DIELECTRIC STUDIES OF FACTORS INFLUENCING THE ENERGY BARRIERS TO MOLECULAR AND GROUP REORIENTATION

by

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SUMMARY

Dielectric relaxation times and energy barrier parameters of polar organic molecules were determined in dilute solution at microwave frequencies using a coaxial line apparatus, which has not previously been employed for low loss measurements, and a bridge technique.

A study has been made of factors affecting the reorientating processes of rotatable polar groups substituted mainly on aromatic molecules, where two mechanisms, molecular and intramolecular, are present. Previous work has shown that acetyl and methoxy groups possess a mobility which reduces the observed relaxation time to a value below that of molecular relaxation. The size of reduction depends on the resultant dipole moment direction, as illustrated by the results of the p-halo and p-alkylacetophenones, and also on the magnitude of the intramolecular relaxation time, a tendency was observed for acetyl reorientation to lengthen with increasing conjugation to the parent molecule. Viscous solution studies further clarified these intramolecular processes. Placing a single chlorine atom ortho to an acetyl group was found to increase its mobility, while inserting two neighbouring groups, as in 2,4,6-trimethylacetophenone and 9-acetylanthracene appeared to prevent acetyl rotation completely.

Of the o-substituted alkoxy benzenes examined an intramolecular process was only detected in o-fluoroanisole. Measurement of cholesterylmethylether provided an accurate value of the aliphatic methoxy relaxation time (and, therefore, a minimum value for the aromatic parameter), since complete separation of molecular and intramolecular absorption occurred.

A similar, but smaller study to the acetyl compounds was carried out on aldehyde derivatives. Analysis of results proved difficult as the aldehydes' dielectric behaviour was found to be dependent on the nature of the solvent. An internal mechanism was detected in the p-halobenzaldehydes, but not in benzaldehyde nor 2-naphthaldehyde.

A series of ortho and meta halo substituted iodobenzenes were measured for comparison with the analogous acetyl and alkoxy derivatives, and the results, with others, used to suggest a possible correlation between a molecule's moment of inertia and its relaxation time.

PREFACE

The work described in this thesis was carried out at the University of Aston in Birmingham from January 1966 to October 1967 and from this last date till September 1969 at Lakehead University, Ontario, Canada. I would like to thank my supervisor, Professor S.Walker, for his constant interest and invaluable advice and my co-supervisor, Dr.A.Holt, for guiding me through the organic sections of this work.

I am also grateful to my dielectric postgraduate colleagues for many interesting discussions and to Mr.B.K.Morgan for maintaining the equipment and helping in many ways.

Working in two countries has left me indebted to many people for their interest and opinions; may it suffice to thank Professor Parker and the staff of the Chemistry Department at Aston, together with the staffs of the Chemistry, Mathematics and Physics Departments at Lakehead.

Finally, may I humbly thank my wife who travelled 4,000 miles with me, giving unfailing support in many ways without which this work may never have been completed.

P.F.MOUNTAIN.

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CHAPTER 1

EXPERIMENTAL METHODS AND BASIC THEORY

INTRODUCTION

This thesis is an account of the dielectric examination at microwave frequencies of some dilute solutions of polar organic molecules, to determine their relaxation mechanisms and to estimate the energy barriers involved in these processes. Although the original dielectric theory was formulated by Debye(108) at the beginning of this century, the growth of this field has been restricted by the limited hardware available. It is only in recent years with the advancement of electronics that measurement in the microwave region has become a practical feasibility. Even so a considerable amount of papers have been published, reporting the behaviour of molecules in the liquid or solution state, detected by dielectric measurements. Predominant amongst the publishers are Professor C.P.Smyth and his colleagues at Princeton, U.S.A., and many references to their work are included in the subsequent discussions. The majority of small/medium sized molecules have their maximum dielectric absorption in the region of 10^9 - 10^{10} c/s, and an essential requirement for dielectric dispersion studies (especially where two relaxation processes are present) is a sufficiently wide frequency coverage over this range. The availability in this laboratory of a frequency range of 0.9 - 70 G c/s enables the determination of a far larger number of microwave points than have hitherto been employed in this type of study and further assists in the interpretation of the results.

Measurement of the above frequencies have been carried out using two types of apparatus, a bridge technique (70 - 6.7 G c/s) and a coaxial line method (2.5 - 0.9 G c/s). Previous students of this laboratory have successfully employed the former techniques and have fully described the equipment(1)(2)(16)(17)(56). Similarly much of the theory has been dealt with in these accounts and of course in the standard texts(15)(88)(147), therefore, to avoid needless repetition an attempt has been made in this chapter to discuss only the bare essentials. The latter apparatus has been used previously by Grant and his co-workers(148)(149)(150) for the study of medium and high loss liquids, but no apparent use has been made of it for dilute solutions with low losses and thus the cell (for convenience referred to as the 'Grant cell') and theory are described. An account is also given of subsidiary measurements and methods used for purification of materials and the physical constants of the latter are tabulated.

A. Dielectric Parameters

ε': The dielectric constant of a medium may be defined as the ratio of a field strength in a vacuum to that in the medium for the same distribution of charge. It may also be defined, as it is measured on the heterodyne beat apparatus, as the ratio of the capacitance C of a condenser filled with the material to the capacitance C_0 of the empty condenser; $\varepsilon' = \frac{C}{C_0}$ . . . . (1:1)

Although it is called a constant, ε' for polar materials depends on the frequency of the applied alternating field and some workers, therefore, prefer to describe it as the 'electrical permittivity'(88).

ε'': When an oscillator is exposed to radiant energy it may absorb certain characteristic frequencies, molecules in a liquid absorb electric waves and this absorption gives a loss of power, termed dielectric loss.

This parameter may be defined by the loss angle, which is the angle, δ, between the vector for the total current and that for the charging current, so that

$$\tan\delta = \frac{\text{loss current}}{\text{charging current}} = \frac{\varepsilon''}{\varepsilon'} \qquad (1:2)$$

Thus, when absorption occurs, the dielectric constant is treated as a complex quantity

$$\varepsilon^* = \varepsilon' - i\,\varepsilon'' \qquad (1:3)$$

ε_0: The static dielectric constant is the value ε' is increased to when the frequency and ε'' approaches zero.

ε_∞: The optical dielectric constant is the value ε' is decreased to when the frequency approaches ∞ and ε'' again approaches zero.

τ: When a field applied to a dielectric is removed, the decay of the polarization with time is called "dielectric relaxation". Since the decay is assumed to be an exponential function of time, the relaxation time, τ, is defined as the time required for the polarization, P, to decrease to $^1/e$ of its value at the instant when the field is removed, P_0,

$$P = P_0\, e^{-t/\tau} \qquad (1:4)$$

where $t = \tau$ for the definition.

Thus for frequencies higher than 10^8 c/sec. there is a time lag between the response of small polar molecules in solution to the behaviour of an applied field. For rigid symmetrical molecules, such as chlorobenzene only one relaxation time, corresponding to a molecular process τ_1, will be observed;for a non-rigid molecule such as acetophenone, whose resultant dipole moment is not along a symmetry axis, however, two relaxation times will be detected, one corresponding to molecular relaxation τ_1, the other to group relaxation τ_2 (intramolecular).

A third parameter discussed in this thesis, the mean relaxation time τ_0, in effect does not have any physical meaning, but is the value at which the dielectric loss is at a maximum and about which the other relaxation times, if there are more than one, are symmetrically distributed. So for chlorobenzene τ_0 will effectively equal τ_1 , while for acetophenone τ_0 will be shorter than the molecular relaxation time.

B. Apparatus

(i) The Bridge Method: As mentioned earlier this technique has already been fully described(32) (together with the method of measurement(17) and the errors involved(2)), by previous students, and will not be discussed here. The actual frequencies used in this work, with their letter notation and the possible error involved in the dielectric constant are tabulated below, the dielectric loss was obtained to an accuracy of ∿±0.002 for all the bridge points.

LETTER CHARACTERISING WAVEBAND	OPERATING FREQUENCY G c/s	ANGULAR FREQUENCY $\omega \times 10^{-10}$	POSSIBLE ERROR IN ε'
O	70	43.9823	± 0.008
Q	(35.11 (34.86	(22.06 (21.9063	± 0.006
K	23.98	15.083	± 0.003
P	16.2	10.18	± 0.005

LETTER CHARACTERISING WAVEBAND	OPERATING FREQUENCY G c/s	ANGULAR FREQUENCY $\omega \times 10^{-10}$	POSSIBLE ERROR IN ε'
X	9.313	5.8508	± 0.003
C	6.7	4.2097	± 0.003

TABLE 1:1 MICROWAVE BRIDGE FREQUENCIES EMPLOYED.

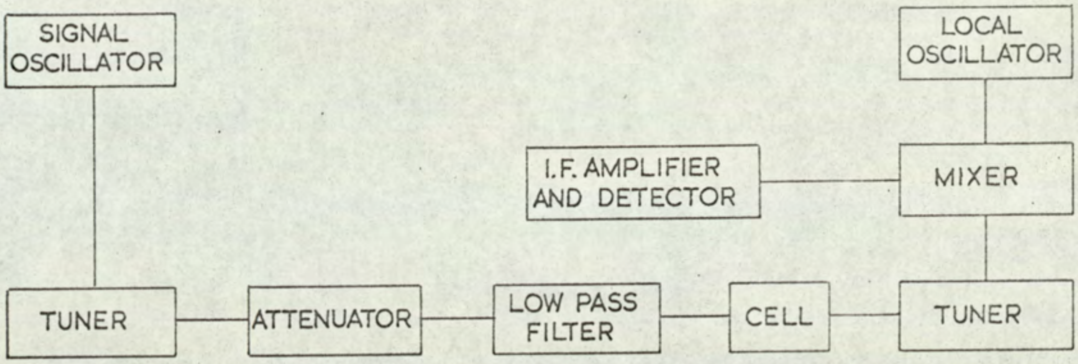
Further corrections to results obtained on the first three frequencies are given in Section E.

(ii) The Coaxial-line Method

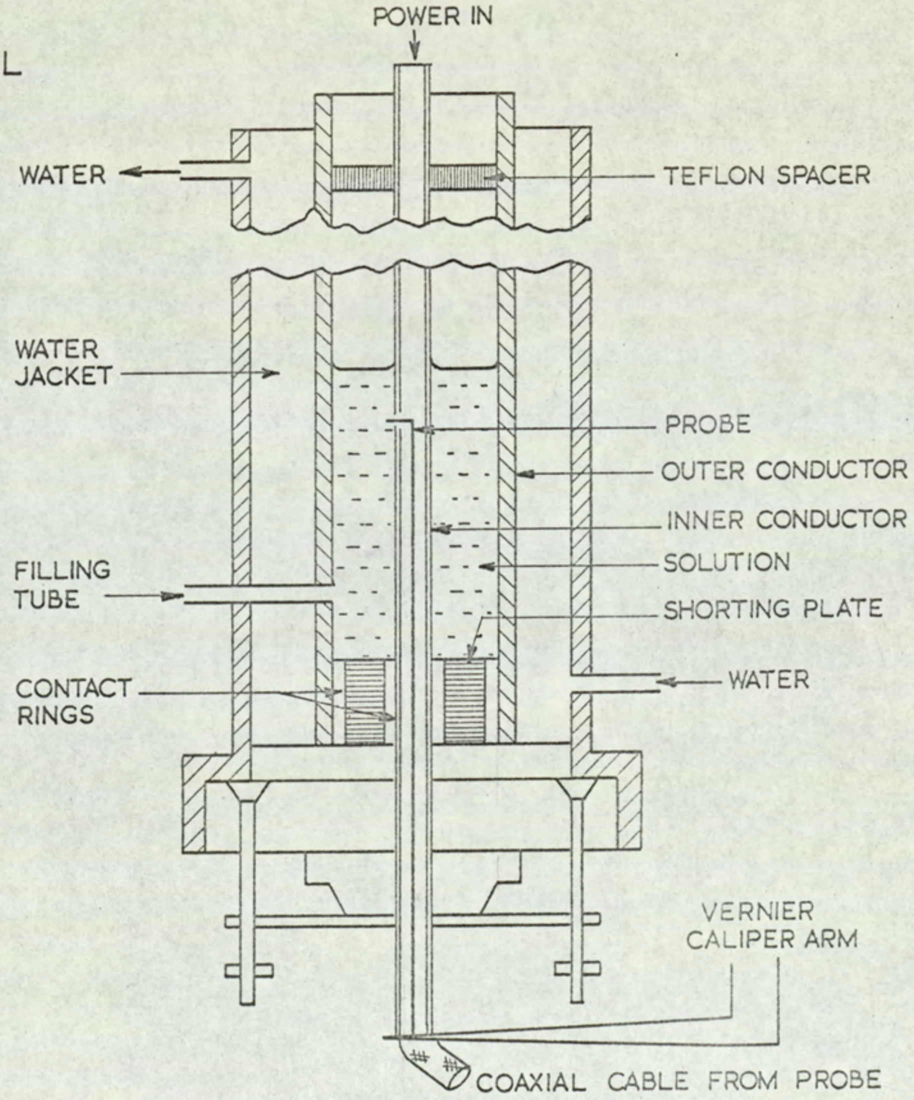
Below the frequence of 6.7 G c/s the bridge technique becomes impractical as a measurement requires a large amount of solution and thus, solute, for molecules with a dipole moment of 2-3D and, therefore, another method requiring less material is required.
An adaptation of a coaxial-line technique proposed by Grant and his co-workers(148-150) has been found to be suitable for dilute solutions. Apart from using less than 50 ml. of solution, depending on the size of the cell, this method has the advantage that a number of frequencies (between 0.9 and 2.5 G c/s) and temperatures may be measured without removing the sample, also as the latter is completely enclosed a larger temperature range is feasible.
A further advantage of this technique is that the electric field vector is sampled within the liquid under investigation and thus, difficulties from reflections at the air-liquid interface do not arise.

FIG. 1:1 THE COAXIAL LINE APPARATUS

(a.) SCHEMATIC DIAGRAM



(b.) CELL



A schematic diagram of the apparatus is shown in Fig. 1:1:a, where it can be seen that radiation from the signal generator enters the cell containing the specimen solution, the resulting electric vector of the standing wave pattern is sampled by a probe and the output is mixed with the signal from a local oscillator. The latter is tuned to a frequency 30 Mc/s away from the input signal and the resulting beat frequency is amplified and measured on an I.F. amplified which has a calibrated db scale that allows the power level to be determined at the probe position within the liquid.

The frequency of the input radiation was checked using a Rohde and Swartz U.H.F. Resonance Fequency meter type WAL.BH 4321/2 and to prevent pulling of this oscillator a pad attenuator was employed, while harmonics generated by the source were eliminated by attaching low pass filters, corresponding to the frequency being determined, to the cell. Tuners were inserted in the line on either side of the cell, to match the impedance of the circuit components and all connectors between the above were of the locking type (General Radio Type QBL) to reduce reflections in the line and avoid any stray electromagnetic fields. The major components of the circuit are listed below in Table 1:2

COMPONENT	FREQUENCY RANGE G c/s	SUPPLIER	MODEL
Oscillators	2.5 - 0.5	Rohde and Swartz	SLRD
	2.0 - 0.9	General Radio	1218B
Tuners	2.0 - 0.9	General Radio	874LTL
		Microlab	S305N

COMPONENT	FREQUENCY RANGE G c/s	SUPPLIER	MODEL
Low-pass filters	<0.5, <1.0 <2.0, <4.0	General Radio	874F( )L
Cell		Lakehead University	
Mixer	2.5 - 0.5	General Radio	MRAL
I.F.Amplifier and meter	30	General Radio	1236

TABLE 1:2. GRANT CELL COMPONENTS.

The grant Cell itself is essentially a length of coaxial line terminated by a shortcircuit (cf Fig. 1:1:b), the coaxial line consisting of an outer conductor (i.d. 14.3 mm) and an inner conductor (o.d. 4.1 mm). To ensure good electrical contact all three components were made out of silver and to further increase the contact, silver collars were inserted between both conductors and the short circuit. The centre conductor passes through a telescopic tube, ensuring axial movement along the cell, which is supported by two machined teflon plugs and is connected to the centre contact of the input locking connector. The probe emerges through a small opening in the tubular centre conductor, sealed in it by a plug of polyethylene which prevents any solution entering the tube, and its position within the cell is determined by a vernier calliper, accurate to within 0.02 mm. The specimen solution is introduced to the centre conductor by a small tube at the base of the cell and a water jacket enables thermostating by the usual means.

THEORY

The electric field intensity of an electromagnetic plane wave on entering a solution is given by

$$E = E_0 e^{i\omega t} \tag{1:5}$$

where E_0 is the amplitude of the electric vector, ω is the angular frequency and t is time(15). After travelling a distance x through the solution the field strength is reduced to:

$$E = E_0 e^{i\omega t}\, e^{-\gamma x} \tag{1:6}$$

γ being known as the propagation coefficient of the solution and is defined by

$$\gamma = \alpha + i\beta \tag{1:7}$$

Thus a reappraisal of equation 1:6 gives

$$E = \left[E_0 e^{-\alpha x}\right]\left[\cos(\omega t - \beta x) + i \sin(\omega t - \beta x)\right] \tag{1:8}$$

from which it can be seen that by travelling a distance x the amplitude of the wave has been reduced by $e^{-\alpha x}$, therefore, α is known as the attenuation constant, and is a measure of the reduction in the wave's electrical intensity per cm of solution. Equation 1:5 has similarly been diminished in the last term, the phase of the wave, by βx radians and hence β is known as the phase constant.

