Chapter 1) by solution of the τ_1 , τ_2 , C_1 , ϵ_0 and ϵ_∞ data tabulated in the relevant chapters.

Weight fraction (w_2) and density (d) data are also given in the following tables.

The following notation has been used for the solvents employed:-

Cyclohexane	CHx
p-Xylene	p-Xyl
Carbontetrachloride	CTC
1,4-Dioxan	Diox
Decalin	Dec

Table 1 Experimental Results Discussed in Chapter 2

Solute	Solvent	t (^oC)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
Acetophenone w_2 =0.02030	CHx	15	70	2.033	0.0248	2.053	0.0245
			35.11	2.066	0.0401	2.066	0.0424
			23.98	2.076	0.0503	2.081	0.0520
			16.20	2.103	0.0576	2.101	0.0574
			9.313	2.128	0.0531	2.130	0.0535
			6.7	2.141	0.0459	2.144	0.0462

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
Acetophenone w_2 =0.02030	CHx	25	70	2.040	0.0275	2.040	0.0255
			35.11	2.052	0.0377	2.055	0.0425
			23.98	2.066	0.0502	2.070	0.0504
			16.20	2.096	0.0532	2.089	0.0535
			9.313	2.112	0.0476	2.115	0.0477
			6.7	2.123	0.0400	2.127	0.0406
Acetophenone w_2 =0-0.03 Results are in the a'-a" form of the Cole-Cole plot in this case.	CHx	25	70	1.186	1.1443	1.164	1.2539
			34.86	2.118	2.1084	1.898	2.1092
			23.98	2.917	2.4981	2.644	2.5170
			16.20	3.531	2.5491	3.599	2.697
			9.313	4.408	2.5147	4.909	2.456
Acetophenone w_2 =0.02168	CHx	40	70	1.999	0.0331	2.017	0.0313
			35.11	2.038	0.0461	2.037	0.0478
			23.98	2.051	0.0534	2.055	0.0526
			16.20	2.077	0.0536	2.074	0.0517
			9.313	2.092	0.0442	2.097	0.0422
			6.7	2.105	0.0346	2.106	0.0345
Acetophenone w_2 =0.02046	CHx	50	70	1.990	0.0320	2.003	0.0310
			35.11	2.016	0.0435	2.024	0.0450
			23.98	2.032	0.0493	2.041	0.0477
			16.20	2.063	0.0471	2.058	0.0450
			9.313	2.065	0.0353	2.076	0.0349
			6.7	2.080	0.0287	2.083	0.0277
Acetophenone w_2 =0.01828	p-Xyl	15	70	2.292	0.0242	2.297	0.0224
			35.11	2.305	0.0387	2.308	0.0404
			23.98	2.320	0.0515	2.321	0.0517
			16.20	2.337	0.0602	2.341	0.0606
			9.313	2.376	0.0635	2.373	0.0619
Acetophenone w_2 =0.01967	p-Xyl	25	70	2.264	0.0259	2.282	0.0255
			35.11	2.296	0.0419	2.296	0.0450
			23.98	2.312	0.0538	2.311	0.0563
			16.20	2.330	0.0646	2.332	0.0639
			9.313	2.367	0.0621	2.365	0.0625
Acetophenone w_2 =0.02239	p-Xyl	40	70	2.257	0.0316	2.260	0.0325
			35.11	2.267	0.0551	2.280	0.0545
			23.98	2.303	0.0633	2.299	0.0648
			16.20	2.320	0.0708	2.324	0.0689
			9.313	2.363	0.0631	2.357	0.0613
Acetophenone w_2 =0.02163	p-Xyl	50	70	2.240	0.0342	2.244	0.0332
			35.11	2.265	0.0522	2.265	0.0529
			23.98	2.281	0.0602	2.284	0.0603

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
Acetophenone w_2 =0.02163	p-Xyl	50	16.20	2.310	0.0634	2.307	0.0612
			9.313	2.339	0.0538	2.335	0.0515
Acetophenone w_2 =0.01685	p-Xyl	60	70	2.223	0.0260	2.223	0.0267
			35.11	2.242	0.0401	2.341	0.0408
			23.98	2.263	0.0464	2.256	0.0448
			16.20	2.275	0.0457	2.272	0.0438
			9.313	2.292	0.0370	2.291	0.0350
Acetophenone w_2 =0.02070	Dec	15	35.11	2.209	0.0351	2.210	0.0327
			23.98	2.214	0.0429	2.218	0.0445
			16.20	2.227	0.0561	2.233	0.0570
			9.313	2.255	0.0673	2.265	0.0676
			6.7	2.282	0.0685	2.286	0.0666
Acetophenone w_2 =0.02263	Dec	25	35.11	2.198	0.0383	2.199	0.0375
			23.98	2.209	0.0504	2.210	0.0499
			16.20	2.222	0.0600	2.228	0.0620
			9.313	2.256	0.0696	2.262	0.0692
			6.7	2.275	0.0682	2.283	0.0659
Acetophenone w_2 =0.02263	Dec	40	35.11	2.185	0.0439	2.180	0.0433
			23.98	2.192	0.0533	2.194	0.0549
			16.20	2.213	0.0643	2.215	0.0633
			9.313	2.244	0.0645	2.249	0.0625
			6.7	2.257	0.0572	2.266	0.0554
Acetophenone w_2 =0.01914	Dec	50	35.11	2.158	0.0376	2.162	0.0381
			23.98	2.170	0.0463	2.175	0.0470
			16.20	2.194	0.0539	2.193	0.0524
			9.313	2.221	0.0507	2.220	0.0495
			6.7	2.232	0.0446	2.233	0.0432
Acetophenone w_2 =0.02070	Dec	60	35.11	2.150	0.0449	2.152	0.0456
			23.98	2.163	0.0535	2.168	0.0538
			16.20	2.195	0.0591	2.189	0.0567
			9.313	2.218	0.0519	2.216	0.0501
			6.7	2.232	0.0436	2.229	0.0422
4-Acetyl-pyridine w_2 =0.02438	p-Xyl	15	35.11	2.304	0.0314	2.308	0.0322
			23.98	2.308	0.0421	2.317	0.0432
			16.20	2.332	0.0573	2.332	0.0545
			9.313	2.366	0.0585	2.364	0.0612
			6.7	2.382	0.0569	2.383	0.0569
4-Acetyl-pyridine w_2 =0.02347	p-Xyl	25	70	2.277	0.0193	2.284	0.0178
			35.11	2.297	0.0305	2.293	0.0318
			23.98	2.298	0.0400	2.302	0.0409
			16.20	2.319	0.0499	2.317	0.0490
			9.313	2.346	0.0507	2.344	0.0513