A standing wave is created by the short circuit reflecting the incident radiation back towards the source, the field strength of which is given by $E = E_0\, e^{i\omega t}\, (e^{\gamma x} - e^{-\gamma x})$ (1:9)

since the two combining waves are travelling in opposite directions ($+x$ and $-x$) . From this equation it can be shown(148) that the amplitude at a distance $x$cm from the short circuit is

$$E = E_0 \left[2(\cosh 2\alpha x - \cos 2\beta x)\right]^{\frac{1}{2}} \qquad (1:10)$$

By differentiating this and solving for the positions of the maxima and and minima of the standing wave, the values of x at which they occur are given by:

$$2\beta x = n\pi + (-1)^n \sin^{-1} \left[-(\alpha/\beta) \sinh 2\alpha x\right] \qquad (1:11)$$

where n is an integer, odd for the maxima and even for the minima(150). In this thesis only minima were measured. For low loss solutions $\beta >> \alpha$ and, therefore,

$$\beta = \frac{n\pi}{2x} \qquad (1;12)$$

The standing wave ratio, $r = \left(\frac{\text{amplitude of minimum}}{\text{amplitude of maximum}}\right)$ may be obtained from equation 1:10

$$r^2 = \frac{E_{min}{}^2}{E_{max}{}^2} = \frac{(\cosh 2\alpha x_1 - \cos 2\beta x_1)}{(\cosh 2\alpha x_2 - \cos 2\beta x_2)} \qquad (1:13)$$

for medium/low loss liquids this simplifies to

$$r \simeq \frac{\sinh \alpha x_1}{\cosh \alpha x_2} \simeq \sinh \alpha x_1 \qquad (1:14)$$

where x_1 and x_2 are the distance of the minimum and the maximum respectively from the short circuit. For low losses, pairs of positions of minima and maxima will occur where $x_1 = 2x_2$ exactly, so sinh $\alpha x_2 = {}^{r}/_{2}$ and in the limiting case equation 1:14 reduces to $\alpha = \frac{r}{x_2}$ (1:15)

EXPERIMENTAL PROCEDURE AND CALCULATIONS

After the oscillators had been allowed to stabilise, the apparatus was normally checked and the short circuit position determined by measuring cyclohexane, the dielectric constant of which was accurately known. For the greatest accuracy this was accomplished by taking the vernier reading 3 db either side of the minimum; the minimum position x_1, being midway between the two points; the short circuit's position, s/c, was then determined from

$$s/c = x - x_1 \qquad (1:16)$$

where $x = \pi \frac{C}{\sqrt{\varepsilon'_{\text{solvent}}}}$ and $c = \frac{\lambda_o^{\,2}}{4\pi^2}$

λ_o being the free space wavelength $= \frac{\text{velocity of light}}{\text{frequency}}$

At frequencies where more than one minima occurred (x_1, x_2, etc.), the short circuit was determined by

$$s/c = x_2 - 2x_1 \qquad (1;17)$$

The latter could not be measured directly since the vernier calliper was attached to the inner conductor at a position which prevented the probe from being damaged by contact with the shorting plate.

This procedure was repeated at several frequencies to ensure that the short circuit was functioning correctly, a check on the apparatus at the higher frequencies was to determine the solvent dielectric constant, using

$$\varepsilon' = \beta^2 c \tag{1:18}$$

where

$$\beta = \frac{\pi}{x_2 - x_1} = \frac{\pi}{x_0} \tag{1:19}$$

$(x_0 = x_n - x_{n-1}$ or $x_1 + s/c)$

and compared with the theoretical value.

The minima positions of a low loss specimen solution are also measured in a likewise manner, the distance between the 3db points on either side of them (Δ)providing a measure of the standing wave ratio.

$$r = \frac{\pi\Delta}{\lambda_m} \tag{1:20}$$

where λ_m = length of the wave in the liquid = $2x_0^2$. This procedure, known as the double minimum method, uses the electrical distance which separates two points, on either side of a minimum, at which the output is twice the minimum value(152). Thus, knowing the attenuation and phase constants (equations 1:12 and 1:15) the dielectric constant and loss of the specimen solution may be calculated.

$$\varepsilon' = (\beta^2 - \alpha^2)c \tag{1:21}$$

$$\varepsilon'' = \alpha\beta c \tag{1:22}$$

When a series of minima occurred, either the mean x_0 was used or independent calculations made and the resulting dielectric parameters averaged; equation 1:17 could also be used as a further check on the short circuit. Any solvent or wall loss was measured and substracted from the apparent loss of the solution. Grant and his co-workers deduced much of the above theory on the assumption that the circuit was perfectly reflecting and that the probe had no perturbing effect on the field, they found that errors in α resulted if these two conditions were not fulfilled. Cooke, in this laboratory, tested the efficiency of the short circuit and the suitability of the probe using acetone and found that the cell was satisfactory up to a frequency of 2.5 G c/s(97).

(iii) Heterodyne Beat Apparatus

The static dielectric constant, ε_0, was measured at 2Mc/s on a Wiss-Tech-Werkstatten Dipolmeter type DM01. During each measurement the instrument was calibrated with dry air, pure cyclohexane, p-xylene and toluene, the latter was specifically used for dielectric constants higher than 2.3. The ε_0 values were found to be reproducible to ± 0.002 or better.

(iv) Infrared Spectra

The spectra reported in chapter 2 were recorded on a Beckman IR 12 infrared spectrophotometer.

(v) Additional Measurements

Refractive indices were measured using either an Abbe refractometer type 58273 manufactured by Carl Zeiss or a

Bellingham and Stanley refractometer of the Pulfrich type, at the frequency of the sodium D line. Viscosities were determined with the applicable range of Ubbelohde viscometer, and the densities by using a pyknometer of the type used by Cumper, Vogel and Walker(153).

C Essential Equations

(i) For molecules such as chlorobenzene which can be characterised by a single relaxation time the complex dielectric constant (Equation 1:3) may be related to the relaxation time and angular frequency of the applied field by:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} = \varepsilon' - i\varepsilon'' \qquad (1:23)$$

On separation into real and imaginary parts

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \qquad (1:24)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \qquad (1:25)$$

These latter are known as the Debye dispersion equations, and elimination of $\omega\tau$ from them gives the relationship between ε' and ε'':

$$\left(\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2 \qquad (1:26)$$

which is the equation of a circle. The locus of ε' and ε'' in an Argand diagram is, therefore, a semi-circle of radius $\varepsilon_0 - \varepsilon_\infty/2$ the centre lying on the abscissa and is known as a Cole-Cole plot(154).

(ii) For systems with more than one relaxation time, the centre of the semi-circle lies below the abscissa and the Argand diagram is found to be an arc which corresponds to a clockwise rotation of the semi-circle about the ε_∞ point; for this case equation 1:23 is modified to:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\omega\tau_0)^{1-\alpha}} \qquad (1:27)$$

where α is known as the distribution coefficient and is a measure of the spread of relaxation times about τ_0 and has the range $1>\alpha>0$.

Separation of the above equation into real and imaginary parts yields:

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)\left[1 + (\omega\tau_0)^{1-\alpha} \sin(\alpha \frac{\pi}{2})\right]}{1 + 2\,(\omega\tau_0)^{1-\alpha} \sin(\alpha\frac{\pi}{2}) + \omega\tau_0{}^{2(1-\alpha)}} \qquad (1:28)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)(\omega\tau_0)^{1-\alpha} \cos(\alpha^{\pi}/2)}{1 + 2\,(\omega\tau_0)^{1-\alpha} \sin(\alpha^{\pi}/2) + \omega\tau_0{}^{2(1-\alpha)}} \qquad (1:29)$$

known as the Cole-Cole equations.

(iii) For multiple discrete relaxation times Budo(155) assumed that the complex dielectric constant could be represented by the superimposition of overlapping Debye absorptions, for two relaxation times such a behaviour is described by the equations:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\left[\frac{C_1}{1 + \omega^2\tau_1{}^2} + \frac{C_2}{1 + \omega^2\tau_2{}^2}\right] \qquad (1:30)$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)\left[\frac{C_1\omega\tau_1}{1 + \omega^2\tau_1^{\ 2}} + \frac{C_2\omega\tau_2}{1 + \omega^2\tau_2^{\ 2}}\right] \tag{1:31}$$

$$C_1 + C_2 = 1 \tag{1:32}$$

where C_1 and C_2 are the weighting factors of the two contributing absorptions.

(iv) A further Debye equation relates the dielectric constant of a substance to its dipole moment (μ):

$$\mu^2 = \frac{9kT\,(\varepsilon_0 - \varepsilon_\infty)\,C}{4\pi N\,(\varepsilon_0 + 2)(\varepsilon_\infty + 2)} \tag{1:33}$$

where C is the concentration in moles/litre, k is Boltzmann's constant, N is Avogadro's number and T the absolute temperature. For dilute solutions (weight fraction of solute $\omega_2 < 0.15$), the denominator of the above may be modified by extrapolation to infinite dilution, at which

$$(\varepsilon_0 + 2)(\varepsilon_\infty + 2) = (\varepsilon_1 + 2)^2 \tag{1:34}$$

$$\text{so} \quad \mu = 0.012812\left[\frac{3T(\varepsilon_0 - \varepsilon_\infty)\,M_2}{(\varepsilon_1 + 2)^2\,\omega_2\,d_1}\right]^{\frac{1}{2}} \tag{1:35}$$

where M_2 is the molecular weight of the solute, ε_1 and d_1, the dielectric constant and density of the solvent respectively. An alternative method for determining μ is that of Guggenheim(66) which involves $n_D^{\ 2}$ (where n_D is the refractive index for the sodium D line) in place of ε_∞, this approximation in the Guggenheim technique ($\varepsilon_\infty \neq n_D^2$) may explain the tendency to obtain slightly lower moments by the microwave procedure. The ε_∞ value contains an additional atom polarisation contribution over that included in n_D^2 and the difference of $\varepsilon_\infty - n_D^2$ when sufficiently large, may indicate a high frequency absorption region, e.g. libration of a group$^{(70)}$.

(v) Any system undergoing a physical or chemical transformation, the rate of which depends on a factor of the type $e^{-\alpha/T}$, can be treated in terms of absolute rate theory. Eyring recognised the similarity between dielectric relaxation and the rates of chemical reactions and suggested that dipole orientation could be treated by the statistical mechanical methods of absolute rate theory$^{(156)}$. Thus for a dipole orientating between two equilibrium positions separated by a potential energy barrier of height $\Delta G^\ddagger$, Eyring deduced the following expression:

$$\tau = \frac{1}{K} = \frac{\sigma h e^{\Delta G^\ddagger/RT}}{kT} \qquad (1:36)$$

where h, k and R have their normal meanings, K is the dipole jump rate and σ is a transmission coefficient, (normally taken to be unity) which is the probability that once the dipole reaches the top of the energy barrier (activated state) it will continue to move in the same direction, to a new position of orientation.

Since $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, equation 1:36 may be rewritten as

$$\tau = \frac{h}{kT}\, e^{(\Delta H^\ddagger/RT - \Delta S^\ddagger/R)} \qquad (1:37)$$

From these two relationships $\Delta G^{\ddagger}$, the free energy of activation and $\Delta H^{\ddagger}$, the enthalpy may be obtained:

$$\Delta G^{\ddagger} = 2.303\ RT \left[\log \tau + \log {}^{kT}/h\right] \qquad (1:38)$$

$$\log \tau\ T = \frac{1}{T} \cdot \frac{\Delta H^{\ddagger}}{2.303R} + \left[\log \frac{h}{k} - \frac{\Delta S^{\ddagger}}{2.303R}\right] \qquad (1:39)$$

D. Treatment of Results

(i) Computer Analysis

Four types of program were used to calculate

(a) ε' ε'' from the microwave bridge data

(b) τ_0 α ε_∞ from ε_0 and the results from (a)

(c) $\tau_1 \tau_2$ C_1 from ε_0 ε_∞ and the results from (a)

(d) and two of τ_1 τ_2 C_1 with the third fixed at a particular value.

The programs were originally compiled in Autocode for an Elliot 803 computer by M.D.Magee and R.B.Dagnall of Aston University.
At Lakehead these programs were rewritten in I.B.M. P.L./1 for a I.B.M. 360-40 computer using the same subroutine format with minor changes (viz: step sizes) required for the more sophisticated computer.
For a full account of the errors involved in the various relationships and an assessment of the programs, see reference (2).

(a) The equations and constants for the bridge method may be found in preceding theses$^{(1)(2)(17)(32)}$, the slopes of attenuation versus volume and phase versus volume were found by the method of least squares as the lines can be described by the equation:

$$y = mx + c \tag{1:40}$$

and so the slope,

$$m = \frac{\Sigma xy - \bar{y}\,\Sigma x}{\Sigma x^2 - \bar{x}\,\Sigma x} \tag{1:41}$$

where x = volume added

y = attenuation or phase change.

The computer "recognises" the frequency being determined by the magnitude of m and assigns the appropriate constants for calculation of ε' and ε". It also determines the standard deviations of the slopes, from which it computes the errors in ε' and ε" according to the theory of transmission of errors; this provides a useful check on the reliability of the results.

(b) The remaining three programs all use the same basic format; guesses of the required parameters are inserted into the appropriate equations and values of ε' and ε" are calculated and compared with the observed values by use of a function A,

where $$A = \sum(\varepsilon''_{obs} - \varepsilon''_{calc}) + \sum\left(\frac{\varepsilon'_{obs} - \varepsilon'_{calc}}{n}\right)^2 \tag{1:42}$$

the second term containing a scaling factor η chosen to reduce the errors in ε' to about the same magnitude as those in ε",

for the bridge frequencies $n = 4$

for the Grant cell frequencies $n = 6$

The computer takes each variable in turn and augments it by given step sizes so that A is reduced, the variables have upper and lower limits within which the computer works, the step sizes are reduced till two complete cycles fail to improve A, then the final values of the variables and the dielectric constant and loss at each frequency are recorded together with the current step sizes, the final function value and the number of evaluations of A performed during the program. The size of A indicates how well the final analysis fits the experimental points, also depending, of course, on the number of frequencies used in the calculation - for reliable results no less than four points (excluding ε_0) are required.

To determine τ_0 α ε_∞ the Cole-Cole equations (1:28) and (1:29) are used; the input data including the following:- number of microwave points, dielectric constants and losses with the appropriate angular frequency and value of n, guesses of the three variables, ε_0 and the solvents dielectric constant to provide a restraint for ε_∞.

In principle ε_∞ could be measured, but this is experimentally difficult and is not generally attempted by workers in the field of dielectric absorption. The Cole-Cole equations assume the data to lie on a sector of a circle, the lower intercept of which on the ε' axis being taken to be ε_∞. The computer program thus gives a value for ε_∞ which best fits, mathematically, the experimental data and this value is then used in the remaining two types of program which employ the Budo equations (1:30 - 32) for determining molecular and intramolecular relaxation times. There has been some discussion in the literature on the validity of applying both the Cole-Cole and the Budo relationships to one set of experimental data$^{(95)}$, but Magee$^{(2)}$ has shown that the ε_∞ value obtained from the former is accurate (depending on the τ_1/τ_2 ratio and C_1) within the limits.

$$\varepsilon_\infty \text{ (true)} \geqslant \varepsilon_\infty \text{ (Cole-Cole)} \qquad (1:43)$$

$$\varepsilon_\infty \text{ (true)} \leqslant \varepsilon_\infty \text{ (Cole-Cole)} + 0.42\alpha\left[\varepsilon_0 - \varepsilon_\infty \text{ (Cole-Cole)}\right] \qquad (1:44)$$

The ε_∞ obtained from the computer has, therefore, been used with these limitations borne in mind; in certain cases, however, for example, viscous solution and large molecule studies where the τ_1/τ_2 ratio is large the Cole-Cole and Budo equations have been found to be inadequate and graphical methods (cf (ii) a and (ii) b) have been employed to determine the relaxation parameters.

(c) For calculation of τ_1 τ_2 and C_1 by the Budo computer analysis the same input data is inserted as in (b) with the exclusion of the solvent dielectric constant and the inclusion of ε_∞, together with the expected limits of the relaxation times.

(d) Sometimes the computer gives τ_1 τ_2 C_1 parameters which, although the best mathematical fit of the experimental results, do not coincide with what is already known about the molecule ($\tau_1 \neq \tau$ of similar sized rigid molecule, τ_2 and C_1 are at odds with the results at other temperatures - cf. Chapter 2 for full explanation) and, therefore, no physical meaning can be assigned to them. If, after changing ε_∞ within the limits quoted above, no distinct change occurs and the physical evidence warrants it, one of the three parameters may be fixed and only two varied in the Budo relationship. The computer input is, thus, identical to that in (c). Care must be exercised with the results to ensure that the final A function is of normal proportions.

(ii) Graphical Methods

(a) τ_o may be obtained by plotting the function $\log \frac{v}{u}$ against $\log \omega$, this follows from the relation

$$\frac{v}{u} = (\omega\tau_o)^{1-\alpha} \qquad (1:45)$$

where v is the distance between ε_o and an experimental point on the Cole-Cole arc at an angular frequency ω, and u is the distance from that point to ε_∞. The intercept with the abscissa at $\log \frac{v}{u} = o$ gives $\log \omega_{max}$, from which τ_o may be evaluated:

$$\tau_o = \frac{1}{\omega_{max}} \qquad (1:46)$$

(b) By eliminating ε_∞ from the Debye dispersion equations (1:24 and 1:25) a useful expression relating ε' and ε'' is obtained

$$\varepsilon' = \varepsilon_0 - \tau\,(\omega\varepsilon'') \qquad (1:47)$$

For systems showing Debye behaviour (one relaxation time) or where the ratio τ_1/τ_2 (given the notation k) is small a linear plot of ε' vs $\varepsilon''\omega$ may be drawn, the slope of which is equivalent to the mean relaxation time. Since ε_0 is the most accurate measured dielectric parameter, the line is normally forced through this point. As k increases the plot becomes a curve, the limiting slopes corresponding roughly to τ_1 and τ_2(90), when k is increased still further and the absorptions due to the two relaxation mechanisms completely separate (cf Chapter 4), two distinct slopes are obtained from which the relaxation times may be determined with greater accuracy.