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
4-Acetyl-pyridine w_2 =0.02216	p-Xyl	40	70	2.261	0.0227	2.257	0.0182
			35.11	2.262	0.0312	2.267	0.0326
			23.98	2.276	0.0377	2.278	0.0409
			16.20	2.295	0.0486	2.294	0.0463
			9.313	2.320	0.0424	2.319	0.0428
4-Acetyl-pyridine w_2 =0.02734	p-Xyl	60	70	2.230	0.0245	2.231	0.0244
			35.11	2.246	0.0399	2.247	0.0408
			23.98	2.266	0.0491	2.261	0.0484
			16.20	2.289	0.0505	2.281	0.0505
			9.313	2.305	0.0430	2.305	0.0418
4-Acetyl-pyridine w_2 =0.02348	Dec	40	70	2.153	0.0201	2.157	0.0180
			35.11	2.173	0.0313	2.167	0.0313
			23.98	2.179	0.0383	2.177	0.0388
			16.20	2.193	0.0418	2.192	0.0436
			9.313	2.213	0.0424	2.215	0.0408
ω,ω,ω-Trifluo-roacetophenone w_2 =0.03516	CHx	15	70	2.037	0.0260	2.049	0.0237
			35.11	2.060	0.0458	2.058	0.0445
			23.98	2.061	0.0550	2.069	0.0597
			16.20	2.092	0.0800	2.087	0.0771
			9.313	2.125	0.0965	2.128	0.0969
ω,ω,ω-Trifluo-roacetophenone w_2 =0.04868	CHx	25	70	2.014	0.0331	2.044	0.0334
			35.11	2.070	0.0633	2.058	0.0625
			23.98	2.072	0.0834	2.073	0.0835
			16.20	2.095	0.1076	2.099	0.1076
			9.313	2.155	0.1333	2.158	0.1329
ω,ω,ω-Trifluo-roacetophenone w_2 =0.02541	CHx	40	70	1.985	0.0220	2.006	0.0200
			35.11	2.011	0.0357	2.014	0.0361
			23.98	2.022	0.0465	2.025	0.0475
			16.20	2.044	0.0603	2.042	0.0589
			9.313	2.069	0.0648	2.076	0.0647
ω,ω,ω-Trifluo-roacetophenone w_2 =0.03345	p-Xyl	15	70	2.285	0.0277	2.288	0.0271
			35.11	2.300	0.0502	2.298	0.0508
			23.98	2.307	0.0643	2.310	0.0681
			16.20	2.337	0.0920	2.330	0.0879
			9.313	2.377	0.1116	2.374	0.1132
ω,ω,ω-Trifluo-roacetophenone w_2 =0.04002	p-Xyl	25	70	2.267	0.0344	2.293	0.0318
			35.11	2.299	0.0598	2.303	0.0603
			23.98	2.320	0.0827	2.318	0.0813
			16.20	2.333	0.1047	2.343	0.1051
			9.313	2.391	0.1316	2.399	0.1315

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
ω,ω,ω-Trifluoroacetophenone w_2 =0.02463	p-Xyl	40	70	2.247	0.0238	2.248	0.0224
			35.11	2.259	0.0389	2.258	0.0419
			23.98	2.271	0.0573	2.269	0.0555
			16.20	2.276	0.0693	2.289	0.0692
			9.313	2.327	0.0777	2.328	0.0779
ω,ω,ω-Trifluoroacetophenone w_2 =0.03002	p-Xyl	60	70	2.225	0.0305	2.221	0.0294
			35.11	2.230	0.0521	2.235	0.0542
			23.98	2.261	0.0718	2.252	0.0703
			16.20	2.276	0.0839	2.279	0.0836
			9.313	2.324	0.0847	2.326	0.0839
2-Acetonaphthone w_2 =0.02379	p-Xyl	25	70	2.273	0.0102	2.278	0.0109
			35.11	2.283	0.0220	2.281	0.0209
			23.98	2.286	0.0275	2.286	0.0290
			16.20	2.301	0.0386	2.293	0.0390
			9.313	2.315	0.0544	2.311	0.0536
			6.7	2.325	0.0606	2.327	0.0608
p-Methoxyacetophenone w_2 =0.01659	p-Xyl	25	70	2.269	0.0137	2.274	0.0133
			35.11	2.287	0.0246	2.278	0.0252
			23.98	2.286	0.0331	2.284	0.0347
			16.20	2.295	0.0466	2.295	0.0452
			9.313	2.319	0.0571	2.318	0.0565
			6.7	2.332	0.0585	2.334	0.0595
Cyclohexylmethylketone w_2=0.01640	p-Xyl	15	35.11	2.313	0.0359	2.311	0.0362
			23.98	2.321	0.0434	2.324	0.0432
			16.20	2.347	0.0458	2.341	0.0460
			9.313	2.360	0.0407	2.363	0.0404
Cyclohexylmethylketone w_2 =0.01707	p-Xyl	25	35.11	2.299	0.0365	2.300	0.0370
			23.98	2.313	0.0429	2.313	0.0429
			16.20	2.336	0.0441	2.330	0.0441
			9.313	2.351	0.0373	2.350	0.0372
Cyclohexylmethylketone w_2 =0.01767	p-Xyl	40	35.11	2.287	0.0399	2.280	0.0387
			23.98	2.294	0.0426	2.294	0.0433
			16.20	2.310	0.0424	2.311	0.0423
			9.313	2.330	0.0343	2.329	0.0328
Cyclohexylmethylketone w_2 =0.01894	p-Xyl	50	35.11	2.267	0.0409	2.268	0.0402
			23.98	2.282	0.0427	2.281	0.0437
			16.20	2.302	0.0416	2.298	0.0412
			9.313	2.318	0.0319	2.314	0.0308
Cyclohexylmethylketone w_2 =0.01997	p-Xyl	60	35.11	2.256	0.0448	2.255	0.0433
			23.98	2.271	0.0435	2.271	0.0439
			16.20	2.286	0.0381	2.286	0.0391
			9.313	2.303	0.0299	2.300	0.0279

Table 2. Experimental Results Discussed in Chapter 3.

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
Anisole w_2 =0.09125	p-Xyl	15	35.11	2.324	0.0414	2.330	0.0449
			23.98	2.344	0.0559	2.351	0.0547
			16.20	2.376	0.0616	2.369	0.0594
			9.313	2.406	0.0541	2.397	0.0528
			6.7	2.423	0.0427	2.410	0.0451
Anisole w_2 =0.10531	p-Xyl	25	35.11	2.327	0.0553	2.329	0.0560
			23.98	2.345	0.0653	2.349	0.0647
			16.20	2.373	0.0662	2.374	0.0660
			9.313	2.408	0.0555	2.404	0.0556
			6.7	2.418	0.0470	2.417	0.0470
Anisole w_2 =0.10531	p-Xyl	40	35.11	2.307	0.0551	2.313	0.0552
			23.98	2.324	0.0604	2.334	0.0612
			16.20	2.358	0.0609	2.357	0.0593
			9.313	2.386	0.0456	2.383	0.0463
			6.7	2.392	0.0372	2.392	0.0367
Anisole w_2 =0.09502	p-Xyl	50	35.11	2.290	0.0478	2.294	0.0487
			23.98	2.310	0.0520	2.312	0.0511
			16.20	2.333	0.0477	2.331	0.0470
			9.313	2.348	0.0359	2.349	0.0345
			6.7	2.357	0.0256	2.355	0.0267
Anisole w_2 =0.09125	p-Xyl	60	35.11	2.270	0.0459	2.275	0.0461
			23.98	2.298	0.0452	2.291	0.0457
			16.20	2.312	0.0421	2.306	0.0402
			9.313	2.325	0.0300	2.321	0.0289
			6.7	2.324	0.0219	2.326	0.0224
Anisole w_2 =0.05967	CHx	25	70	2.047	0.0208	2.044	0.0184
			34.86	2.057	0.0268	2.057	0.0280
			23.98	2.064	0.0290	2.068	0.0303
			16.20	2.069	0.0295	2.078	0.0288
			9.313	2.094	0.0229	2.090	0.0228
Anisole w_2 =0.07920	CHx	25	70	2.058	0.0267	2.057	0.0248
			34.86	2.072	0.0364	2.073	0.0381
			23.98	2.086	0.0401	2.088	0.0406
			16.20	2.097	0.0385	2.102	0.0386
			9.313	2.121	0.0311	2.114	0.0306
p-Methyl-anisole w_2 =0.09835	p-Xyl	15	70	2.309	0.0274	2.314	0.0276
			35.11	2.333	0.0435	2.330	0.0437
			23.98	2.346	0.0523	2.346	0.0512
			16.20	2.362	0.0527	2.365	0.0541
			9.313	2.394	0.0486	2.391	0.0480