(c) A direct, but more cumbersome method of determining ω_{max} and, thus, the relaxation time is by plotting the dielectric loss against the angular frequency. For this type of plot molecules exhibiting Debye behaviour give a sharp symmetrical peak, whereas those with more than one relaxation time exhibit broader curves which are frequently asymmetrical, especially as the size of k increases. When k is very large two maxima will occur and several authors have used this method to estimate the relaxation times of such systems by determining the Debye absorption attributable to each process(21)(73)(57). The ε'' vs log ω plot requires more frequency determinations than any other method to provide only approximate relaxation times, since in the majority of cases the top of the maxima is broad and estimation of ω_{max} is difficult.

E. Solvent Parameters

(i) Dielectric Constants and Densities

The solvent dielectric constants and densities employed as standard parameters in the static constant and dipole moment determinations were obtained from the normal sources(157)(158). The variation of the former with temperature (t) was calculated by

$$\varepsilon_a' = \varepsilon_b' - x\,(t_a - t_b) \qquad (1:48)$$

when the temperature in question was close to reported values, or, if this was not the case by

$$\log \varepsilon_a' = \log \varepsilon_b' - \alpha\,(t_a - t_b) \qquad (1:49)$$

where x and α are constants applicable to a particular solvent. ε' was also periodically checked by measurement of cyclohexane and p-xylene at X band frequency. The values used are listed in Table 1:3.

TABLE 1:3

Solvent Parameters at Various Temperatures

Solvent Temperature ^{0}C	Cyclohexane ε_1	Cyclohexane d_1	p-xylene ε_1	p-xylene d_1	Toluene ε_1
15	2.031	0.7831	2.278	0.8654	2.410
25	2.016	0.7739	2.263	0.8567	2.383
32.5	2.003	0.7668	2.246	0.8501	2.364
40	1.990	0.7596	2.234	0.8435	2.348
50	1.973	0.7502	2.219	0.8347	2.325
60	1.957	0.7406	2.206	0.8261	2.298

d_1 = density in gms/ml

(ii) p-Xylene Corrections

Above 16.2 G c/s, p-xylene has a small but detectable dielectric absorption and corrections for this were made to measurements on solutions employing this solvent. The dielectric constant and loss of p-xylene were determined at O, Q and K band frequencies periodically, although the variance from batch to batch was normally found to be well within the experimental errors of the technique, and the mean corrections are presented in Table 1:4

where ε' correction factor, (ε_{corr}) = ε_1(p-xylene) - ε'(p-xylene)

and is added to the solution value, so

$$\varepsilon'_{true} = \varepsilon'_{meas} + \varepsilon_{corr} \qquad (1:50)$$

while the ε" correction factor (ε''_{corr}) = ε" (p-xylene) which is substracted from the solution value

$$\varepsilon''_{true} = \varepsilon''_{meas} - \varepsilon''_{corr} \qquad (1:51)$$

Frequency Temperature	ε'_{corr} O	ε'_{corr} Q	ε'_{corr} K	ε''_{corr} O	ε''_{corr} Q	ε''_{corr} K
15	0.0127	- 0.0083	0.0049	0.0075	0.0048	0.0038
25	0.011	- 0.0094	0.0040	0.0073	0.0045	0.0033
32.5	0.010	- 0.0102	0.0034	0.0072	0.0043	0.0030
40	0.0088	- 0.0111	0.0027	0.0071	0.0041	0.0027
50	0.0072	- 0.0122	0.0018	0.0070	0.0038	0.0024
60	0.0058	- 0.0134	0.0009	0.0068	0.0034	0.0019

TABLE 1:4 P-XYLENE CORRECTIONS (ε_{corr}) FOR O, Q AND K FREQUENCIES AT VARIOUS TEMPERATURES

F. Purification of Materials

(i) Solvents

Cyclohexane and p-xylene were purified by refluxing over sodium followed by distillation through a two foot column packed with glass rings. They were stored in well closed amber bottles over sodium wire, the purity being checked periodically by dielectric constant measurements and gas liquid chromatography analysis. A high degree of purity was attained for toluene, which was employed as a secondary standard in the ε_0 determination, by using a preparative gas-liquid chromatography technique. Nujol, purchased from a local drugstore, was placed under vacuum for an hour to remove dissolved gas which might be present and then used without further purification.

(ii) Solutes

The chemicals were obtained from commercial sources and their identity checked by either, Mass Spectrometry using a Hitachi RMU-7 double focusing mass spectrometer, or N.M.R. integral analysis, employing a Varian A60-A N.M.R.spectrometer.

Liquids were dried over a suitable drying agent, when necessary, and distilled on a Nester Faust spinning band column of either 30 or 125 theoretical plates; a small, constant boiling point centre fraction being collected and the purity confirmed by gas-liquid chromatography.

Solids were recrystallised at least twice (with charcoal, if required) until a constant melting point was obtained, dried by phosphorus pentoxide under vacuum, and if G.L.C. analysis proved impossible the purity was established by infra-red spectroscopy.

Halogen substituted molecules are frequently light sensitive and so solutions of these compounds were stored in darkened glassware immediately after purification. Aldehydes are also known to be easily oxidised by atmospheric oxygen by a free radical process (auto-oxidation) and to prevent this a small amount of catechol ($\sim 0.1\%$) was added to the solute after purification and analysis. The purification and storing of liquid aldehydes were carried out under an atmosphere of nitrogen, any acid present being removed by washing with aqueous sodium carbonate and to ensure that no acid remained the infra-red spectrum of the final product was examined.

The purification of the solutes is summarised in Table 1:5, which is divided into sections (a) to (e) corresponding to the compounds discussed in Chapters 2 to 6 respectively, of this thesis. The reported melting and boiling point values are uncorrected and an explanation of the abbreviations used may be found at the end of the table.

TABLE 1:5 PURIFICATION OF SOLUTES

	Solute	Purification	Liquid Drying Agent	Melting Point °C	Boiling Point °C	Dist. Pressure mm.
(a)	p-fluoroacetophenone	S.B.			198-200	750
	p-chloroacetophenone	D/V			82- 83	3
	p-bromoacetophenone	D/V			110-113	7
	p-iodoacetophenone	R petrol-ether (60-100)		81-83		
	p-methylacetophenone	S.B./V	Sodium sulphate		129-131	8
	p-ethylacetophenone	S.B./V	"		128	12
	2-acetonaphthone	R petrol-ether (60-80)		54-55		

Solute	Purification	Liquid Drying Agent	Melting Point °C	Boiling Point °C	Dist. Pressure mm
1-acetylcyclohexene	preparative G.L.C.				
Trans.4-phenyl-3-buten-2-one	R petrol-ether (60-110)		40-41		
2-acetylphenanthrene	R methanol/C		144-145		
3-acetylphenanthrene	R petrol-ether (60-110)/C		72-73		
9-acetylphenanthrene	R petrol-ether (60-40)/C		73-74		
acetophenone	S.B.	magnesium sulphate		199	756
4-acetylpyridine	S.B.			214-215	735
(b) 2-chloroacetophenone	S.B.			226-228	737
2,5-dichloroaceto phenone	S.B.			251-253	745
2,4,6-trimethyl-acetophenone	S.B.			238-240	748
9-acetylanthracene	R 95% ethanol-water		74-76		
(c) 2-fluoroanisole	S.B.			159	731
2-bromoanisole	S.B.			220-222	740
2-iodoanisole	W.dilute caustic potash and sodium thiosulphate, D over calcium			77- 79	5-6
2,4,6-tribromoanisole	R ethanol		87-88		
2,6-dimethylanisole	S.B.			182	746
phenetole	S.B./V	calcium sulphate		62	13

Solute	Purification	Liquid Drying Agent	Melting Point °C	Boiling Point °C	Dist. Pressure mm
2-bromophenetole	S.B.			228-230	739
2-ethoxynaphthalene	R methanol/water		35-37		
cholesterylmethyl-ether	received pure from Sigma Chem.Co. U.S.A.		83		
(d) benzaldehyde	W 10% sodium carbonate/water and D/VN	Magnesium, sulphate		(i) 71 (ii) 39-41	11 1.8
2-naphthaldehyde	W 10% sodium carbonate/water and D/VN		59-60	130-133	4.5
crotonaldehyde	S.B./N	calcium sulphate		105	740
terephthalaldehyde	R methanol/water/C		114-116		
p-nitrobenzaldehyde	R petrol-ether (60-80)		107-108		
p-fluorobenzaldehyde	S.B./VN			76-77	20
p-chlorobenzaldehyde	D/VN, R ethanol/water		47-48	72-75	3
p-bromobenzaldehyde	received pure from Koch-Light Labs.Ltd. Eng.		57-58		
(e) o-diiodobenzene	R ethanol		24-25		
o-bromoiodobenzene	S.B./V light excluded	calcium sulphate		121-123	6.5
o-chloroiodobenzene	S.B./V light excluded	calcium sulphate		96-97	8
m-diiodobenzene	R ethanol/ether		34-35		

Solute	Purification	Liquid Drying Agent	Melting Point ^oC	Boiling Point ^oC	Dist. Pressure mm.
m-bromoiodobenzene	S.B./V			114-116	9
2-iodonaphthalene	R ethanol/water/C		52-53		

Abbreviations:		
	S.B.	Spinning band distillation
	D	fractionally distilled
	V	under vacuum
	VN	under vacuum with a nitrogen atmosphere
	R	recrystallised with
	C	charcoaled
	W	washed with

G. Presentation of Results

The relaxation times (τ), weight contributions (C), distribution coefficient (α), dipole moment (μ) and where applicable, energy barrier parameters to rotation ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) and the $\varepsilon_{\infty} - n_D$ term are listed in tabular form in the relevant chapter. While the experimentally determined parameters, static dielectric constant (ε_o), dielectric constant and loss (ε', ε''), refractive index (n_D), densities and weight fraction may be found in the appendix. Also listed in the same appendix table (Table A:2) are the calculated dielectric constant and loss determined from equations 1:28 - 1:32, and the dielectric constant at infinite frequency (ε_{∞}).

CHAPTER 2

ACETYL GROUP ROTATION IN AROMATIC AND ALIPHATIC MOLECULES.

ACETYL GROUP ROTATION IN AROMATIC AND ALIPHATIC MOLECULES

Introduction

There has been considerable interest shown by chemists in the behaviour of the acetyl group on aromatic and aliphatic molecules. Physical chemical investigations have included dipole, I.R., N.M.R. and U.V. measurements. However, published work on microwave dielectrics in this field has been comparatively small and the consequences limited for the following reasons: workers have either studied at too few frequencies or measured molecules which have a high weighting to molecular rotation and thus the true effect of the acetyl group cannot be gauged accurately, if at all.

To combat the latter of these failings, this present work was initiated to study molecules which had very little or no weighting to molecular relaxation, and it was hoped that only acetyl relaxation would be observed. This was to be achieved in the following manner: the majority of the acetyl group dipole, results from the attraction by the oxygen of the π electrons in the double bond of the carbonyl group - thus the resultant dipole in an aromatic methyl ketone, such as acetophenone is directed away from the benzene ring at an angle θ to the C_1-C_4 axis of the ring. Placing in the para position an electron withdrawing group of such a magnitude that the angle of the resultant dipole θ to the C_1-C_4 axis was 90° would produce a molecule which would have virtually no intermolecular reorientation in the microwave region. The correction of the other failing of past workers was to simply measure at no fewer than five microwave frequencies.

A co-worker in this laboratory has also made a study of acetyl compounds(1) and for reasons that will become apparent later, this work was extended to other acetyl derivatives in which the orientation of the resultant dipole to the main axis was varied; the degree of conjugation of the carbonyl group was also changed and several different solvent conditions were used. Owing to the increased amount of data this chapter has been sectionalised into the following parts:

(a) Parasubstituted acetophenones
(b) The effect of conjugation on acetyl group rotation
(c) Large acetyl molecules
(d) Studies in viscous solutions
(e) Conclusions and summary

Although each section is a separate research topic in its own right, it is felt that the evidence obtained should be treated as a whole, since the sections are interrelated. The main object of this study is to determine the extent of acetyl group rotation in various aliphatic and

TABLE 2:1 DIELECTRIC RELAXATION PARAMETERS AND DIPOLE MOMENTS OF CERTAIN ACETYL COMPOUNDS

(a) PARA-SUBSTITUTED ACETOPHENONES.

COMPOUND	SOLVENT	TEMP.	τ_o	τ_1	τ_2	C_1	α	μ
		°C		$\times 10^{12}$	sec			D
p-fluoro acetophenone	p-xylene	15	16.5	31.1	13.9	0.25	0.03	2.29
		25	14.2	25.4	12.1	0.25	0.02	2.29
		40	11.4	17.4	10.0	0.25	0	2.24
		50	10.0	13.3	9.0	0.25	0	2.25
		60	8.8	11.7	8.0	0.25	0	2.24
	cyclohexane	15	13.0	31.0	10.5	0.25	0.06	2.29
		25	10.7	20.7	8.9	0.25	0.04	2.26
		40	8.7	11.5	7.9	0.25	0.01	2.24
		50	7.9	10.8	7.0	0.25	0	2.24
p-chloro acetophenone	p-xylene	40	12.3	14.6	12.0	0.25	0	2.24
	cyclohexane	15	14.7	32.6	12.1	0.25	0.05	2.25

COMPOUND	SOLVENT	TEMP °C	τ_o	τ_1 $\times 10^{12}$ sec	τ_2	C_1	α	μ D
	cyclohexane	25	12.7	23.4	10.7	0.25	0.04	2.25
		40	10.1	17.7	8.6	0.25	0.03	2.25
p-bromo acetophenone	p-xylene	15	18.5	31.5	15.8	0.25	0.02	2.27
		40	12.7	17.6	11.5	0.25	0	2.25
	cyclohexane	15	16.1	42.0	13.3	0.25	0.04	2.29
		25	14.0	37.0	10.8	0.25	0.07	2.32
		40	11.4	26.1	9.3	0.25	0.04	2.31
p-iodo acetophenone	p-xylene	15	18.0	47.4	14.2	0.25	0.08	2.40
		25	15.4	33.9	12.7	0.25	0.06	2.39
		40	12.3	22.6	10.4	0.25	0.03	2.33
		50	11.4	21.5	9.6	0.25	0	2.33
	cyclohexane	25	14.8	48.1	11.6	0.25	0.08	2.33
		40	11.4	34.6	9.0	0.25	0.09	2.33

COMPOUND	SOLVENT	TEMP	τ_o	τ_1	τ_2	C_1	α	μ
		°C		$\times 10^{12}$ sec				D
P-methyl	p-xylene	25	18.4	28.6	9.9	0.55	0.08	3.13
Acetophenone		50	13.4	18.3	7.9	0.6	0.04	3.12
	cyclohexane	25	16.0	28.0	8.7	0.55	0.09	3.15
		50	11.2	16.8	5.5	0.63	0.08	3.16
P-ethyl	p-xylene	25	22.7	32.3	9.8	0.71	0.09	3.16
Acetophenone		50	15.5	21.2	8.1	0.68	0.05	3.11
	cyclohexane	25	20.4	31.3	7.7	0.69	0.12	3.20
		50	14.1	22.9	6.3	0.63	0.10	3.19

(b) THE EFFECT OF CONJUGATION ON ACETYL GROUP ROTATION.

2-Acetonaph-	p-xylene	15	34.9	44.2	13.1	0.8	0.08	3.04
thone		25	30.3	37.0	14.8	0.78	0.05	3.03

COMPOUND	SOLVENT	TEMP	τ_o	τ_1	τ_2	C_1	α	μ
		°C		x10^{12}sec				D
	p-xylene	40	23.1	29.2	12.8	0.73	0.04	3.00
		50	20.7	25.2	10.8	0.78	0.04	2.98
	cyclohexane	25	28.2	35.7	9.7	0.8	0.07	2.97
		40	21.6	24.1	8.7	0.88	0.03	2.99
1-acetyl cyclohexene	p-xylene	15	16.0	58.3	13.7	0.17	0.06	3.15
		32.5	13.0	50.6	11.0	0.17	0.06	3.18
		50	10.1	25.0	9.2	0.13	0.02	3.10
trans 4-phenyl-3-buten-2-one	p-xylene	15	29.1	65.5	17.4	0.44	0.11	3.20
		60	15.1	28.2	9.8	0.46	0.08	3.15

(c) LARGE ACETYL MOLECULES.

COMPOUND	SOLVENT	TEMP. °C	τ_o	τ_1	τ_2	C_1	α	μ	$\epsilon_\infty - n_D^2$
			$\times 10^{12}$ sec						
2-acetyl Phenanthrene	p-xylene	60	30.7	40.2	10.0	0.80	0.09	3.08	0.03
3-acetyl Phenanthrene	p-xylene	25	49.2	57.1 50.7*	13.5 15.3*	0.85	0.07	3.01	0.043
9-acetyl Phenanthrene	p-xylene	15	50.0†	68.5*	6.0*	–	0.07	2.80	0.061
		25	40.7†	50.4*	5.9*	-	0.09	2.85	0.059
		50	29.9†	32.3*	4.9*	-	0.04	2.79	0.050

(d) STUDIES IN VISCOUS SOLUTIONS AT 25°C

COMPOUND	SOLVENT	SOLVENT VISCOSITY η c.p.s.	τ_o	τ_1	τ_2	α	μ
			$\times 10^{12}$ sec				
Acetophenone	Nujol	166	65.0†	85*	8.5*	0.19	2.82
4-Acetyl Pyridine	Nujol + P-xylene	53.7	43.9†	68*	15*	0.20	2.28
4-Bromo Acetophenone	Nujol + Cyclohexane	62	103†			0.123	2.20
	Nujol	166	194†			0.212	2.27
3-Acetyl Phenanthrene	Nujol + P-xylene	9.0	181†	190*	15*	0.10	3.00

† τ_o calculated from log v/μ vs log ω plot.