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
p-Methyl-anisole w_2 =0.09216	p-Xyl	25	70	2.299	0.0255	2.299	0.0240
			35.11	2.311	0.0386	2.314	0.0396
			23.98	2.330	0.0453	2.328	0.0466
			16.20	2.345	0.0503	2.346	0.0484
			9.313	2.370	0.0398	2.369	0.0406
p-Methyl-anisole w_2 =0.09216	p-Xyl	32.5	70	2.274	0.0284	2.292	0.0246
			35.11	2.311	0.0384	2.308	0.0398
			23.98	2.324	0.0437	2.324	0.0451
			16.20	2.338	0.0442	2.341	0.0444
			9.313	2.356	0.0361	2.361	0.0343
p-Methyl-anisole w_2 =0.09216	p-Xyl	40	70	2.269	0.0297	2.276	0.0295
			35.11	2.306	0.0425	2.297	0.0429
			23.98	2.319	0.0455	2.313	0.0448
			16.20	2.335	0.0404	2.329	0.0411
			9.313	2.341	0.0318	2.345	0.0300
p-Methyl-anisole w_2 =0.09216	p-Xyl	50	70	2.256	0.0284	2.260	0.0285
			35.11	2.281	0.0409	2.280	0.0411
			23.98	2.304	0.0424	2.296	0.0423
			16.20	2.313	0.0376	2.311	0.0377
			9.313	2.324	0.0271	2.325	0.0264
p-Methyl-anisole w_2 =0.09835	p-Xyl	60	70	2.234	0.0328	2.248	0.0314
			35.11	2.276	0.0405	2.271	0.0424
			23.98	2.289	0.0412	2.287	0.0416
			16.20	2.304	0.0364	2.301	0.0354
			9.313	2.310	0.0251	2.312	0.0239
p-Bromo-anisole w_2 =0.04912	p-Xyl	15	35.11	2.292	0.0244	2.298	0.0248
			23.98	2.305	0.0336	2.303	0.0333
			16.20	2.316	0.0420	2.312	0.0433
			9.313	2.336	0.0599	2.331	0.0585
			6.7	2.346	0.0659	2.348	0.0667
p-Bromo-anisole w_2 =0.04970	p-Xyl	25	35.11	2.283	0.0257	2.285	0.0263
			23.98	2.290	0.0356	2.291	0.0350
			16.20	2.304	0.0450	2.300	0.0453
			9.313	2.326	0.0601	2.322	0.0606
			6.7	2.338	0.0677	2.340	0.0669
p-Bromo-anisole w_2 =0.04970	p-Xyl	40	35.11	2.265	0.0279	2.260	0.0287
			23.98	2.268	0.0384	2.267	0.0380
			16.20	2.281	0.0486	2.279	0.0480
			9.313	2.303	0.0594	2.303	0.0596
			6.7	2.320	0.0624	2.322	0.0623

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
p-Bromo-anisole w_2 =0.04970	p-Xyl	50	35.11	2.251	0.0300	2.247	0.0300
			23.98	2.258	0.0396	2.255	0.0386
			16.20	2.271	0.0472	2.267	0.0478
			9.313	2.290	0.0584	2.292	0.0578
			6.7	2.305	0.0590	2.311	0.0585
p-Bromo-anisole w_2 =0.04912	p-Xyl	60	35.11	2.232	0.0298	2.229	0.0304
			23.98	2.237	0.0393	2.237	0.0389
			16.20	2.250	0.0468	2.250	0.0472
			9.313	2.275	0.0557	2.275	0.0545
			6.7	2.288	0.0523	2.292	0.0536
Trifluoro-methoxybenzene w_2 =0.03029	CHx	10	70	2.045	0.0103	2.031	0.0100
			34.86	2.036	0.0170	2.035	0.0174
			23.98	2.028	0.0213	2.039	0.0224
			9.313	2.073	0.0387	2.057	0.0390
Trifluoro-methoxybenzene w_2 =0.04001	CHx	10	70	2.044	0.0147	2.032	0.0137
			34.86	2.039	0.0221	2.038	0.0239
			23.98	2.039	0.0303	2.043	0.0307
			9.313	2.087	0.0512	2.069	0.0516
Trifluoro-methoxybenzene w_2 =0.02501	CHx	25	34.86	2.013	0.0158	2.022	0.0154
			23.98	2.018	0.0200	2.026	0.0207
			16.20	2.033	0.0261	2.033	0.0265
			9.313	2.060	0.0312	2.048	0.0315
Trifluoro-methoxybenzene w_2 =0.03074	CHx	25	70	2.016	0.0129	2.017	0.0125
			34.86	2.020	0.0193	2.023	0.0203
			23.98	2.023	0.0257	2.028	0.0255
			16.20	2.034	0.0323	2.035	0.0317
			9.313	2.057	0.0378	2.052	0.0390
Trifluoro-methoxybenzene w_2 =0.03517	CHx	25	34.86	2.016	0.0220	2.020	0.0222
			23.98	2.022	0.0284	2.026	0.0293
			16.20	2.039	0.0368	2.035	0.0367
			9.313	2.062	0.0435	2.054	0.0437
Trifluoro-methoxybenzene w_2 =0.03998	CHx	25	70	2.017	0.0140	2.019	0.0134
			34.86	2.018	0.0248	2.025	0.0248
			23.98	2.028	0.0336	2.031	0.0331
			16.20	2.042	0.0411	2.042	0.0425
			9.313	2.080	0.0508	2.065	0.0514
Trifluoro-methoxybenzene w_2 =0.04531	CHx	25	34.86	2.022	0.0282	2.027	0.0284
			23.98	2.030	0.0378	2.034	0.0376
			16.20	2.043	0.0468	2.046	0.0477
			9.313	2.083	0.0575	2.072	0.0576

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
Trifluoro-methoxybenzene w_2 =0.03074	CHx	40	70	1.986	0.0125	1.990	0.0120
			34.86	1.985	0.0205	1.995	0.0212
			23.98	1.995	0.0271	2.001	0.0272
			16.20	2.013	0.0333	2.011	0.0331
			9.313	2.031	0.0353	2.029	0.0373
Trifluoro-methoxybenzene w_2 =0.03998	CHx	40	70	1.986	0.0157	1.986	0.0151
			34.86	1.981	0.0263	2.001	0.0271
			23.98	2.005	0.0354	2.008	0.0353
			16.20	2.023	0.0428	2.021	0.0435
			9.313	2.047	0.0459	2.045	0.0483
Trifluoro-methoxybenzene w_2 =0.03029	CHx	60	70	1.959	0.0130	1.962	0.0127
			34.86	1.959	0.0218	1.969	0.0218
			23.98	1.967	0.0281	1.975	0.0276
			16.20	1.981	0.0310	1.986	0.0324
			9.313	1.995	0.0298	2.004	0.0322
Trifluoro-methoxybenzene w_2 =0.04001	CHx	60	70	1.955	0.0176	1.964	0.0173
			34.86	1.962	0.0288	1.972	0.0290
			23.98	1.975	0.0363	1.981	0.0363
			16.20	1.995	0.0412	1.995	0.0422
			9.313	2.010	0.0395	2.018	0.0417
Trifluoro-methoxybenzene w_2 =0.02112	Dec	15	34.86	2.166	0.0104	2.172	0.0104
			23.98	2.166	0.0132	2.178	0.0133
			16.20	2.181	0.0176	2.181	0.0176
			9.313	2.188	0.0245	2.189	0.0245
Trifluoro-methoxybenzene w_2 =0.02112	Dec	25	34.86	2.156	0.0110	2.162	0.0094
			23.98	2.160	0.0135	2.163	0.0131
			16.20	2.158	0.0175	2.167	0.0181
			9.313	2.176	0.0249	2.176	0.0254
Trifluoro-methoxybenzene w_2 =0.03003	Dec	40	34.86	2.138	0.0161	2.144	0.0156
			23.98	2.137	0.0215	2.147	0.0208
			16.20	2.151	0.0257	2.153	0.0273
			9.313	2.168	0.0355	2.168	0.0347
Trifluoro-methoxybenzene w_2 =0.03003	Dec	70	34.86	2.101	0.0198	2.106	0.0187
			23.98	2.103	0.0248	2.111	0.0246
			16.20	2.117	0.0295	2.120	0.0305
			9.313	2.138	0.0343	2.138	0.0335
2-Methoxy-naphthalene w_2 =0.08588	p-Xyl	25	70	2.289	0.0140	2.294	0.0107
			35.11	2.293	0.0174	2.299	0.0192
			23.98	2.302	0.0217	2.305	0.0245
			16.20	2.322	0.0289	2.314	0.0288
			9.313	2.337	0.0321	2.327	0.0313
			6.7	2.342	0.0311	2.335	0.0315

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
2-Methoxy-naphthalene w_2 =0.09033	CHx	40	70	2.024	0.0136	2.038	0.0135
			35.11	2.047	0.0181	2.047	0.0198
			23.98	2.053	0.0211	2.053	0.0217
			16.20	2.062	0.0232	2.059	0.0223
			9.313	2.071	0.0238	2.068	0.0231
			6.7	2.077	0.0225	2.074	0.0237
Difluoromethyl phenyl ether w_2 =0.02118	CHx	25	70	2.028	0.0157		
			34.86	2.026	0.0191		
			23.98	2.033	0.0213		
			16.20	2.046	0.0237		
			9.313	2.062	0.0240		
Difluoromethyl phenyl ether w_2 =0.03456	CHx	25	70	2.041	0.0232		
			34.86	2.050	0.0314		
			23.98	2.050	0.0358		
			16.20	2.068	0.0381		
			9.313	2.095	0.0389		
Difluoromethyl pentafluoro-phenyl ether w_2 =0.06362	CHx	25	70	2.021	0.0138		
			34.86	2.014	0.0184		
			23.98	2.026	0.0201		
			16.20	2.043	0.0209		
			9.313	2.055	0.0184		
Methoxypenta-fluorobenzene w_2 =0.04142	CHx	15	70	2.041	0.0165	2.043	0.0159
			34.86	2.049	0.0233	2.052	0.0246
			23.98	2.055	0.0269	2.059	0.0287
			16.20	2.065	0.0326	2.068	0.0325
			9.313	2.088	0.0364	2.083	0.0368
Methoxypenta-fluorobenzene w_2 =0.04782	CHx	15	70	2.041	0.0179	2.044	0.0175
			34.86	2.057	0.0268	2.054	0.0278
			23.98	2.060	0.0325	2.062	0.0329
			16.20	2.072	0.0368	2.072	0.0375
			9.313	2.098	0.0433	2.090	0.0425
Methoxypenta-fluorobenzene w_2 =0.03116	CHx	25	70	2.027	0.0123	2.022	0.0122
			34.86	2.027	0.0179	2.032	0.0183
			23.98	2.039	0.0207	2.037	0.0210
			16.20	2.041	0.0242	2.043	0.0236
			9.313	2,057	0.0262	2.054	0.0267
Methoxypenta-fluorobenzene w_2 =0.03781	CHx	25	70	2.029	0.0147	2.027	0.0146
			34.86	2.034	0.0214	2.035	0.0221
			23.98	2.039	0.0261	2.041	0.0257
			16.20	2.046	0.0293	2.049	0.0294
			9.313	2.069	0.0325	2.064	0.0330

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
Methoxypenta-fluorobenzene w_2=0.04908	CHx	25	70	2.034	0.0188	2.030	0.0187
			34.86	2.041	0.0285	2.040	0.0298
			23.98	2.051	0.0360	2.049	0.0349
			16.20	2.059	0.0387	2.060	0.0390
			9.313	2.080	0.0427	2.078	0.0428
Methoxypenta-fluorobenzene w_2=0.03116	CHx	40	70	2.002	0.0131	2.000	0.0125
			34.86	2.002	0.0183	2.007	0.0186
			23.98	2.003	0.0209	2.012	0.0216
			16.20	2.016	0.0237	2.019	0.0242
			9.313	2.038	0.0247	2.031	0.0254
Methoxypenta-fluorobenzene w_2=0.03781	CHx	40	70	2.005	0.0165	2.004	0.0149
			34.86	2.006	0.0220	2.012	0.0218
			23.98	2.012	0.0266	2.019	0.0249
			16.20	2.017	0.0295	2.026	0.0278
			9.313	2.045	0.0301	2.040	0.0299
Methoxypenta-fluorobenzene w_2=0.04066	CHx	60	70	1.971	0.0165	1.970	0.0181
			34.86	1.976	0.0246	1.980	0.0249
			23.98	1.986	0.0289	1.988	0.0278
			16.20	1.989	0.0299	1.997	0.0301
			9.313	2.015	0.0276	2.012	0.0293
Methoxypenta-fluorobenzene w_2=0.04515	CHx	60	70	1.971	0.0186	1.974	0.0200
			34.86	1.981	0.0270	1.985	0.0270
			23.98	1.991	0.0306	1.994	0.0299
			16.20	1.995	0.0332	2.003	0.0321
			9.313	2.023	0.0305	2.019	0.0311
Pentafluoro-benzene w_2=0.09456	CHx	25	70	2.025	0.0274	2.024	0.0259
			34.86	2.039	0.0417	2.042	0.0413
			23.98	2.051	0.0461	2.057	0.0461
			16.20	2.073	0.0451	2.075	0.0448
			9.313	2.093	0.0342	2.094	0.0341
Pentafluoro-benzene w_2=0.04813	CHx	25	70	2.013	0.0143	2.020	0.0130
			34.86	2.024	0.0210	2.029	0.0206
			23.98	2.034	0.0237	2.037	0.0229
			16.20	2.041	0.0219	2.046	0.0221
			9.313	2.053	0.0168	2.055	0.0167

Table 3. Experimental Results Discussed in Chapter 4.