* τ_1 τ_2 " " ε' vs $\varepsilon''\omega$ plot.

Table 2:2:a ENERGY BARRIERS TO ACETYL GROUP RELAXATION $\Delta G_2^{\ddagger}$

SOLVENT		CYCLOHEXANE			P-XYLENE			DECALIN		
COMPOUND	T °c	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
		- Kcal mole^{-1}		- e.u.	- Kcal mole^{-1}		e.u.	- Kcal mole^{-1}		- e.u.
	15	2.20	1.2	-3.4	2.33	1.3	-3.6	2.56	1.6	-3.3
	25	2.18	1.2	-3.3	2.36	1.3	-3.6	2.56	1.6	-3.2
	40	2.23	1.2	-3.3	2.42	1.3	-3.6	2.59	1.6	-3.2
Acetophenone	50	2.28	1.2	-3.3	2.41	1.3	-3.4	2.65	1.6	-3.3
	60				2.49	1.3	-3.6	2.63	1.6	-3.1
p-Fluoro	15	2.37	1.3	-3.7	2.53	1.7	-2.9			
Acetophenone	25	2.38	1.3	-3.6	2.55	1.7	-2.9			
	40	2.45	1.3	-3.7	2.60	1.7	-2.9			
	50	2.47	1.3	-3.6	2.63	1.7	-2.9			
	60				2.66	1.7	-2.9			

COMPOUND	T °c	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	15	2.45	1.6	-3.0						
p-Chloro	25	2.48	1.6	-3.0						
Acetophenone	40	2.50	1.6	-2.9						
p-Bromo	15	2.50	1.7	-2.8	2.60	1.5	-3.9			
Acetophenone	25	2.49	1.7	-2.7	2.65	1.5	-4.0			
	40	2.55	1.7	-2.7	2.68	1.5	-3.9			
p-iodo	15				2.54	1.5	-3.8			
Acetophenone	25				2.59	1.5	-3.8			
	40				2.62	1.5	-3.7			
	50				2.67	1.5	-3.6			
p-methyl	25	2.36	1.4	-3.2	2.44	1.2	-4.5			
Acetophenonone	50	2.32	1.4	-2.9	2.55	1.2	-4.5			
p-ethyl	25	2.29	0.9	-4.6	2.43	0.9	-5.3			
Acetophenone	50	2.40	0.9	-4.6	2.57	0.9	-5.4			

COMPOUND	T°C	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}_{2}$	$\Delta H^{\ddagger}_{2}$	$\Delta S^{\ddagger}_{2}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
1-Acetyl Cyclohexene	15				2.52	1.6	-3.2			
	32.5				2.58	1.6	-3.2			
	50				2.65	1.6	-3.3			
2-Aceto Naphthalene	15				2.50	1.8	-2.4			
	25				2.67	1.8	-2.9			
	40				2.75	1.8	-3.0			
	50				2.75	1.8	-2.9			

TABLE 2:2 : b $\Delta G_1^\ddagger$ ENERGY BARRIERS TO MOLECULAR RELAXATION

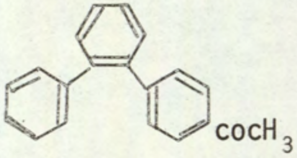
		CYCLOHEXANE			P-XYLENE			DECALIN		
COMPOUND	T°c	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
		-Kcal mole^{-1}		e.u.	-Kcal mole^{-1}		e.u.	Kcal mole^{-1}		e.u.
	15	2.61	2.2	-1.4	2.73	2.3	-1.5	2.89	2.6	-1.0
Acetophenone	25	2.68	2.2	-1.6	2.81	2.3	-1.7	2.94	2.6	-1.1
	40	2.65	2.2	-1.4	2.76	2.3	-1.5	2.91	2.6	-1.0
	50	2.65	2.2	-1.4	2.78	2.3	-1.5	2.94	2.6	-1.1
	60				2.76	2.3	-1.4	2.95	2.6	-1.1
p-Methyl	25	2.93	1.9	-3.5	2.94	2.8	-0.5			
Acetophenone	50	3.03	1.9	-3.6	3.08	2.8	-0.9			
p-Ethyl	25	3.12	1.8	-4.6	3.14	2.6	-1.8			
Acetophenone	50	3.23	1.8	-4.6	3.18	2.6	-1.8			
p-Fluoro	15				2.99	3.6	+2.1			
Acetophenone	25				3.00	3.6	+2.0			
	40				2.95	3.6	+2.1			
	60				2.91	3.6	+2.1			

COMPOUND	T °C	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
p-Bromo Acetophene	15	3.16	2.9	-0.9						
	25	3.22	2.9	-1.1						
	40	3.19	2.9	-0.9						
2-Aceto-Naphthone	15				3.2	2.4	-2.8			
	25				3.22	2.4	-2.8			
	40				3.26	2.4	-2.8			
	50				3.30	2.4	-2.8			

TABLE 2:3: a LITERATURE VALUES OF RELAXATION TIMES OF ACETOPHENONE AND DERIVATIVES, TOGETHER WITH ENTHALPIES OF ACTIVATION FOR MOLECULAR RELAXATION (1) AND FOR INTRAMOLECULAR RELAXATION (2) IN Kcals/mole.

COMPOUND	SOLVENT	TEMP.	τ_o	τ_1	τ_2	C_1	μ	$\Delta H^{\ddagger}$	REF
		°C		x 10^{12} sec					
Acetophenone	Benzene	25	11.8	11.2 (calc)					9
	Carbon Tet.	25	13.0	13.8 (calc)					
	" "	19.5	11.9				2.96		25
	Benzene	20		13.4	1→3	0.95			14
	p-xylene	15	14.3	24.5	10.8	0.33	2.83	2.2(1)	1
		25	12.8	22.0	9.7	0.33	2.84	1.9(2)	
		40	10.2	16.6	7.9	0.33	2.82		
		50	9.0	14.4	6.8	0.33	2.80		
	cyclohexane	15	11.5	18.2	8.9	0.33	2.84	1.8(1)	
		25	10.2	17.2	7.8	0.33	2.82	2.2(2)	
		40	8.0	13.0	6.0	0.33	2.84		

COMPOUND	SOLVENT	TEMP. °c	τ_0	τ_1	τ_2	C_1	μ	$\Delta H^{\ddagger}$	REF
			$\times 10^{12}$ sec						
	Decalin	15	20.1	31.4	15.4	0.33	2.76	2.2(1)	
		25	17.5	22.1	13.4	0.33	2.74	2.3(2)	
		40	13.1	20.2	10.3	0.33	2.74		
Acetylcyclohexane	p-xylene	15	9.9	24.0	8.8	0.13	2.59		
		25	9.0	34.4	8.2	0.13	2.58	1.3(2)	
		40	7.6	10.5	7.2	0.13	2.53		
2-Acetyl Pyridine	Benzene	20	7.88					2.3	26
		20	16.8						27
4 Acetyl Pyridine	Benzene	20		12.8	1.4	0.88			
	p-xylene	25	14.2				2.30		1
		40	11.2				2.27	1.9(2)	
	decalin	40	11.6				2.22		
	Cyclohexane	20	16.4						28
o-Hydroxy Acetophenone	Cyclohexane	40	13.8	- Rigid due to Hydrogen Bonding -					28
	Decalin	20	31.0						
		40	24.0						

COMPOUND	SOLVENT	TEMP °C	τ_o	τ_1	τ_2	C_1	μ	$\Delta H^{\ddagger}$	REF
			$\times 10^{12}$ sec						
para-Chloroacetophenone	Benzene	20		14.3	2→3	0.92	2.34		14
2-Acetonaphthone	Benzene	20		33	7.3	0.86	3.15	1.8(1)	10
		30		30	7.0	0.86		1.1(2)	
		40		27	6.4	0.86			
		50		23	6.0	0.85			
4-Acetyl-o-Terphenyl	Benzene	20		100	7.5	0.88	3.12	2.5(1)	10
		30		88	6.8	0.86		1.1(2)	
		40		78	6.2	0.87			
		50		65	5.7	0.85			
p-Phenylacetophenone	Benzene	20	45.3	51	8.0	0.88	3.11	2.0(1)	11
		40	35.3	41	6.5	0.88		1.5(2)	
		60	27.0	30	4.9	0.89			

COMPOUND	SOLVENT	TEMP.	τ_o	τ_1	τ_2	C_1	μ	$\Delta H^{\ddagger}$	REF
		°C	$\times 10^{12}$ sec						
1,4-Diacetobenzene	Benzene	20	24.6	27.0	7.7	0.85	2.91	1.3	11
		40	19.0	22.0	6.2	0.84	2.86		
		60	16.2	18.0	4.9	8.82			

TABLE 2:3: b LITERATURE VALUES OF RELAXATION PARAMETERS FOR RIGID AND NON-RIGID MOLECULES STUDIED IN VISCOUS SOLUTIONS.

COMPOUND	SOLVENT	TEMP °C	SOLVENT VISCOSITY c.p.s.	τ_o	τ_1 $\times 10^{12}$ sec	τ_2	C_1	REF
	p-xylene	25	0.60	9.0	39.6	8.0	0.15	1
Anisole	Declain	20	2.61	10.8	21.9	7.0	0.35	73
		40		9.0	18.2	6.0	0.32	
	Nujol	20	211.00	19.2	69.0	7.2	0.40	
		40	61.10		46.0	6.6	0.40	
p-Bromoanisole	p-xylene	25	0.60	27.1	31.3	7.4	0.88	1
p-Chloroanisole	Nujol	20	211.00	200.0	380	10.5	0.79	73
		40	61.10		210	10.0	0.77	
p-Methylanisole	p-xylene	25	0.60	9.0	not analysed		0.00	1
	Nujol	20	211.00	16.3	100	11.5	0.30	73

COMPOUND	SOLVENT	TEMP °C	SOLVENT VISCOSITY c.p.s.	τ_o	τ_1	τ_2	C_1	REF
p-Phenylanisole	Nujol	20	211.00		345	14.6	0.44	73
		40	61.10		195	14.2	0.35	
2-Methoxy	Decalin	20	2.61	33.1	94	15.8	0.49	
Naphthalene	Nujol	20	211.00		912	20.0	0.58	
2-Ethoxy	Declain	20	2.61	56.2	122	24.5	0.45	
Naphthalene	Nujol	20	211.00	290.0	1212	24.5	0.60	
Nitrobenzene	Benzene	25	0.603	11.3				74
	Nujol	25	137.80	40.3				
4-Nitrotoluene	Benzene	25	0.603	20.6				
	Nujol	25	137.80	133.3				
2-Methyl-								
Naphthalene	Nujol	20	211.0	148.0				75
2-Bromobiphenyl	Nujol	20	226.1	407.3				62
4-Bromobiphenyl	Nujol	20	211.0	25.80				61
"	"	40	61.1	797.00				

COMPOUND	SOLVENT	TEMP	SOLVENT VISCOSITY	τ_o	τ_1	τ_2	C_1	REF
		°C	c.p.s.	$\times 10^{12}$ sec				
2-iodobiphenyl	Nujol	20	226.1	595.6				62
4-iodobiphenyl	Nujol	20	226.1	3349.0				
		40	65.3	1276.0				
Diphenyl Ether	Benzene	25	0.603	4.65				74
	Nujol	25	137.8	5.60				
	"	20	$\sim$200.0	6.20				76

aromatic molecules and the activation energy required for these processes.

Discussion of Results

Before a detailed discussion of the acetyl results is given, it would appear advisable to clarify the theoretical weight factor calculations, as these parameters are so important in the discussion of non-rigid molecules.

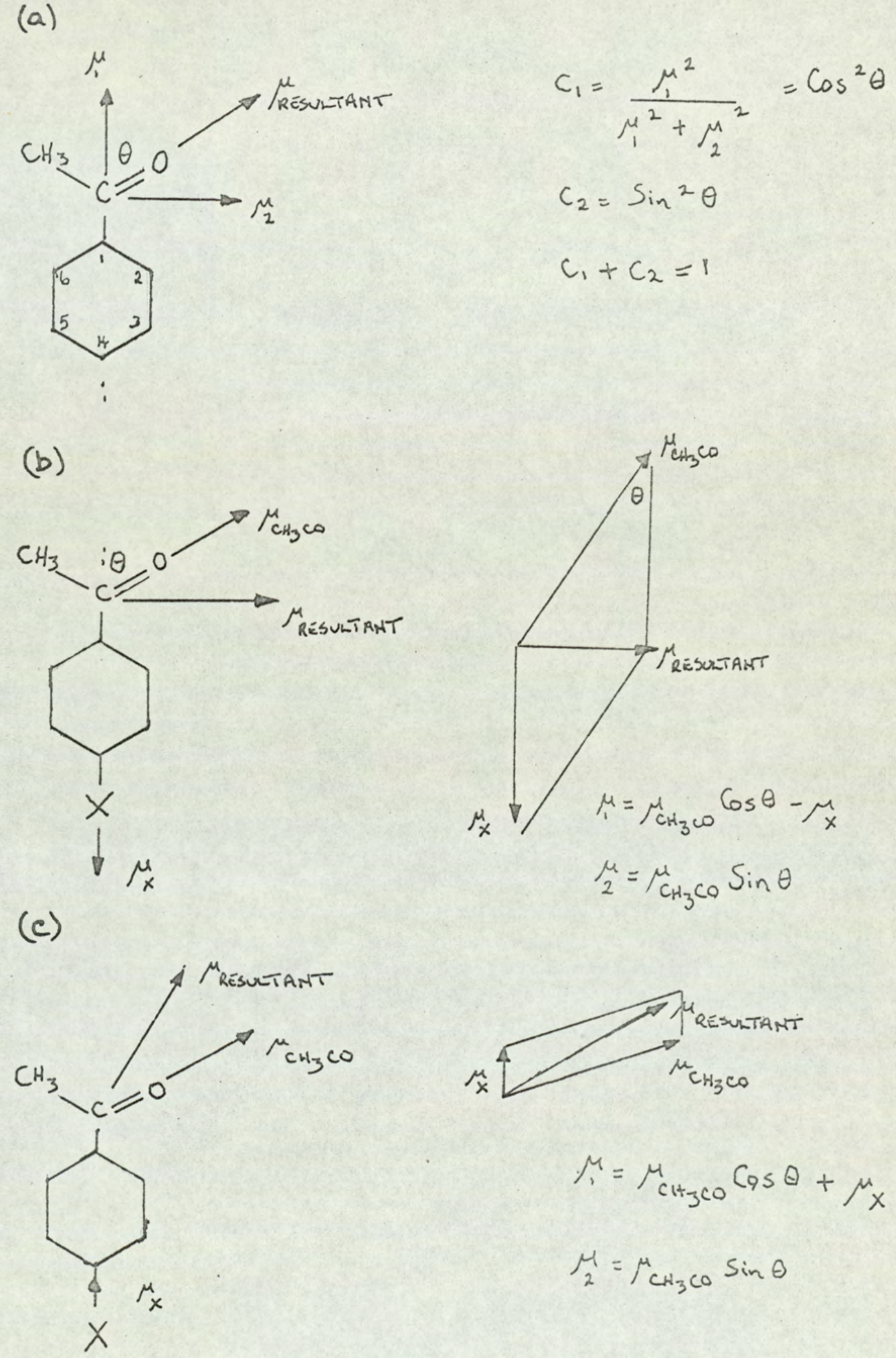
For two simultaneous independent Debye mechanisms, the Budo theory (2) gives the following equations for their weight factors C_1 and C_2.

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

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

where f_1 and f_2 are the mole fractions of the polar components of dipole moments μ_1, μ_2 of the two relaxation mechanisms.

Considering acetophenone (a monosubstituted benzene whose resultant moment is not along a symmetry axis) and it is assumed for the moment that the acetyl group is free to rotate, then the dipole moment of molecules of this type can be resolved into two



$$C_1 = \frac{\mu_1^2}{\mu_1^2 + \mu_2^2} = \cos^2\theta$$

$$C_2 = \sin^2\theta$$

$$C_1 + C_2 = 1$$

$$\mu_1 = \mu_{CH_3CO}\cos\theta - \mu_X$$

$$\mu_2 = \mu_{CH_3CO}\sin\theta$$

$$\mu_1 = \mu_{CH_3CO}\cos\theta + \mu_X$$

$$\mu_2 = \mu_{CH_3CO}\sin\theta$$

FIG 2:1 WEIGHTING FACTORS FOR ACETOPHENONE AND DERIVATIVES BY GROUP MOMENTS.

components, one along the C_1-C_4 axis, the other parallel to the C_2-C_6 axis perpendicular to the former. The latter component μ_2 (Fig. 2:1) is free to rotate intramolecularly while the other, μ_1, involves rotation of the whole molecule. Since the concentrations of the components are identical, being part of the same molecule, the above equations abbreviate to:

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

or $$C_1 = \frac{(\mu \, \mathrm{Cos}\theta)^2}{(\mu \mathrm{Cos}\theta)^2 + (\mu \mathrm{Sin}\theta)^2} = \mathrm{Cos}^2\,\theta$$

similarly $$C_2 = \mathrm{Sin}^2\,\theta$$

where θ is the angle of the acetyl group moment to the long C_1-C_4 axis. It is interesting to note that the weight factors do not depend on the size of the dipole moment in monosubstituted compounds but on the angle of inclination θ.