Solute	Solvent	t (^{o}C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}
Benzophenone w_2=0.03168	CHx	25	70	2.023	0.0176
			34.86	2.045	0.0289
			23.98	2.048	0.0396
			16.20	2.068	0.0477
			9.313	2.088	0.0603
			6.7	2.109	0.0575
Benzophenone w_2=0.03168	CHx	40	70	1.997	0.0186
			34.86	2.023	0.0316
			23.98	2.027	0.0421
			16.20	2.058	0.0524
			9.313	2.077	0.0560
			6.7	2.089	0.0498
Decafluoro-benzophenone w_2=0.13612	p-Xyl	15	70	2.290	0.0080
			34.86	2.294	0.0126
			23.98	2.290	0.0151
			16.20	2.303	0.0225
			9.313	2.305	0.0282
Decafluoro-benzophenone w_2=0.13612	p-Xyl	25	70	2.275	0.0084
			34.86	2.276	0.0119
			23.98	2.280	0.0149
			16.20	2.282	0.0225
			9.313	2.288	0.0280
Decafluoro-benzophenone w_2=0.10404	p-Xyl	40	70	2.244	0.0066
			34.86	2.245	0.0102
			23.98	2.243	0.0153
			16.20	2.258	0.0177
			9.313	2.265	0.0230
Decafluoro-benzophenone w_2=0.10404	p-Xyl	60	70	2.209	0.0057
			34.86	2.218	0.0123
			23.98	2.212	0.0151
			16.20	2.225	0.0189
			9.313	2.233	0.0215
Dicyclohexyl-ketone w_2=0.03620	CHx	25	70	2.041	0.0217
			34.86	2.043	0.0313
			23.98	2.051	0.0395
			16.20	2.075	0.0442
			9.313	2.094	0.0511
			6.7	2.106	0.0479
Dicyclohexyl-ketone w_2=0.03620	CHx	40	70	2.011	0.0219
			34.86	2.024	0.0346
			23.98	2.032	0.0444
			16.20	2.063	0.0463

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}
Dicyclohexyl-ketone (cont.) w_2 =0.03620	CHx	40	9.313	2.076	0.0463
			6.7	2.089	0.0409
Diethylether w_2 =0.06519	CHx	15	70	2.073	0.0490
			34.86	2.123	0.0431
			23.98	2.132	0.0339
			16.20	2.143	0.0240
			9.313	2.143	0.0155
Diethylketone w_2 =0.03580	CHx	15	70	2.124	0.1148
			34.86	2.217	0.1130
			23.98	2.229	0.1052
			16.20	2.292	0.0821
			9.313	2.303	0.0538
Diethylketone w_2 =0.01457	CHx	15	70	2.073	0.0462
			34.86	2.106	0.0434
			23.98	2.110	0.0392
			16.20	2.139	0.0305
			9.313	2.139	0.0193
4-Benzoyl-pyridine w_2 =0.03901	p-Xyl	25	70	2.285	0.0162
			34.86	2.304	0.0272
			23.98	2.301	0.0354
			16.20	2.315	0.0520
			9.313	2.331	0.0718
			6.7	2.347	0.0841
4-Benzoyl-pyridine w_2 =0.03758	p-Xyl	40	70	2.247	0.0159
			34.86	2.264	0.0292
			23.98	2.269	0.0402
			16.20	2.285	0.0547
			9.313	2.307	0.0719
			6.7	2.326	0.0836
m-Dibenzoyl-benzene w_2 =0.03045	p-Xyl	25	70	2.278	0.0078
			34.86	2.292	0.0147
			23.98	2.293	0.0210
			16.20	2.300	0.0309
			9.313	2.305	0.0440
			6.7	2.333	0.0606
m-Dibenzoyl-benzene w_2=0.03045	p-Xyl	60	70	2.190	0.0092
			34.86	2.232	0.0181
			23.98	2.237	0.0233
			16.20	2.243	0.0341
			9.313	2.255	0.0468
			6.7	2.271	0.0524

Table 4. Experimental Results Discussed in Chapter 5.

Solute	Solvent	t (^{o}C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
p-Dimethoxy-	CHx	15	70	2.065	0.0281	2.071	0.0275
benzene			35.11	2.085	0.0419	2.088	0.0432
w_2 =0.05818			23.98	2.093	0.0499	2.104	0.0492
			16.20	2.129	0.0494	2.123	0.0497
			9.313	2.147	0.0394	2.145	0.0408
p-Dimethoxy-	CHx	25	70	2.055	0.0337	2.065	0.0327
benzene			35.11	2.085	0.0480	2.088	0.0497
w_2 =0.06586			23.98	2.102	0.0534	2.106	0.0536
			16.20	2.133	0.0504	2.126	0.0506
			9.313	2.148	0.0396	2.147	0.0379
p-Dimethoxy-	CHx	40	70	2.041	0.0356	2.046	0.0355
benzene			35.11	2.077	0.0494	2.072	0.0501
w_2 =0.06751			23.98	2.100	0.0504	2.091	0.0507
			16.20	2.118	0.0454	2.109	0.0444
			9.313	2.121	0.0316	2.124	0.0306
p-Dimethoxy-	CHx	50	70	2.007	0.0319	2.020	0.0320
benzene			35.11	2.053	0.0404	2.044	0.0417
w_2 =0.05818			23.98	2.059	0.0411	2.059	0.0400
			16.20	2.078	0.0331	2.072	0.0334
			9.313	2.084	0.0223	2.082	0.0221
p-Diacetyl-	p-Xyl	15	70	2.302	0.0180	2.303	0.0153
benzene			34.86	2.309	0.0262	2.308	0.0276
w_2 =0.02688			23.98	2.314	0.0344	2.315	0.0370
			16.20	2.322	0.0507	2.326	0.0479
			9.313	2.352	0.0606	2.351	0.0605
			6.7	2.367	0.0616	2.370	0.0629
p-Diacetyl-	p-Xyl	25	70	2.282	0.0147	2.284	0.0123
benzene			34.86	2.285	0.0210	2.288	0.0220
w_2 =0.02074			23.98	2.296	0.0283	2.294	0.0293
			16.20	2.301	0.0372	2.303	0.0374
			9.313	2.326	0.0470	2.323	0.0460
			6.7	2.337	0.0463	2.337	0.0470
p-Diacetyl-	p-Xyl	25	70	2.294	0.0205	2.291	0.0171
benzene			34.86	2.292	0.0296	2.298	0.0309
w_2 =0.02886			23.98	2.305	0.0390	2.305	0.0412
			16.20	2.319	0.0543	2.318	0.0527
			9.313	2.346	0.0647	2.346	0.0647
			6.7	2.367	0.0654	2.367	0.0658

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
p-Diacetyl-	p-Xyl	25	70	2.294	0.0205	2.291	0.0171
benzene			34.86	2.292	0.0296	2.298	0.0309
w_2 =0.02886			23.98	2.305	0.0390	2.305	0.0412
			16.20	2.319	0.0543	2.318	0.0527
			9.313	2.346	0.0647	2.346	0.0647
			6.7	2.367	0.0654	2.367	0.0658
p-Diacetyl-	p-Xyl	40	70	2.263	0.0189	2.264	0.0175
benzene			34.86	2.271	0.0318	2.271	0.0320
w_2 =0.02688			23.98	2.287	0.0432	2.280	0.0425
			16.20	2.297	0.0506	2.296	0.0527
			9.313	2.327	0.0603	2.326	0.0584
p-Diacetyl-	p-Xyl	60	70	2.233	0.0203	2.231	0.0189
benzene			34.86	2.241	0.0348	2.240	0.0345
w_2 =0.02688			23.98	2.249	0.0438	2.251	0.0449
			16.20	2.272	0.0532	2.268	0.0534
			9.313	2.300	0.0552	2.298	0.0537
			6.7	2.310	0.0467	2.313	0.0472
α,α'-Dichloro-	p-Xyl	15	70	2.318	0.0311	2.316	0.0304
p-xylene			35.11	2.332	0.0414	2.336	0.0421
w_2 =0.03981			23.98	2.344	0.0445	2.351	0.0448
			16.20	2.370	0.0435	2.366	0.0430
			9.313	2.382	0.0340	2.384	0.0345
α,α'-Dichloro-	p-Xyl	25	70	2.296	0.0283	2.296	0.0275
p-xylene			35.11	2.311	0.0352	2.315	0.0356
w_2 =0.03321			23.98	2.322	0.0362	2.327	0.0364
			16.20	2.343	0.0339	2.340	0.0329
			9.313	2.350	0.0241	2.352	0.0246
α,α'-Dichloro-	p-Xyl	40	70	2.259	0.0259	2.272	0.0249
p-xylene			35.11	2.286	0.0302	2.290	0.0321
w_2 =0.03321			23.98	2.303	0.0323	2.301	0.0315
			16.20	2.314	0.0281	2.312	0.0274
			9.313	2.321	0.0191	2.321	0.0194
α,α'-Dichloro-	p-Xyl	50	70	2.274	0.0344	2.272	0.0340
p-xylene			35.11	2.305	0.0427	2.297	0.0428
w_2 =0.04513			23.98	2.313	0.0393	2.313	0.0401
			16.20	2.323	0.0335	2.325	0.0329
			9.313	2.332	0.0229	2.335	0.0215
α,α'-Dichloro-	p-Xyl	60	70	2.249	0.0332	2.247	0.0331
p-xylene			35.11	2.274	0.0375	2.271	0.0375
w_2 =0.03981			23.98	2.288	0.0323	2.284	0.0331
			16.20	2.298	0.0266	2.293	0.0259
			9.313	2.298	0.0181	2.299	0.0164

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
α,α'-Dichloro- p-xylene w_2 =0.01496	CHx	25	70	2.024	0.0137	2.031	0.0135
			35.11	2.042	0.0148	2.041	0.0153
			23.98	2.043	0.0136	2.046	0.0136
			16.20	2.055	0.0112	2.0501	0.0108
			9.313	2.050	0.0061	2.053	0.0070
Benzyl chloride w_2 =0.05589	p-Xyl	15	70	2.313	0.0364	2.329	0.0302
			35.11	2.337	0.0423	2.345	0.0430
			23.98	2.348	0.0483	2.357	0.0511
			16.20	2.374	0.0635	2.373	0.0592
			9.313	2.394	0.0626	2.405	0.0624
			6.7	2.413	0.0570	2.423	0.0569
Benzyl chloride w_2 =0.05171	p-Xyl	25	70	2.272	0.0305	2.305	0.0273
			35.11	2.315	0.0420	2.321	0.0425
			23.98	2.332	0.0490	2.335	0.0494
			16.20	2.352	0.0558	2.352	0.0542
			9.313	2.371	0.0532	2.379	0.0531
			6.7	2.386	0.0469	2.394	0.0471
Benzyl chloride w_2 =0.05171	p-Xyl	40	70	2.273	0.0319	2.279	0.0290
			35.11	2.290	0.0429	2.297	0.0442
			23.98	2.314	0.0521	2.313	0.0499
			16.20	2.326	0.0512	2.331	0.0515
			9.313	2.349	0.0451	2.355	0.0450
			6.7	2.359	0.0392	2.366	0.0376
Benzyl chloride w_2 =0.05589	p-Xyl	50	70	2.260	0.0360	2.267	0.0307
			35.11	2.288	0.0446	2.286	0.0442
			23.98	2.303	0.0491	2.300	0.0493
			16.20	2.320	0.0525	2.318	0.0509
			9.313	2.338	0.0474	2.342	0.0443
			6.7	2.350	0.0388	2.353	0.0367
Benzyl chloride w_2 =0.05171	p-Xyl	60	70	2.237	0.0253	2.243	0.0256
			35.11	2.262	0.0415	2.260	0.0416
			23.98	2.286	0.0493	2.275	0.0480
			16.20	2.297	0.0480	2.294	0.0485
			9.313	2.311	0.0376	2.316	0.0388
			6.7	2.324	0.0339	2.324	0.0309
Benzyl chloride w_2 =0.05955	CHx	25	70	2.058	0.0383	2.068	0.0372
			35.11	2.082	0.0449	2.090	0.0452
			23.98	2.087	0.0478	2.104	0.0475
			16.20	2.123	0.0497	2.118	0.0487
			9.313	2.134	0.0438	2.141	0.0450
			6.7	2.150	0.0381	2.152	0.0390

Solute	Solvent	t (°C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}	ϵ'_{calc}	ϵ''_{calc}
p-Dibenzoyl-benzene w_2=0.009144	p-Xyl	60	70	2.205	0.0028	2.205	0.0036
			34.86	2.206	0.0059	2.206	0.0070
			23.98	2.208	0.0095	2.207	0.0098
			16.20	2.212	0.0141	2.101	0.0132
			9.313	2.218	0.0179	2.218	0.0171
			6.7	2.223	0.0172	2.223	0.0176
p-Phenylene-diamine w_2=0.03600	Diox	25	70	2.373	0.0383		
			35.11	2.402	0.0426		
			23.98	2.413	0.0407		
			16.20	2.432	0.0425		
			9.313	2.445	0.0304		
Tetrafluoro-hydroquinone w_2=0.05932	Diox	25	70	2.359	0.0462		
			35.11	2.359	0.0514		
			23.98	2.379	0.0729		
			16.20	2.381	0.0842		
			9.313	2.437	0.1154		
Diacetyl w_2=0.19775 d=0.8141	CHx	25	70	2.217	0.0364		
			34.86	2.231	0.0255		
			23.98	2.238	0.0197		
			16.20	2.247	0.0141		
			9.313	2.248	0.0107		
Diacetyl w_2=0.30089 d=0.8351	CHx	25	70	2.352	0.0695		
			34.86	2.376	0.0511		
			23.98	2.392	0.0420		
			16.20	2.411	0.0289		
			9.313	2.410	0.0209		
Diacetyl w_2=0.21649 d=1.4048	CTC	15	70	2.638	0.0975		
			34.86	2.689	0.0803		
			23.98	2.706	0.0694		
			16.20	2.733	0.0531		
			9.313	2.741	0.0406		
Diacetyl w_2=0.29946 d=1.3436	CTC	15	70	2.786	0.1521		
			34.86	2.839	0.1230		
			23.98	2.889	0.1020		
			16.20	2.925	0.0870		
			9.313	2.939	0.0594		
Dibenzoyl w_2=0.01005	CTC	15	70	2.260	0.0074		
			34.86	2.264	0.0121		
			23.98	2.270	0.0193		
			16.20	2.276	0.0256		
			9.313	2.280	0.0342		
			6.7	2.281	0.0438		