For disubstituted acetophenones where the substituent X is in the para position, the treatment is similar and is shown in Fig. 2:1:b and 2:1:c where X is electron withdrawing and donating respectively. Hence, the resultant dipole of the molecule will either be smaller (b) or larger (c) than that of acetophenone, and conversely the angle between the resultant and the C_1-C_4 axis will increase (b) or decrease (c) depending on the behaviour of the substituent X. Thus, placing an electron withdrawing group in the 4 position will reduce the μ_1 term (molecular relaxation) while not affecting the μ_2 term (intramolecular relaxation) as long as the resultant dipole of the X substituent is along the C_1-C_4 axis.

There are two ways of determining μ_1 and μ_2 from bond moments and bond angles, and from group moments and the angle of inclination of the group moment to the C_1-C_4 axis. The former method has been favoured by many workers but suffers from the fact that in using aliphatic bond moments it frequently neglects mesomeric effects which are important in aromatic molecules.

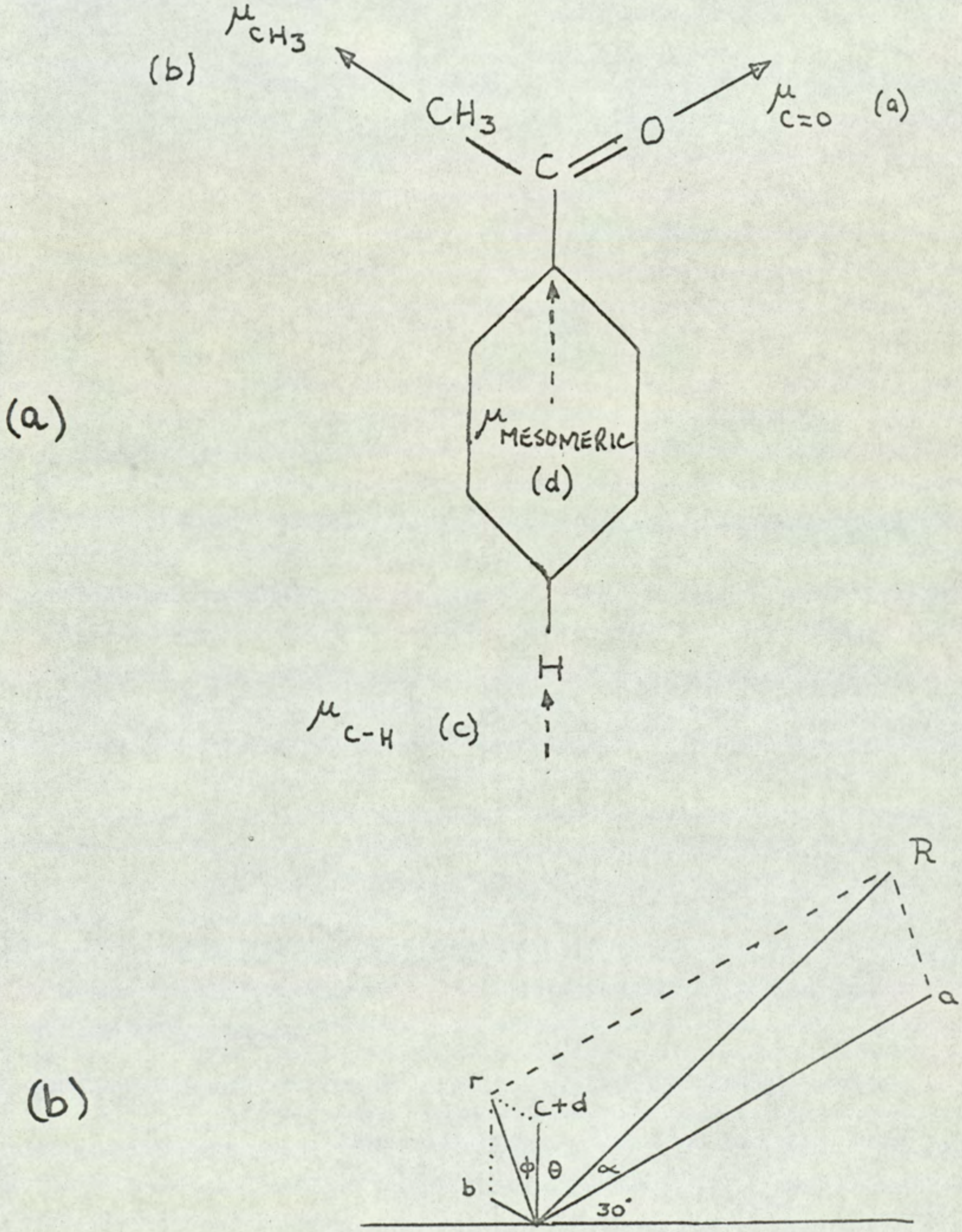
Group Moments

As aromatic rings have been found to have no dipole moment, when substituents are introduced into the benzene ring, the resulting dipole is normally taken to be that of the group(3). Thus, the remaining unknown parameter required to calculate the weight factor is the angle of inclination of this group moment. This is usually calculated from a knowledge of the moments of a parasubstituted compound which can be related to the moments of the monosubstituted parent molecule. So, a parahaloacetophenone's moment ($\mu_{\chi\phi cocH_3}$) may be related to acetophenone ($\phi cocH_3$)and the halobenzene ($\phi\chi$) using the following equation:

$$\mu^{2}_{\chi\phi coH_3} = \mu^{2}_{\phi cocH_3} + \mu^{2}_{\phi\chi} - 2\mu_{\phi cocH_3}\,\mu_{\phi\chi}\cos\theta$$

where θ = the inclination of the acetyl group moment to the main axis. The dipole moments should all be determined in the same solvent, preferably at one temperature. So, by taking the moment of 4-bromoacetophenone in p-xylene at 15°C to be 2.27D and the moments of acetophenone (1) and bromobenzene (5) under the same conditions to be 2.83D and 1.59D respectively, the resulting angle θ = 53°15'. Similar calculations using 4-chloroacetophenone, 4-acetylpyridine and 4-nitroacetophenone as the para substituted compound yield 54° 23', 52°32', and 55°. Taking an angle θ = 54° (the approximate mean of the above) produces a molecular weighting factor ($C_1 = \cos^2\theta$) for acetophenone of 0.33. Using the value of 2.83D for the acetyl group moment also gives a molecular weighting factor for parabromoacetophenone of 0.001, while a value of 0.4D for the group moment of an aromatic alkyl substituent (5) (the dipole being directed towards the ring) produces a c_1 value for paramethylacetophenone of 0.45. This form of calculation suggests that the parahaloacetophenones are ideal compounds for studying intra-molecular rotation ($C_2 \sim 1.0$). The above method of determining θ does assume that there is no mesomeric interaction between the

FIG. 2:2 CALCULATION OF THE DIRECTION OF ACETOPHENONE'S DIPOLE USING BOND MOMENTS.



acetyl group and the para-substituent.

Bond Moments

This procedure involves more assumptions than the previous method and is normally taken to be less accurate. For example, with acetophenone it must be assumed that the carbonyl group and the alkyl group make angles of 120° with each other and the long axis. Silver and Wood estimated a similar value for the H-C-O angle in benzaldehyde for use in I.R. measurements (6).

The resultant dipole of acetophenone as mentioned previously is 2.83D and considering bond moments, this must comprise of:

(a) a carbonyl group moment

(b) an aliphatic CH_3 moment, which is equivalent to a C-H (aliphatic) bond moment, since carbon is tetrahedral

(c) a moment due to the para substituted hydrogen

(d) a mesomeric moment (cf Fig. 2:2)

Using the accepted values for b, c and d(7), a may be determined.

(b) μ C-H (aliphatic) = 0.3D

(c) μ C-H (aromatic) = 0.4D

(d) μ mesomeric = 0.17D

Setting out these moments in a vector diagram (Fig. 2:2:b) the resultant (**r**) of moments b, c and d may be obtained by using the cosine theorem:

$$r^2 = (c+d)^2 + (b)^2 + 2(c+d)(b)\text{Cos } 60°$$

$$\therefore r = 0.77D$$

and also the angle (ϕ) this resultant makes with the major C_1-C_4 axis

$$b^2 = r^2 + (c+d)^2 + 2r\,(c+d)\text{ Cos }\phi$$

where $\phi = 19°26'$

Thus, as the resultant of the molecule (R) is now made up of r and a separated by an angle of ($\phi+\theta+\alpha$), 'a' being the only unknown may be determined

$$R^2 = r^2 + a^2 + 2ar\text{ Cos }(\phi+\theta+\alpha)$$

where $\phi + \alpha = 90° - 30°$

Thus $a = 2.57D$

That this value is of the correct order, can be seen by comparing it with the dipole of benzophenone (8)(2.96D) which must consist of the sum of the carbonyl moment, plus an aromatic C-H moment (assuming the carbonyl bridge angle is 120°).

α can also be determined by a similar cosine theorem calculation and therefore θ which is found to be 44°13. This figure differs by 10° from the resultant dipole angle of inclination determined using group moments and gives some idea of the errors involved. If, however, the value for θ=44° is used, the following weight factors emerge:

for acetophenone $C_1 = 0.51$
p-halocetophenones $C_1 = 0.25$
p-alkylacetophenones $C_1 = 0.61$

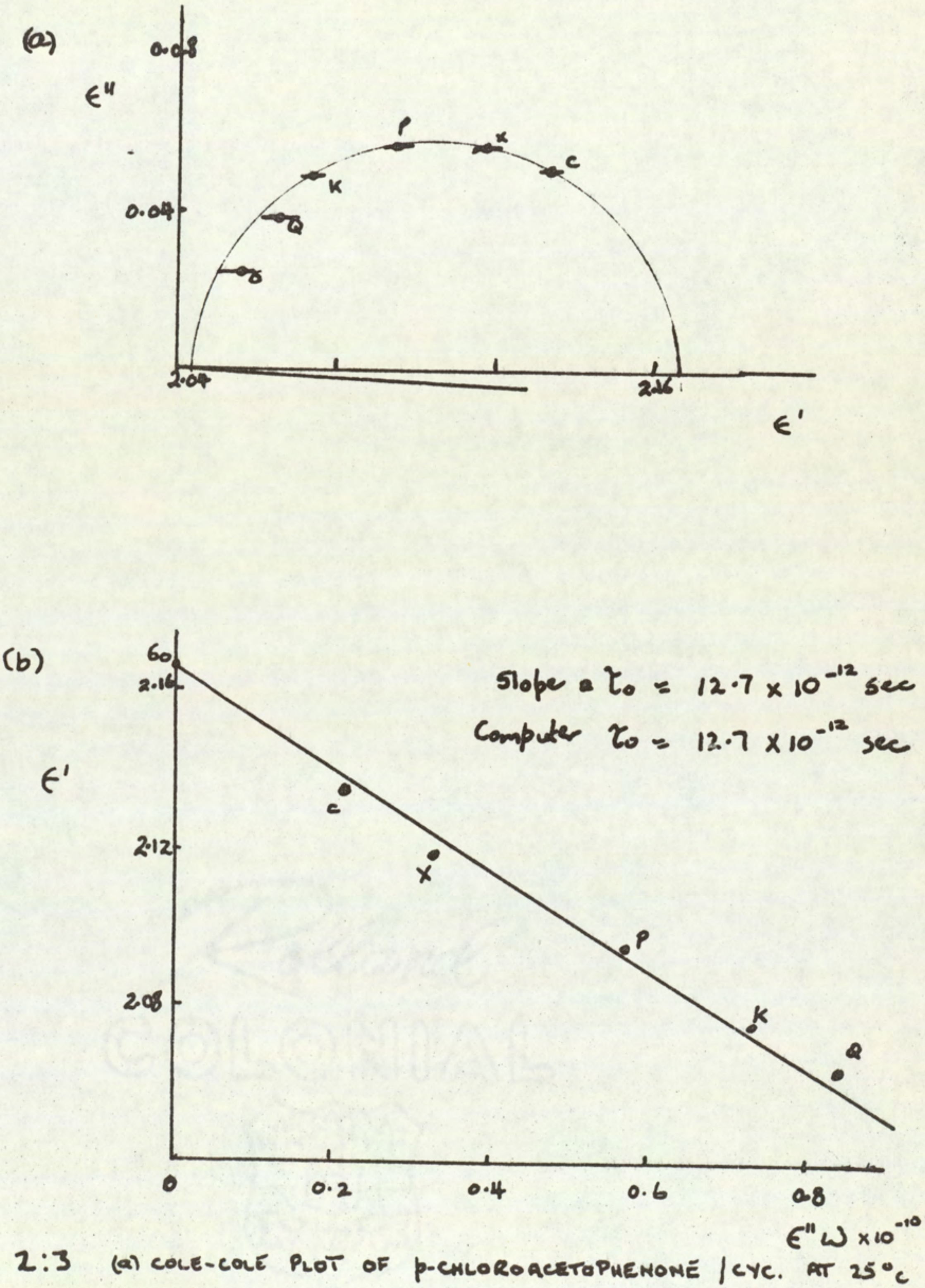
Here again, the parahalocetophenones have a low molecular orientation weighting, suggesting that they would be ideal compounds to study acetyl intramolecular relaxation.

(a) PARA SUBSTITUTED ACETOPHENONES

E. Fischer(9) originally measured acetophenone dielectrically, his results gave some indication that the acetyl group may rotate; since then Smyth and his co-workers(10)(13) as well as Klages and Knobloch[14] have measured several aromatic acetyl derivatives and have concluded that the acetyl group is mobile in such systems as acetophenone, where the acetyl is free from steric hindrance. More recently in this laboratory, Farmer(1) has measured acetophenone in several solvents and reached the same conclusions.

Normal practice for confirming the presence of two relaxation times in a molecule's dielectric absorption is to compare its mean relaxation time with that of a rigid molecule of similar shape and size.(15)(18) If intramolecular relaxation is present, this parameter will be lower than that of the rigid compound. The degree of lowering will depend on the magnitudes of τ_1, τ_2 and C_1, obviously if C_1 is small, the mean relaxation of the non-rigid molecule will tend towards the value of τ_2 and conversely, if large, towards that of τ_1 (comparable with the value of the rigid molecule). Crossley(16) and Hassell(17) have constructed theoretical tables, with various values of the above parameters to illustrate this dependence. These tables are reproduced in the appendix (Table A.1) to assist in a critical assessment of the results presented in this thesis.

p-Fluoro, chloro, bromo and iodoacetophenones were measured in cyclohexane and p-xylene solutions at several temperatures. (Table 2:1:a). The relaxation times of the p-haloacetophenones in p-xylene are longer than those obtained for the cyclohexane solutions. Such a lengthening of τ has been observed for nearly all the molecules studied in this laboratory and has been attributed to the interaction of the polar group with the Π electrons of the p-xylene. A typical Cole-Cole plot is shown in Fig. 2:3:a where it can be seen that the microwave points are distributed evenly over the majority of the dielectric absorption region. Graphs of ε' vs $\varepsilon''W$ (Fig. 2:3:b gave single straight lines whose slopes agreed with the τ_0 values obtained using the



Slope = $\tau_0 = 12.7 \times 10^{-12}$ sec

Computer $\tau_0 = 12.7 \times 10^{-12}$ sec

FIG 2:3 (a) COLE-COLE PLOT OF p-CHLOROACETOPHENONE / CYC. AT 25°C
(b) ε' VS ε''ω " " " "

Cole-Cole computer programme. Comparison of these values with the p-halotoluenes(17) (Table 2:4), which are virtually rigid molecules, shows that the acetyl compounds have much lower relaxation times, although they are larger in size. p-Bromoacetophenone may also be compared with p-bromoanisole as this compound has been shown to have a high C_1 (0.9).(1) Here again there is a significant difference in values. This data provides strong evidence of the intramolecular process in these p-substituted acetophenones. That the τ_o value obtained for p-fluoracetophenone is of the same order as that of acetophenone itself indicates that the C_1 value of the former is less than the latter, as suggested by the theoretical calculations.

TABLE 2:4

A τ_o COMPARISON OF P-HALOACETOPHENONES WITH MOLECULES OF SIMILAR SIZE

Compound	Solvent	Temp.°C	τ_o
p-chloracetophenone	cyclohexane	25	12.7
	p-xylene	40	12.3
p-chlorotoluene	cyclohexane	25	16.8
	p-xylene	40	14.0
p-bromoacetophenone	p-xylene	15	18.5
	" "	40	12.7
p-bromoanisole	" "	15	32.2
	" "	40	21.9

Compound	Solvent	Temp.°C	τ_o
p-bromotoluene	p-xylene	40	17.4
p-fluroacetophenone	cyclohexane	25	10.7
acetophenone	"	25	10.4

However a $C_1 \simeq 0.1$, as required by group moments, in effect makes $\tau_o = \tau_2$, since it is inadvisable to analyze such data into contributions from two relaxation times. Yet observation of the τ_o values from fluoro to iodoacetophenone shows a definite increase of τ with increasing molecular size. This increase is small in comparison with the increase obtained by Hassell (17) for the mono-substituted halobenzenes (cf. Fig. 2:4), although it may indicate the presence of some molecular rotation in the τ_os.

Farmer (1) analyzed his acetophenone data into two relaxation times by fixing the C_1 to the value predicted by group moments i.e. $C_1 = 0.33$. He justified this value by showing that the molecular relaxation times obtained were of similar order to those of analogous rigid molecules. The intramolecular relaxation times obtained from these analyses were 7.8×10^{-12} sec in cyclohexane at 25°C and in p-xylene at the same temperature, they are much lower than the equivalent τ_o values in the p-haloacetophenone series.

Klages and Knobloch (14) measuring p-chloroacetophenone in benzene at 20°C, produced a time for the molecular rotation of 14.3×10^{-12} sec, for the group rotation $2\text{-}3 \times 10^{-12}$ and a C_1 of 0.92!