Solute	Solvent	t (^{o}C)	Freq. (Gc/s)	ϵ'_{meas}	ϵ''_{meas}
Dibenzoyl w_2=0.01860	CTC	15	70	2.275	0.0143
			34.86	2.277	0.0217
			23.98	2.285	0.0318
			16.20	2.299	0.0435
			9.313	2.306	0.0659
Dibenzoyl w_2=0.01888	CTC	40	70	2.225	0.0173
			34.86	2.230	0.0284
			23.98	2.240	0.0355
			16.20	2.250	0.0499
			9.313	2.266	0.0761
			6.7	2.289	0.0842
Dibenzoyl w_2=0.01427	CHx	40	70	1.998	0.0086
			34.86	1.999	0.0118
			23.98	2.002	0.0163
			16.20	2.008	0.0207
			9.313	2.023	0.0283
			6.7	2.032	0.0280

(2) Published Work.

The following papers have been published :- (i) A Bridge Method at 4.3 mm Wavelength for Dilute Solutions. D.B.Farmer and S.Walker, Tetrahedron, 22, 111 (1966).

(ii) Relaxation Processes of Anisole- and Fluorine-Substituted Anisoles. D.B.Farmer, A.Holt and S.Walker, J.Chem.Phys., 44, 4116 (1966).

(iii) Mesomeric and Coupled Ring Rotation Mechanisms. D.B. Farmer and S.Walker, Trans.Fara.Soc., 63, 966 (1967).

Bibliography

1. C.P.Smyth, 'Dielectric Behaviour and Structure', (McGraw-Hill, New York and London, 1955).

2. C.J.F.Böttcher, 'Theory of Electric Polarization', (Elsevier Publishing Company, 1952).

3. M.Davies, 'Some Electrical and Optical Aspects of Molecular Behaviour', (Pergamon Press Ltd., 1965).

4. W.Kauzmann, Revs.Mod.Phys., 14, 12 (1942).

5. H.Fröhlich, 'Theory of Dielectrics', (Clarendon Press, Oxford, 1958).

6. For details of the individual components of the bridge apparatus see :- A.W.Cross, 'Experimental Microwaves', (W.H. Sanders (Electronics) Ltd., London).

7. W.F.Hassell, M.D.Magee, S.W.Tucker and S.Walker, Tetrahedron, 20, 2137 (1964).

8. C.W.N.Cumper, A.I.Vogel and S.Walker, J.Chem.Soc., 3621 (1956).

9. P.Debye, 'Polar Molecules', (Chemical Catalog Co., New York, 1929).

10. K.S.Cole and R.H.Cole, J.Chem.Phys., 9, 341 (1941).

11. A.Budó, Physik Z., 39, 706 (1938).

12. K.Bergmann, Diss., (Freiburg/Breisgau, West Germany, 1957).

13. K.Bergmann, D.M.Roberti and C.P.Smyth, J.Phys.Chem., 64, 665 (1960).

14. E.L.Grubb and C.P.Smyth, J.Amer.Chem.Soc., 83, 4873 (1961).

15. R.H.Cole, J.Chem.Phys., 23, 493 (1955).

16. W.P.Purcell, K.Fish and C.P.Smyth, J.Amer.Chem.Soc., 82, 6299 (1960).

17. F.K.Fong, R.C.A. Revs., 25, 752 (1966).

18. A.Aihara and M.Davies, J.Coll.Sci., 11, 671 (1956).

19. E.Fischer, Z.Naturforsch., 9a, 909 (1954).

20. H.Hase, Z.Naturforsch., 8a, 695 (1953).

21. J.G.Powles, J.Chem.Phys., 21, 633 (1953).

22. S.H.Glarum, J.Chem.Phys., 33, 1371 (1960).

23. R.C.Miller and C.P.Smyth, J.Amer.Chem.Soc., 79, 3310 (1957).

24. S.Glasstone, K.J.Laidler and H.Eyring,'The Theory of Rate Processes', (McGraw-Hill, New York, 1941).

25. I.F.Halverstadt and W.D.Kumler, J.Amer.Chem.Soc., 64, 2988 (1942).

26. E.A.Guggenheim, Trans.Far.Soc., 45, 714 (1949).

27. W.F.Hassell, Ph.D. Thesis (University of Aston in Birmingham, 1966).

28. R.J.W.Le Fèvre, D.V.Radford and E.P.A.Sullivan, Aust.J. Chem., 20, 623 (1967).

29. A.L.McClellan, 'Tables of Experimental Dipole Moments', (W.H.Freeman and Co., San Francisco, 1963).

30. J.Crossley, S.W.Tucker and S.Walker, Trans.Far.Soc., 62, 576 (1966).

31. E.Forest and C.P.Smyth, J.Phys.Chem., 69, 1302 (1965).

32. M.D.Magee and S.Walker, Trans.Far.Soc., 62, 3093 (1966).

33. F.K.Fong and C.P.Smyth, J.Amer.Chem.Soc., 85, 548 (1963).

34. F.K.Fong and C.P.Smyth, J.Amer.Chem.Soc., 85, 1565 (1963).

35. G.W.Wheland, 'Resonance in Organic Chemistry', (John Wiley and Sons, Inc., New York, 1955).

36. L.Pauling, 'The Nature of the Chemical Bond', (Cornell University Press, 1960).

37. R.N.Jones, W.F.Forbes and W.A.Mueller, Can.J.Chem., 35, 504 (1957).

38. S.K.Freeman, 'Interpretive Spectroscopy', (Reinhold Publishing Co., 1965).

39. E.Fischer, Z.Physik, 127, 49 (1949).

40. L.G.Groves and S.Sugden, J.Chem.Soc., 1992 (1937).

41. J.W.Smith, 'Electric Dipole Moments', (Butterworths Scientific Publications Ltd., 1955).

42. F.C.Frank, Proc.Roy.Soc., A152, 171 (1936).

43. J.R.Partington, 'An Advanced Treatise on Physical Chemistry', Vol.5, p.523, (Longmans, Green and Co., London, 1954).

44. A.R.Katritzky, E.W.Randall and L.E.Sutton, J.Chem.Soc., 1769 (1957).

45. V.Baliah and K.Aparajithan, Tetrahedron, 19, 2177 (1963).

46. A.A.Antony and C.P.Smyth, J.Amer.Chem.Soc., 86, 156 (1964).

47. E.Fischer, Z.Naturforsch., 4a, 707 (1949).

48. P.Knobloch, Ber.Buns., 69, 296 (1965).

49. J.H.Hildebrand and R.L.Scott, 'The Solubility of Non-electrolytes', Chapter 4, (Dover Publications Inc., New York, 1964).