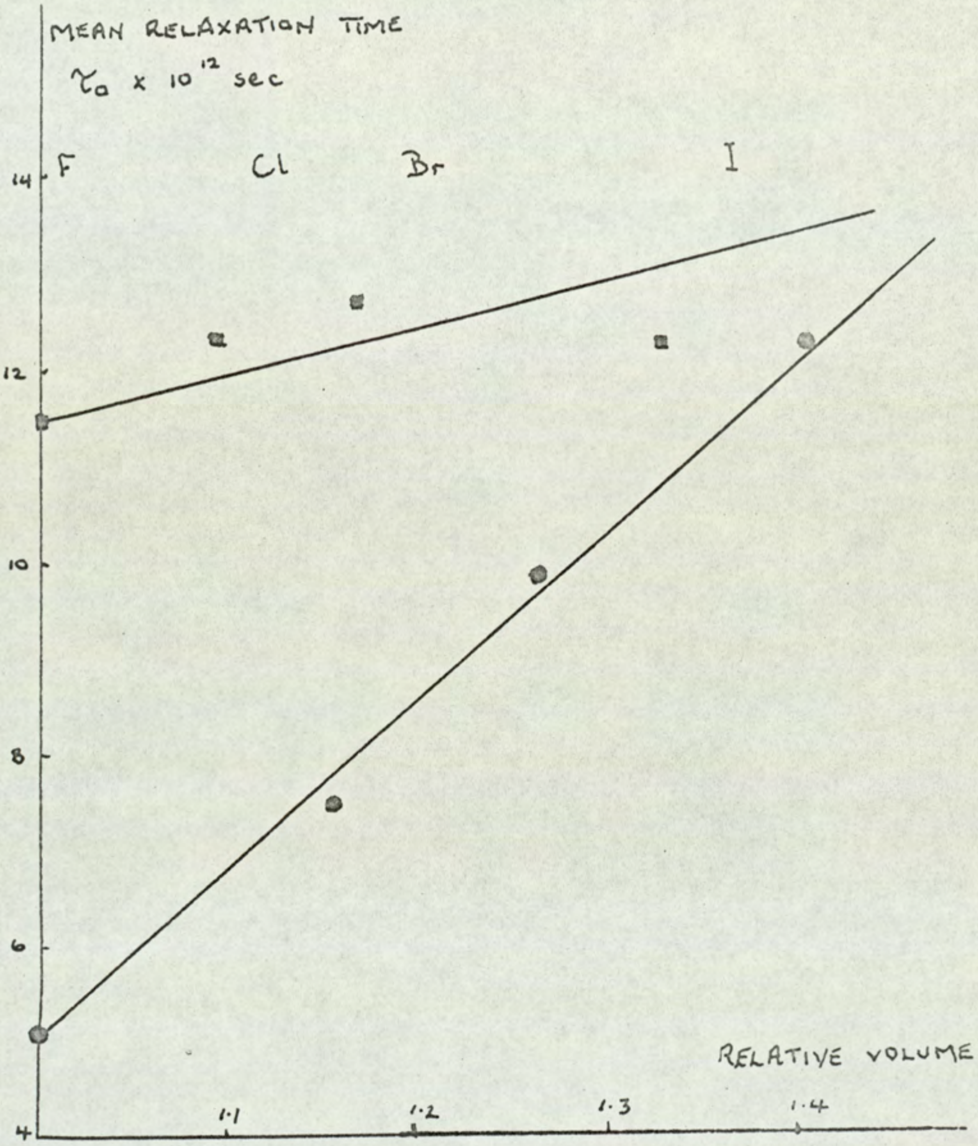


FIG 2:4:i PLOT OF τ_o vs relative volume (CALCULATED FROM COURTALD MODELS AND ATOMIC INCREMENT METHOD) FOR THE HALOBENZENES ● (29) AND THE p-HALOACETOPHENONES ■ IN p-XYLENE AT 40°C – THE FORMER τ WERE EXTRAPOLATED –.

Straightforward analysis of our data gave varying C_1s from 0.1 to 0.9, although the variation in any one compound over a number of temperatures should not be greater than ±0.1. Even though these values may be the best mathematical fit for the dielectric data, if the τ_1 parameter does not compare with the relaxation time of an analogous rigid molecule, the analysis does not have any physical meaning. Klages' and Knobloch's τ_1 value certainly does not compare with that of p-chlorotoluene, although it should, especially with a $C_1 = 0.9$. Their dielectric data is not questioned since it is comparable to our results on p-chloroacetophenone (i.e. τ_1 (Klages) $\approx$ τ_o (p-xylene) at the same temperature), however their form of analysis is questioned.

From the above remarks the following points can be made:

(i) The acetyl group does rotate in the p-haloacetophenones

(ii) C_1 from group moments would appear to be in error for these compounds, since τ_o varies with size or

(iii) The acetyl group does not have the same relaxation time when placed in different electronic conditions and, therefore, τ_2 (p-haloacetophenone) would not have to equal τ_2 (acetophenone).

It is to clarify these last two points that the remaining material in this chapter is examined.

p-alkylacetophenones

p-Methyl and p-ethylacetophenones were measured in cyclohexane and p-xylene solvents at two temperatures. In contrast to the halogens, the alkyl group donates electronic charge to the aromatic system, so increasing the molecular weighting above that of acetophenone. Thus, the mean relaxation times of the alkyl ketones are greater than those of the comparable sized haloacetophenones.

At this stage it is most probably advisable to clarify the term 'similar size' when used in connection with molecular dimensions. When comparing p-chloro, p-bromo and p-methylacetophenones, the word size is too crude a term to differentiate between them, it is more profitable to compare molecular volumes. Several methods are available for estimating the volume of a molecule, two are commonly used; the atomic increment method (19) would appear to be the most popular amongst dielectric workers (20)(21), while others (23) use Courtald models (22) to calculate this parameter. Although both methods are based on Van der Waals radii, the latter tends to give maximum values since normally workers take the three main symmetry axes and calculate the volume as a cylinder or ellipsoid, thus neglecting to take into account the space in between individual atoms. Nor is the former method perfect as it cannot differentiate between isomers which have different volumes. Therefore, in this thesis both methods have been used bearing in mind their deficiencies.

The medium/large αs shown by the p-alkylacetophenones indicate the presence of two relaxation times with relatively equal weighting factors. Indeed analysis confirms this with a $C_1 = 0.6$ (±0.1). With a C_1 of this size, both inter and intra-relaxation times should be accurate to within 10 - 15%. It is interesting to note that this is the value predicted by bond moment calculations.

p-Methylacetophenone has a molecular volume lying between that of p-chloro and p-bromoacetophenone, it is also comparable to that of p-bromoanisole ($C_1 = 0.9$) which has a molecular relaxation time of $30.0\ (\pm 4) \times 10^{-12}$ sec.$^{(1)(14)}$ It can be seen that the τ_1 obtained for the methyl compound agrees with this value, within the experimental error. The increment for molecular relaxation from the p-methyl to p-ethyl derivative would appear to be on the small side ($\sim 3 \times 10^{-12}$ sec) when compared with that obtained by Hassell and Walker$^{(24)}$ in going from toluene to ethylbenzene ($\sim 7 \times 10^{-12}$ sec). Also the volume of p-ethylacetophenone is similar to that of the iodo compound which would be expected to have a $\tau_1 \approx 40 \times 10^{-12}$ at 25°C by an extrapolation of volume vs τ. However, it will be suggested that relaxation may be compared to the volume a molecule sweeps out about its centre of mass, rather than molecular volume (cf Chapter 6). This sort of comparison could explain the difference between the iodo and ethyl compounds. Still, the τ_1s obtained for p-methylacetophenone are most probably the lower limits of the experimental error.

The intramolecular relaxation times of the two alkyl compounds agree with one another, there being no variation with molecular size, this increases the plausibility of the analysis. The magnitude of the τ_2 values is lower than those obtained for the haloacetophenones (if $\tau_o = \tau_2$ for these compounds) being of similar order to those reported by Smyth et al (10)(11) and Farmer (1). It may be concluded from these results that group moment calculations do not predict the observed weighting factors for this type of compound and also the acetyl group rotation does not seem to have been affected by the donation of 0.4D of charge by the alkyl group.

(b) The Effect of Conjugation on Acetyl Group Rotation

Fong and Smyth (10)(11)(12) measured 2-acetonaphthone 4-acetyl-o-terphenyl and p-phenylacetophenone in benzene at several temperatures (<u>cf</u> Table 2:3). On analysis they obtained a consistant C_1 of 0.86 for all three compounds. This is somewhat surprising since in the case of 2-acetonaphthone, for example, the only difference between that and acetophenone is a small amount of charge which flows across the ring systems to the substituent. Bromobenzene has a dipole moment of 1.59D (29) while 2-bromonaphthalene has a value of 1.86D (30), similarly iodobenzene has a dipole moment of 1.39D (29), while 2-iodonaphthalene has one of 1.60D (<u>cf</u> Chapter 6). Thus, the increase of flow of charge in naphthalene compounds in comparison to the analogous benzenes is only 0.2 - 0.3D. The diphenyl compounds have an even smaller flow of charge, 4-iodobiphenyl having a dipole of 1.45D (31). It is hard to envisage an increase in the C_1 from 0.33 for acetophenone (as Farmer (1) suggests) to 0.86 for 2-acetonaphthone, being due to this small change in moment.

2-Acetonaphthone was also measured in this study (cf-Table 2:1:6) in cyclohexane and p-xylene at several temperatures. The dipole moments are lower than those determined by other techniques (Halverstadt-Kumler, (51) Guggenheim (66) etc.) for this compound. This lowering has already been observed for measurements by the microwave procedure (32) and may be explained by the fact that this method, unlike others, does not involve atomic polarization approximations. It is evident that two relaxation processes are present when the τ_o is compared with that of an analogous compound, 2-iodonaphthalene, which has a relaxation time of 43.1 x 10^{-12} sec in cyclohexane at 25°C (cf Table 6:1). Analysis confirms Smyth's large C_1 values, the molecular relaxation times also being comparable. The latter are close enough to that of the iodo compound to suggest that the solution is meaningful in both the mathematical and physical senses; that the intramolecular times are not consistent with temperature is most probably due to their low weighting. However, it can be seen that the τ_2 values are significantly larger than those obtained for the p-alkylacetophenones. It is quite possible that this increase in relaxation time and to some extent the magnification of the

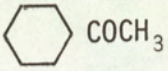
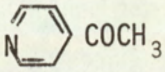
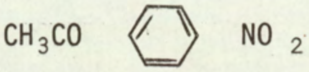
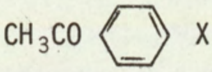
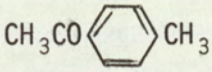
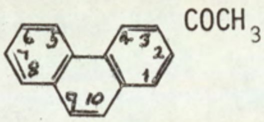
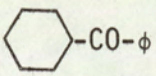
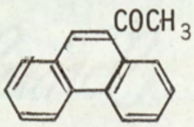
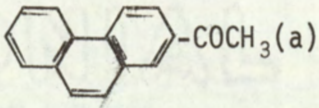
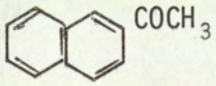
C_1 parameter may be due to the increased double bond character between the acetyl group and the naphthalene nucleus. The extent of the conjugation may be gauged by the position of the infrared carbonyl stretching frequency.

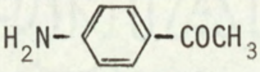
It has long been known $^{(41)(42)}$ that conjugation has a great deal of effect upon the force constant of a group with Π-electron bonds. This is shown qualitatively in the decrease of frequencies on going from a saturated ketone, such as acetylcyclohexane (1713cm^{-1}) to acetophenone (1691 cm^{-1}) and further to benzophenone (1668 cm^{-1}) as can be seen in Table 2:5.

Successful qualitative correlations have been made between Hammett Factors (6), which embrace inductive and mesomeric effects, and the compound stretching frequency of substituted acetophenones $^{(43)}$. Also a semi-quantitative approach comparing bond order with carbonyl bond position has yielded good results $^{(44)}$. Thus, clearly, the major variations in the carbonyl frequencies are due to two main factors: the conjugative capacity of the framework and electro-negativity of the substituents.

It is interesting to note from Table 2:5 that the conjugation between the acetyl group and the ring varies little between that of p-methylacetophenone and acetophenone, while 2-acetonaphthone is closer to that of benzophenone. This indeed, may explain the

TABLE 2:5 I.R. CARBONYL STRETCHING FREQUENCIES

COMPOUND	STRUCTURE	νC=o cm^{-1}	REF.
Acetylcyclohexane		1713	1
Benzaldehyde	ϕCHO	1710	34
4-Acetylpyridine		1706	33
4-Nitroacetophenone		1700	35
4-Haloacetophenones		1692	35
Acetophenone	ϕCOCH$_3$	1691	†
4-Methylacetophenone		1690	40
3-Acetylphenanthrene		1688	†
Cyclohexylphenylketone		1686	36
9-Acetylphenanthrene		1684	†
		1685	39
2-Acetylphenanthrene		1681	†
2-Acetonaphthone		1678	1

COMPOUND	STRUCTURE	$\nu_{c=o}$ cm^{-1}	Ref.
4-Aminoacetophenone		1677	35
Benzophenone	φ co φ	1668	34
1 Acetylcyclohexene		1670	†
		1665	37
Trans 4-phenyl 3-Buten-2-one (Benzalacetone)	 CH=CH.COCH$_3$(a)	1661	51

† This study

All compounds measured in carbon tetrachloride except (a) which was measured in chloroform.

behaviour of the naphthalene compound (unfortunately I.R. data for p-acetylbiphenyl and 4-acetyl-o-terphenyl was not readily available), however it does not explain the p-haloacetophenone results.

Studies have also been carried out on the I.R. carbonyl bond intensities and it has been found that the variations are relatively much larger than the corresponding frequency variations (42). Barrow (34) pointed out that for conjugated ketones the C=0 stretching bond intensity varies directly with the resonance energy of conjugation and this, according to Bellamy (45) depends solely on the mesomeric effect. These results were also confirmed by Thompson and Jameson (43). From this sort of reasoning, together with the evidence of the parallelism of the Hammett constants with the bond positions, leads one to the conclusion that the intensity of the carbonyl bond is a measure of the mesomeric effect alone, while the bond position is a measure of the combined mesomeric and inductive effects.

Jones et al (35) have published details of the I.R. spectra they obtained for the p-haloacetophenones (<u>cf</u> Table 2:6). Although very little change can be seen in the bond positions, a definite intensity trend can be observed in going through the halogen series. A substituent such as the p-amino group which is known to force electrons into the benzene ring to stabilize the quinonoid structure:

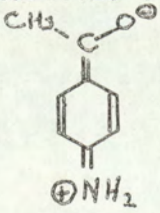


TABLE 2:6

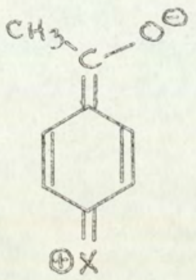
LITERATURE BAND POSITIONS AND INTENSITIES FOR CARBONYL COMPOUNDS

Compound	Wave Numbers CM^{-1}			Integrated Absorption Intensity ($Mole^{-1}$ Liter.CM^{-2} x10^{-4})	
Refs:	35	44	34	35	34
Benzaldhyde			1710		2.1
p-nitroacetophenone	1700	1700		1.93	
acetophenone	1691	1692	1692	2.20	2.1
p-fluroacetophenone	1692			2.17	
p-chloracetophenone	1692	1693		2.25	
p-bromoacetophenone	1693	1693		2.24	
p-iodoacetophenone	1693	1689		2.39	
p-methylacetophenone	1687	1688		2.44	
p-aminoacetophenone	1677			2.38	
benzophenone			1668		2.2

Carbon tetrachloride solutions

was shown to have similar carbonyl bond intensity to that of p-iodoacetophenone.

Although the sequence $F < Cl \sim Br < I$ observed by Jones differs from the mesomeric sequence obtained for dipole moment measurements of the halobenzenes (46), dipole moments do indicate (47) that when an m-directing group (CH_3CO) is substituted in the position para to an op-directing group (X), resonance structures of the type



are important. Therefore a higher intramolecular relaxation time may be expected for the p-haloacetophenones in comparison to acetophenone. p-Methylacetophenone also shows a high intensity carbonyl bond, although the stretching frequency has changed only slightly from that of acetophenone. As the alkyl group donates 0.4D of charge to the aromatic ring (this is illustrated by the size of the dipole moment), increased conjugation of the acetyl group would also be expected in this compound.

To test this hypothesis - that τ_2 increases with conjugation - 1-acetylcyclohexene was measured in p-xylene at three temperatures. From Table 2:5 it can be seen that the carbonyl group in this compound is conjugated to the same extent as that of benzophenone.

Acetylcyclohexane has already been measured (<u>cf</u> Table 2:3) and found to have a much lower τ_o than acetophenone. Normally cyclohexane derivatives are found to have a higher relaxation time than the corresponding benzene compound, thus cyclohexylchloride in benzene(48) at 20°C has a relaxation time of 10.4×10^{-12} whereas that for chlorobenzene is only 8.3×10^{-12} sec,(17) and liquid cyclohexylbromide at 25°C(49) has a relaxation time of 19.1×10^{-12} sec in comparison with 16.8×10^{-12} for liquid bromobenzene at the same temperature(50). Therefore the lowering of the τ_o in the acetylcyclohexane is explained by the increased mobility of the acetyl group due to the lack of the mesomeric effect that is found in acetophenone.

1-Acetyclohexene, although a slightly smaller molecule than the cyclohexane derivative was found to have a τ_o greater than that of acetophenone (*cf* Table 2:7). This increase is not sufficient to indicate the molecule is rigid, as 1-acetylcyclohexene would be expected to have a molecular relaxation time of $\sim 20 \times 10^{-12}$ sec (iodobenzene $\tau = 18 \times 10^{-12}$ sec at 15°C).(29) The lengthening of τ_o in this compound must be due to an increase in τ_2 and/or C_1. In Table 2:7 the two different types of volume calculation have been used(19)(22) and it can be seen that although the two methods do not agree, the same sequence is observed. The poor agreement is due to the limitations in both methods, which have been discussed earlier.

TABLE 2:7

MOLECULAR DIMENSIONS, I.R. AND DIELECTRIC

DATA FOR THE ALIPHATIC AND AROMATIC ACETYL MOLECULE

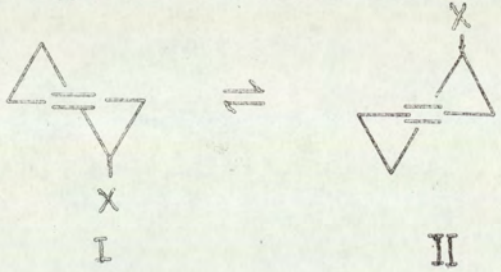
Compound	Vol. Calc. from Atomic increments. $\mathring{A}^3$	Vol. Calc. from Courtald Models $\mathring{A}^3$	I.R. $\nu c{=}o$ cm^{-1}	τ_o p-xy/15°C $\times 10^{-12}$ sec	μ D
Acetylcyclohexane	135.3	132.7	1713	9.9	2.59
Acetophenone	120.9	104.25	1691	14.3	2.83
1-Acetylcyclohexene	130.5	130.23	1665	16.0	3.15

Analysis of 1-acetylcyclohexene into two relaxation times gave a C_1 = 0.16, similar to that obtained for acetylcyclohexane (C_1 = 0.13). It is difficult to see whether this analysis is meaningful or not, as the C_1 is so low there will be a large error in τ_1 and therefore no comparison can be made with analogous rigid molecules. Also it is considered more likely that C_1 as well as τ_2 should increase with conjugation, since the increased dipole (2.59 → 3.15D) would be expected to increase the component μ_2. Theoretical estimations of the C_1 parameter for this type of molecule are complicated by the problem becoming three dimensional in contrast to the two dimensional approach with aromatic systems. As the validity of the latter are still in doubt, C_1 calculations for the cyclic molecules have not been attempted. However if a C_1 of 0 → 0.2 is accepted for acetylcyclohexane it is hard to envisage a C_1 for acetophenone of 0.33

when comparing the τ_os and volumes of the two molecules. It is more difficult to contrast the behaviour of the cyclohexene compound with that of acetophenone since it could be argued that the increase in τ_o is solely due to the increase in size. This of course cannot be verified until rigid cyclohexene molecules have been measured dielectrically.

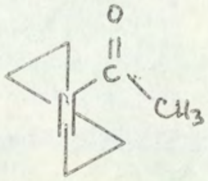
Although the half-chair conformation of cyclohexene was proposed more than a quarter of a century ago, it has only been recently confirmed by electron diffraction (53). The energy barrier between the half-chair conformation and the half boat conformation was found to be greater than 10 kcal/mole.

The energy barrier between half chair forms I and II

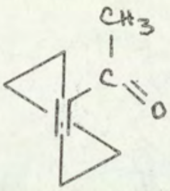


has also recently been measured for 4-bromocyclohexane by an N.M.R. technique and found to be greater than 6 kcals/mole. (77) Energy barriers of this magnitude would not be observed in the microwave region and therefore the cyclohexene ring can be expected to act as a rigid unit. The two main structures of 1-acetylcyclohexene will consist of a S-trans and a S-cis form.

S-trans



S-cis



Braude and Timmons (38) as well as Turner and Voitle (54), from infrared and ultra-violet data, have shown the preferred conformation to be S-trans. Simple dipole moment calculations would tend to confirm this. Assuming the direction of the cyclohexene dipole (0.6D (55)) is along the C = C bond, the predicted moment for S-trans is 3.19D in comparison with that of 2.93D for the S-cis structure.

Trans 4-phenyl-3-buten-2-one(benzalacetone) has also been measured in p-xylene at two temperatures. Consultation of Table 2:5 shows that the carbonyl group in this molecule is conjugated to a greater extent than in 1-acetylcyclohexene. Benzalacetone is similar in size to p-ethylacetophenone, projected τ_os for the conjugated ketone at 25°C and 50°C are 25×10^{-12} sec and 17.5×10^{-12} sec respectively. This increase in τ_o above those of p-ethyl acetophenone could be attributed to increase of double bond character between the acetyl group and the styryl component. Still the τ_o is sufficiently depressed and the distribution coefficient α is large enough to indicate the presence of at least two relaxation times, for in this molecule there are three possible mechanisms:

(i) Three different relaxation processes, one due to molecular re-orientation, one to acetyl rotation and another due to rotation about the Caryl-C vinyl bond; For Crossley(16) has observed an intramolecular reorientation in styrene.

(ii) Two processes, one molecular, the other rotation of the acetyl group about the styryl molecule.

(iii) Similar to (ii) except for rotation of the $CH=CHCOCH_3$ group instead of acetyl rotation. This mechanism may be preferred to (ii) as the carbonyl group is shown to be very conjugated by the I.R. $\nu c=o$ and also analysis into two relaxation times produces a τ_2 much larger than would be expected for acetyl movement. However mechanism (i) cannot be ruled out and since analysis into three relaxation times is complicated and produces large errors, the only tentative conclusion one may draw from this compound is that conjugation appears to increase the mean relaxation time.

Summarizing, it is concluded that there is strong evidence to suggest that conjugation of the carbonyl in 2-acetonaphthone and 1-acetylcyclohexane lengthens the intramolecular process. The C_1 is also expected to increase in these compounds since the additional moment will decrease the angle θ of the resultant dipole to the main symmetry axis ($C_1 = \text{Cos}\theta$), although this was not observed in 1-acetylclohexene. Finally infra-red data has been presented which indicates that conjugation of the carbonyl group may also exist in the p-haloacetophenones.

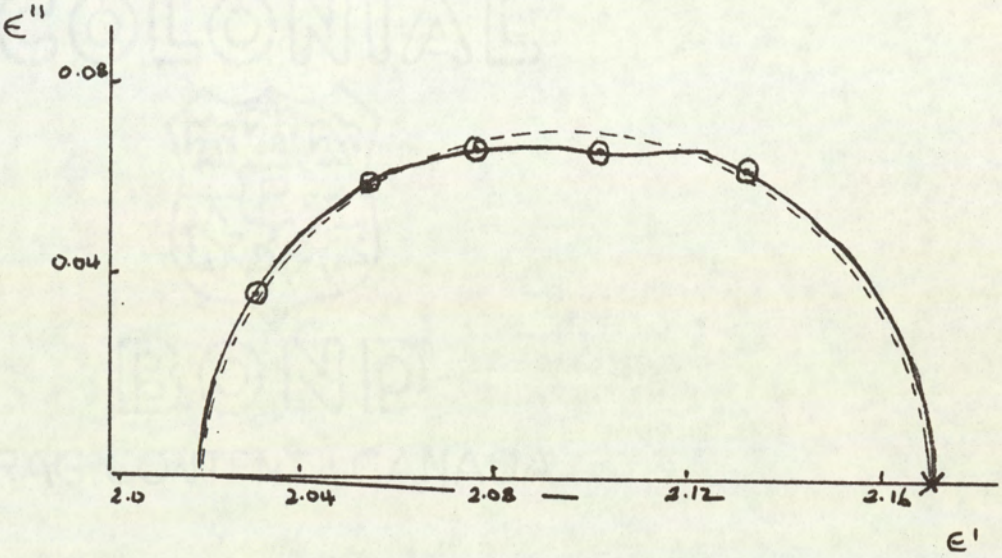
(c) Large Acetyl Molecules

When the ratio of relaxation times τ_1/τ_2 is less than eight, the Cole-Cole plot remains a regular shape, as has already been seen, but as the ratio (given the notation k) becomes progressively greater, separation into two distinct regions begins. This separation starts by a flattening of the curve at the peak and as k increases, eventually two distinct regions will be given. The effect is illustrated by drawing theoretical Cole-Cole plots calculated from the Budo equations (Chapter 1) for various C_1 values(56) (Fig. 2:4). From these plots, which have only been calculated for five bridge frequencies (o.q.k.p+x) it is seen that the separation also depends on the C_1/C_2 ratio. For C_1 values < 0.1 or > 0.9 the plots approximate to the normal Cole-Cole arc form. Also it can be observed that the separation is not marked when the bridge points lie around the maximum of the plot. When the points lie on the high frequency side of the plot the separation is not so obvious, even though k=8. However, when k is much greater than 8, the two regions will become completely separated and the two relaxation times they result from may be very accurately determined. This effect may also be observed by increasing the viscosity of the solvent. Here k is increased by the viscous solvent lengthening τ_1 but not τ_2

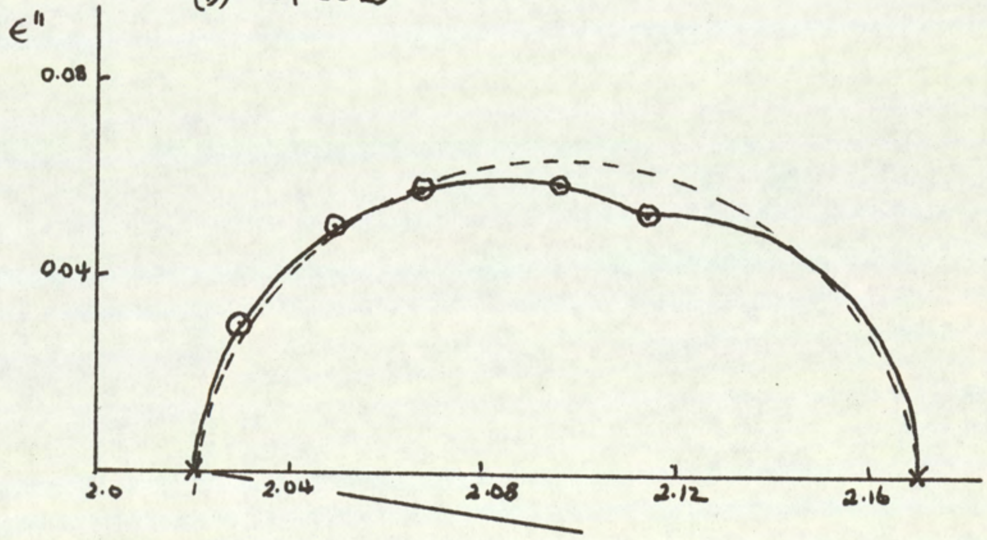
FIG 2:4 THEORETICAL COLE-COLE PLOTS CALCULATED FROM THE BUDO EQUATIONS FOR DIFFERENT VALUES OF C_1

$\tau_1 = 64 \times 10^{-12}$ sec $\tau_2 = 8 \times 10^{-12}$ sec $\epsilon_0 = 2.170$ $\epsilon_\infty = 2.02$

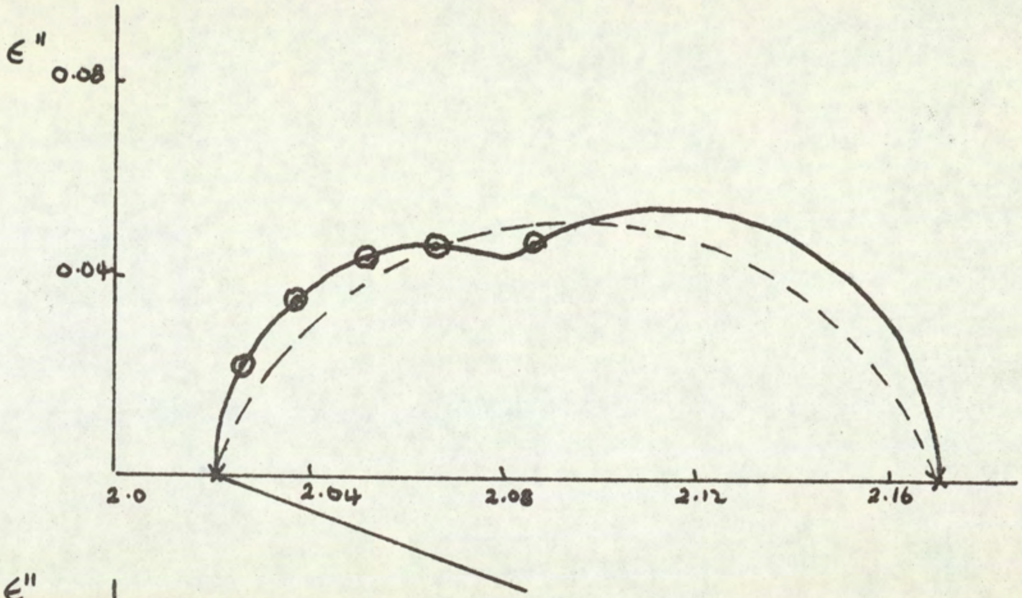
(a) $C_1 = 0.1$

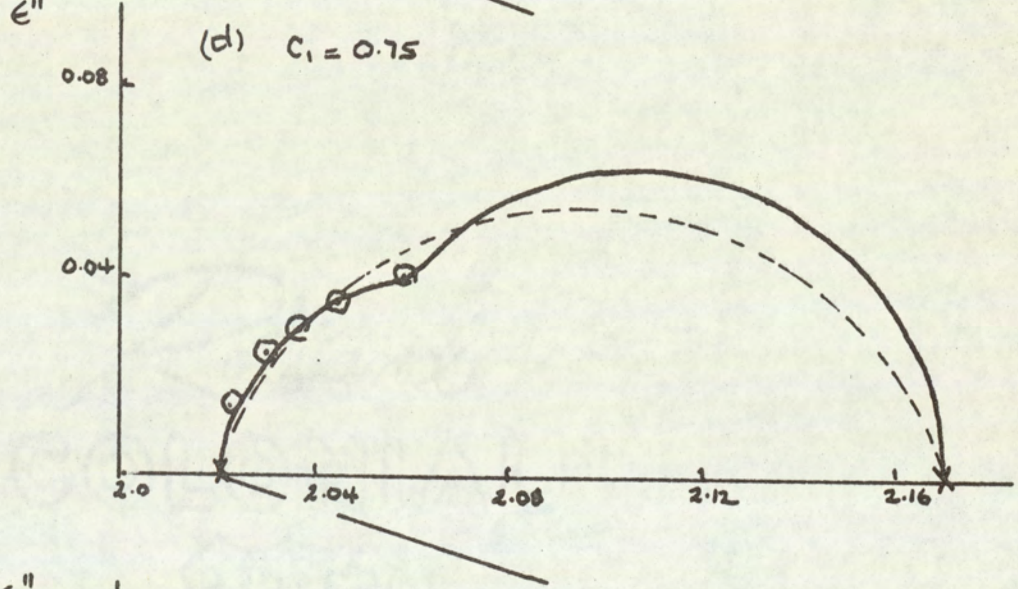


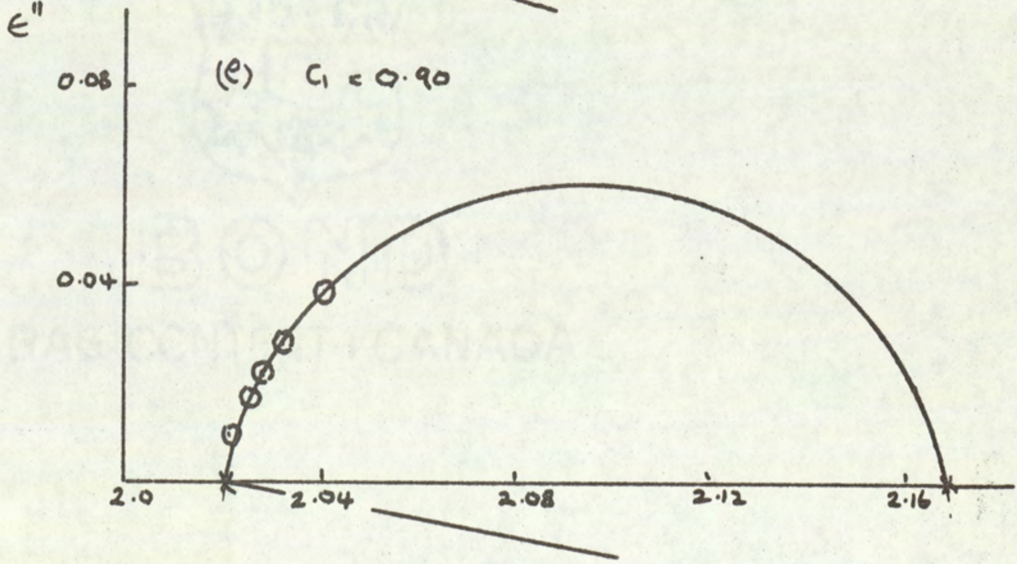
(b) $C_1 = 0.25$



(c) $C_1 = 0.50$




(d) $C_1 = 0.75$


(e) $C_1 = 0.90$

(cf section d). Separation into two absorption regions has already been noticed by Meakins when studying Lupenone $(C_{30}H_{48}O)^{(21)}$ and 2,4,6,-tri-t-butylphenol$^{(57)}$ in decalin solutions. Meakins did not use a Cole-Cole plot to illustrate the distributions of these compounds, nor has he published their dielectric data, so one cannot be constructed, but he plotted ε'' vs log frequency (cf Chapter 1) and obtained two distinct peaks. The higher frequency peak, corresponding to intramolecular absorption and the lower to molecular absorption. Using this sort of plot an accurate knowledge of C_1 can be obtained, since the height of the peaks is proportional to the component dipole from which it originates (cf Chapter 4). Garg and Smyth have also noticed distortion of the Cole-Cole plot, due to several dispersion regions of liquid alcohols$^{(49)(58)}$.