50. J.Crossley, Ph.D. Thesis, (University of Aston in Birmingham, 1967).

51. G.C.Pimentel and A.L.McClellan, 'The Hydrogen Bond', (W.H. Freeman and Co., San Francisco, 1960).

52. V.F.Hufnagel and H.Kilp, Z.Naturforsch., 18a, 769 (1963).

53. F.K.Fong and C.P.Smyth, J.Chem.Phys., 40, 2404 (1964).

54. F.Perrin, J.Phys.Rad., 5, 497 (1934).

55. C.A.Coulson, 'Valence', (Oxford University Press, 1961).

56. P.Knobloch, Z.Naturforsch., 20a, 854 (1965).

57. N.K.Mehrotra and M.C.Saxena, Bull.Chem.Soc.(Japan), 40, 19 (1967).

58. P.F.Mountain, Ph.D. Thesis, (University of Aston in Birmingham, 1968).

59. W.A.Sheppard, J.Amer.Chem.Soc., 87, 2410 (1965).

60. M.T.Rogers, G.M.Barrow and F.G.Bordwell, J.Amer.Chem.Soc., 78, 1790 (1956).

61. F.Hufnagel, Z.Naturforsch., 15a, 723 (1960).

62. D.H.Whiffen, Trans.Far.Soc., 46, 130 (1950).

63. J.McKenna, 'Conformational Analysis of Organic Compounds', (The Royal Institute of Chemistry Lecture Series, No 1, 1966).

64. S.K.Garg and C.P.Smyth, J.Chem.Phys., 46, 373 (1967).

65. E.Forest and C.P.Smyth, J.Amer.Chem.Soc., 86, 3474 (1964).

66. W.E.Vaughan, S.B.W.Roeder and T.Provder, J.Chem.Phys., 39, 701 (1963).

67. A.J.Curtis, P.L.McGeer, G.B.Rathmann and C.P.Smyth, J.Amer. Chem.Soc., 74, 644 (1952).

68. G.Klages and A.Zentek, Z.Naturforsch., 16a, 1016 (1961).

69. 'Tables of Interatomic Distances and Configurations in Molecules and Ions', (The Chemical Society, London, 1958).

70. W.A.Sheppard, J.Amer.Chem.Soc., 85, 1314 (1963).

71. J.W.Williams, Z.Phys.Chem., 138, 75 (1928).

72. S.W.Tucker and S.Walker, J.Chem.Phys., 45, 1302 (1966).

73. S.K.Garg and C.P.Smyth, J.Phys.Chem., 69, 1294 (1965).

74. G.W.Chantry and H.A.Gebbie, Eighth European Conference Molecular Spectroscopy, Copenhagen, 1965.

75. S.K.Garg and C.P.Smyth, J.Chem.Phys., 42, 1397 (1965).

76. N.E.Hill, Proc.Phys.Soc.(London), 82, 723 (1963).

77. S.E.Kammerling and C.P.Smyth, J.Amer.Chem.Soc., 55, 462 (1933).

78. W.E.Vaughan, J.Chem.Phys., 42, 1286 (1965).

79. G.Klages and P.Knobloch, Z.Naturforsch., 20a, 580 (1965).

80. W.Maier, Arch.Sci.(Geneva), 12, 20 (1959).

81. N.J.Leonard and L.E.Sutton, J.Amer.Chem.Soc., 70, 1564 (1948).

82. J.E.Anderson and C.P.Smyth, J.Chem.Phys., 42, 473 (1965).

83. R.D.Nelson and C.P.Smyth, J.Phys.Chem., 69, 1006 (1965).

84. F.Hufnagel, G.Klages and P.Knobloch, Z.Naturforsch., 17a, 96 (1962).

85. W.Gordy, 'Microwave Spectroscopy' in 'Handbuch der Physik', edited by S.Flügge (Springer-Verlog, Berlin, 1957), Vol. XXVIII, pp 8-9.

86. K.Higasi and S.Uyeo, Bull.Chem.Soc.(Japan), 14, 87 (1939).

87. K.Higasi and C.P.Smyth, J.Amer.Chem.Soc., 82, 4759 (1960).

88. K.Higasi, S.Uyeo and S.Yamaguchi, Bull.Inst.Phys.Chem.Res. (Tokyo), 23, 788 (1947).

89. E.Fischer, Naturwiss, 43, 153 (1956).

90. F.K.Fong, J.Chem.Phys., 40, 132 (1964).

91. K.Higasi, Bull.Chem.Soc.(Japan), 35, 692 (1962).

92. L.E.Sutton, Proc.Roy.Soc., A133, 668 (1931).

93. W.E.Vaughan and C.P.Smyth, J.Phys.Chem., 65, 98 (1961).

94. W.P.Purcell and C.P.Smyth, J.Amer.Chem.Soc., 83, 1063 (1961).

95. R.J.W.Le Fèvre and A.J.Williams, J.Chem.Soc., 115 (1960).

96. G.B.Rathmann, A.J.Curtis, P.L.McGeer and C.P.Smyth, J.Chem. Phys., 25, 413 (1956).

97. L.E.Sutton and G.C.Hampson, Trans.Far.Soc., 31, 945 (1935).

98. E.N.DiCarlo and C.P.Smyth, J.Amer.Chem.Soc., 84, 3638 (1962).

99. D.M.Roberti, O.F.Kalman and C.P.Smyth, J.Amer.Chem.Soc., 82, 3523 (1960).

100. H.Mackle and R.G.Mayrick, Trans.Far.Soc., 58, 238 (1962).

101. D.M.Roberti and C.P.Smyth, J.Amer.Chem.Soc., 82, 2106 (1960).

102. K.Chitoku and K.Higasi, Bull.Chem.Soc.(Japan), 36, 1064 (1963).

103. J.Hunt, Private Communication.

104. J.B.Bentley, K.B.Everard, R.J.B.Marsden and L.E.Sutton, J.Chem.Soc., 2957 (1949).

105. R.J.W.Le Fèvre, B.J.Orr and G.L.D.Ritchie, J.Chem.Soc., 3619 (1965).

106. S.W.Tucker, Ph.D. Thesis, (University of London, 1967).

107. G.I.M.Bloom and L.E.Sutton, J.Chem.Soc., 727 (1941).

108. R.S.Rasmussen, D.D.Tunnicliff and R.R.Brattain, J.Amer. Chem.Soc., 71, 1068 (1949).

109. P.H.Cureton, C.G.Le Fèvre and R.J.W.Le Fèvre, J.Chem.Soc., 4447 (1961).

110. J.Crossley and S.Walker, J.Chem.Phys., 45, 4733 (1966).

111. D.A.Pitt and C.P.Smyth, J.Amer.Chem.Soc., 80, 1061 (1958).

112. C.C.Caldwell and R.J.W.Le Fèvre, J.Chem.Soc., 1614 (1939).

113. K.Higasi, Bull.Chem.Soc.(Japan), 13, 158 (1938).