Thus the aim of this section is to measure large acetyl molecules where $k > 8$, in a hope that the two dispersion regions would separate and so provide accurate τ_2 and C_1 values. The largest acetyl molecule commercially available to us, were the acetylphenanthrenes, 2-acetylphenanthrene and 3-acetylphenanthrene were measured at one temperature, while the 9-substituted compound was measured at three. The measurements were carried out in just p-xylene due to the phenanthrene's poor solubility in other solvents. In fact the solubility of 2-acetylphenanthrene was such that only a measurement at 60° could be practically carried out. The Cole-Cole plot for this compound showed no distortion, which is rather surprising since relaxation times obtained for a substituted biphenyl would indicate a $k = 6 \rightarrow 8$ for the phenanthrene molecule. Dipole moment results (15) and present day knowledge indicate clearly that the rings of 4-substituted biphenyls are co-planar to one another and therefore with the lack of dielectric results on rigid substituted phenanthrenes, these molecules may be used as a rough comparison. The German workers Hufnagel and Kilp have published relaxation values for 4-bromobiphenyl at 20°C of 58×12^{-12} sec in benzene (59) and 62×10^{-12} sec in cyclohexane (60). This is obviously a smaller molecule than 2-acetylphenanthrene and therefore a slightly higher relaxation time of $65\text{-}70 \times 10^{-12}$ sec would be expected for the molecular reorientation process at this temperature. Dielectric data of rigid biphenyls at 60° unfortunately are not apparent in the literature and therefore no worthwhile comparison can be made with our measurement. Fong and Smyth (11) have, however, measured p-phenylacetophenone in benzene at 60° C and have obtained a $\tau_o = 27 \times 10^{-12}$ sec at 60°C (Table 2:3) comparable with the value of 30×10^{-12} sec obtained for the 2-acetylphenanthrene. Thus as their τ_o at 25°C is lower than that of the analogous 4-bromobiphenyl it may be concluded that acetyl rotation is occurring in both phenylacetophenone and

2-acetylphenanthrene molecules. The τ_1 Smyth produced on analysis of his results would, however, appear low in the light of the rigid compound, especially considering a $C_1 = 0.88$ would only give an error of 10%. Analysis of the 2-acetylphenanthrene gave a similar C_1, but larger relaxation times. The τ_1 may be justified by the fact that the phenanthrene is a slightly larger molecule, coupled with a comparison of Smyth's low τ_1 value. The intramolecular relaxation time is of similar order to that obtained for 2-acetonaphthone although the error will be large with such a low weighting. The size of τ_2 and the high C_1 may also be explained by increased conjugation between the acetyl group and the ring systems as shown by the I.R. carbonyl stretching frequency (Table 2:5) and the increased dipole. The poor compatibility between Smyth's analysis and that given here is most probably due to p-phenylacetophenone being measured at only three frequencies against five used for the phenanthrene compound. As has already been mentioned, analysis into two relaxation times should have a minimum of four microwave points, although calculation of τ_o at less frequencies than this should still be accurate to within ∿12%.

Thus with $C_1 = 0.8$ and $k = 4$ no distortion of the Cole-Cole plot can be expected for 2-acetylphenanthrene. Smyth and co-workers have also measured 4-bromobiphenyl(61) and

4-iodobiphenyl(62) in viscous solutions, their results indicated that these compounds rotated solely about their short axis. As the molecular component μ of 2-acetylphenanthrene is also along the same axis, there is no reason to suppose that the phenanthrene should not also have a similar molecular reorientation process. The other two phenanthrenes do not have their molecular dipole components along a symmetry axis, yet the magnitude of their τ_os may still be explained by describing their motion perpendicular to the component. 3-Acetylphenanthrene has its molecular component along the $C_3 - C_{11}$ axis (for ring numbering of phenanthrenes (see Table 2:5) its τ_1 motion will, therefore, be perpendicular to this and the volume swept out by it, will almost be comparable to that of 2-acetylphenanthrene. Using Smyth's p-phenylacetophenone as an indication of the change of τ with temperature, the τ_o of these two phenanthrenes can be seen to be roughly compatible, bearing in mind the errors that exist in such assumptions and in the parameters themselves. The molecular component of 9-acetylphenanthrene on the other hand will be the $C_9 - C_{12}$ axis and the resulting volume swept out will be much smaller than the preceding two molecules. This is similarly borne out in the comparison of the τ_os. Once again as with 2-acetonaphthone it would appear that the predominating process in the phenanthrenes is molecular.

Confirmation of this can be seen in the analysis of the

3-acetylphenanthrene data (which includes Grant points), where a high C_1 (0.85) has been given. The accuracy of the τ_1 is difficult to assess as there is a surprising lack of rigid 3 substituted biphenyl data in the literature. 3-chlorobiphenyl has been measured in this laboratory, in cyclohexane at 25°C and a relaxation time of 26.7×10^{-12} sec obtained.(71) This may be contrasted with a value of 32×10^{-12} sec for 4-chlorobiphenyl in benzene at 20°C reported by Le Fevre.(78) Both these results may be judged too low when compared with other biphenyl values although a large difference in τ is also observed between 2-bromo and 2-iodonaphthalenes and may be explained to some extent by rotation about their centre of masses (cf.Chapter 6). Therefore, it would appear that the τ_1 value for 3-acetylphenanthrene of 57.1×10^{-12} sec at 25°C is reasonable, being slightly smaller than the expected τ_1 of 2-acetylphenanthrene at this temperature. The carbonyl stretching in Table 2:5 indicate that this compound has the least conjugated acetyl group of the three phenanthrenes. The C_2 is so low, however, that no difference can be detected between its τ_2 and those already obtained for 2-acetonaphthone and 2-acetylphenanthrene. The τ_1 and τ_2 values obtained from the ε' vs $\varepsilon''\omega$ plot are lower and higher respectively than those given by the computer analysis. That this procedure tends to yield τ_1 values slightly shorter and τ_2 values slightly longer, in comparison with other methods has already been observed by Smyth(65).

Thus here again with $k \sim 4$ and $C_1 = 0.85$ no distortion of the Cole-Cole plot can be expected for 3-acetylphenanthrene.

9-Acetylphehanthrene on the other hand, does show a slight distortion of the Cole-Cole plot (Fig. 2:5:a) which can ben more easily seen by drawing a polarizability plot of the type proposed by Scaife(63) (Fig. 2:5:b). Here the dielectric data may be analyzed by constructing an α plot, α' and α'' being the real and imaginary coordinates of the complex polarizability $\alpha(\omega)$ of a dielectric sphere of unit radius, where

$$\alpha'(\omega) = \alpha' - i\alpha'' = \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{(\varepsilon'-1)(\varepsilon'+2)+\varepsilon''^2 - 3i\varepsilon''}{(\varepsilon'_1+2)^2 + \varepsilon''^2}$$

or more explicitly

$$\alpha'' = \frac{(\varepsilon' - 1)(\varepsilon' + 2) + \varepsilon''^2}{(\varepsilon' + 2)^2 + \varepsilon''^2}$$

$$\alpha'' = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2}$$

This method has only been used here as evidence of the second relaxation mechanism in the high frequency region, since it has the advantage of weighting each mechanism properly, the Cole-Cole plot tends to give a much greater weighting to those mechanisms having low dispersion frequencies than those with shorter relaxation times. The method may also be applied to the determination of relaxation times, where,

$$\alpha(\omega) = \frac{A}{1+i\omega\tau_A} + \frac{B}{1+i\omega T_B}$$

τ_A and τ_B being the intrinsic microscopic relaxation times of the two mechanisms. As of yet, no computer programme has been compiled to analyze this sort of data, but one would be of use if further studies on systems where $k \approx 8$ were contemplated.

It has been found that when separation of two regions occur, the ensuing results cannot be analyzed by the computer method, since the computer attempts to fit the data to one Cole-Cole arc, which is of course impossible. So the relaxation parameters for 9-acetylphenanthrene given in Table 2:1 have been calculated using log $^{v}/\mu$ vs log ω and ε' vs $\varepsilon''\omega$ plots. The latter show quite conclusively the presence of two relaxation processes (cf Fig.2:5:c). Previous workers (23)(64),(65) using this type of plot have, in the main, observed only two microwave points on the smaller slope (τ_2) thus the value for this parameter contained a large error.

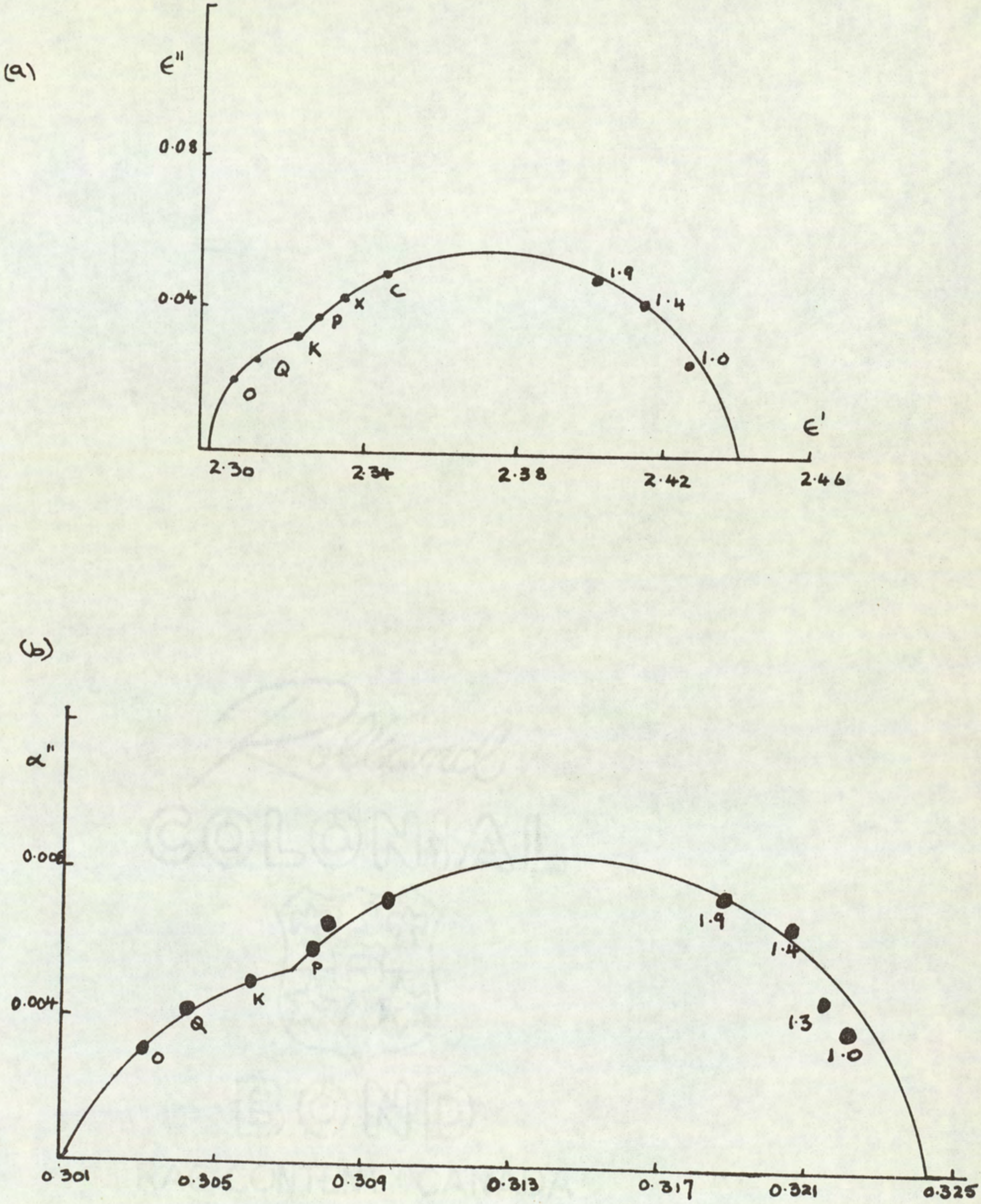


FIG 2:5 (a) COLE-COLE PLOT OF 9-ACETYLPHENANTHRENE | P-XYLENE 25°C

(b) SCAIFE " " " " "

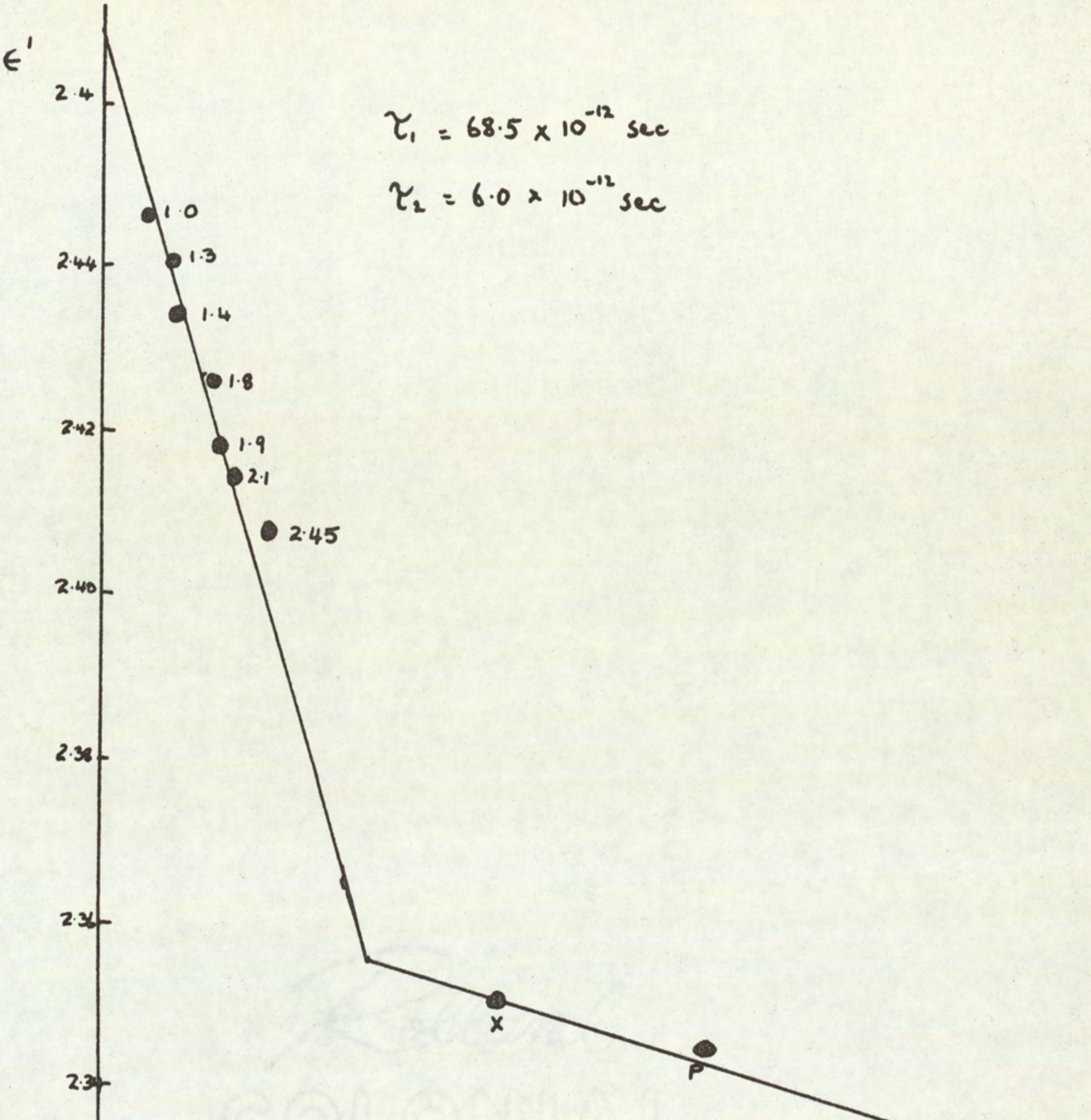


FIG 2:5:C PLOT OF ε' VS ε"ω FOR 9-ACETYLPHENANTHRENE IN P-XYLENE AT 15 °C.

Here there are as many as five microwave points, increasing the accuracy of the τ_2. Also Smyth maintained that the values obtained by this method differed from those calculated by other means$^{(65)}$, due to the effect of the overlap of the two absorption regions on the slopes of the two lines. Here, this effect will minimize as the two regions separate - with these two facts in mind, it is considered that the relaxation times given in Table 2:1 from the ε' vs $\varepsilon''\omega$ plot are as accurate as the weightings allow.

A similar type of plot may be made using Smyth's α' α'' values for 4-acetyl-o-terphenyl$^{(10)}$, a molecule in which $k \geqslant 8$ and where α'' is the slope of the plot of ε'' vs w_2 (weight fraction of solute) and α' the slope of ε' vs w_2.

So $\varepsilon'' = \alpha'' w_2$

$\varepsilon' = \varepsilon_1 + \alpha' w_2$

ε'_1 being the dielectric constant of the solvent.

Thus in a plot of α' vs $\alpha''\omega$ two distinct slopes can be seen (Fig. 2:6), as was observed in the ε' vs $\varepsilon''\omega$ plots for 9-acetylphenanthrene, the τ values produced from the slope $\alpha'/\alpha''\omega$ being slightly higher than those obtained by Smyth by the double arc method$^{(10)}$. No distortion of the Cole-Cole plot was detected, however, with these results, this being probably due to the high molecular weighting reported and the

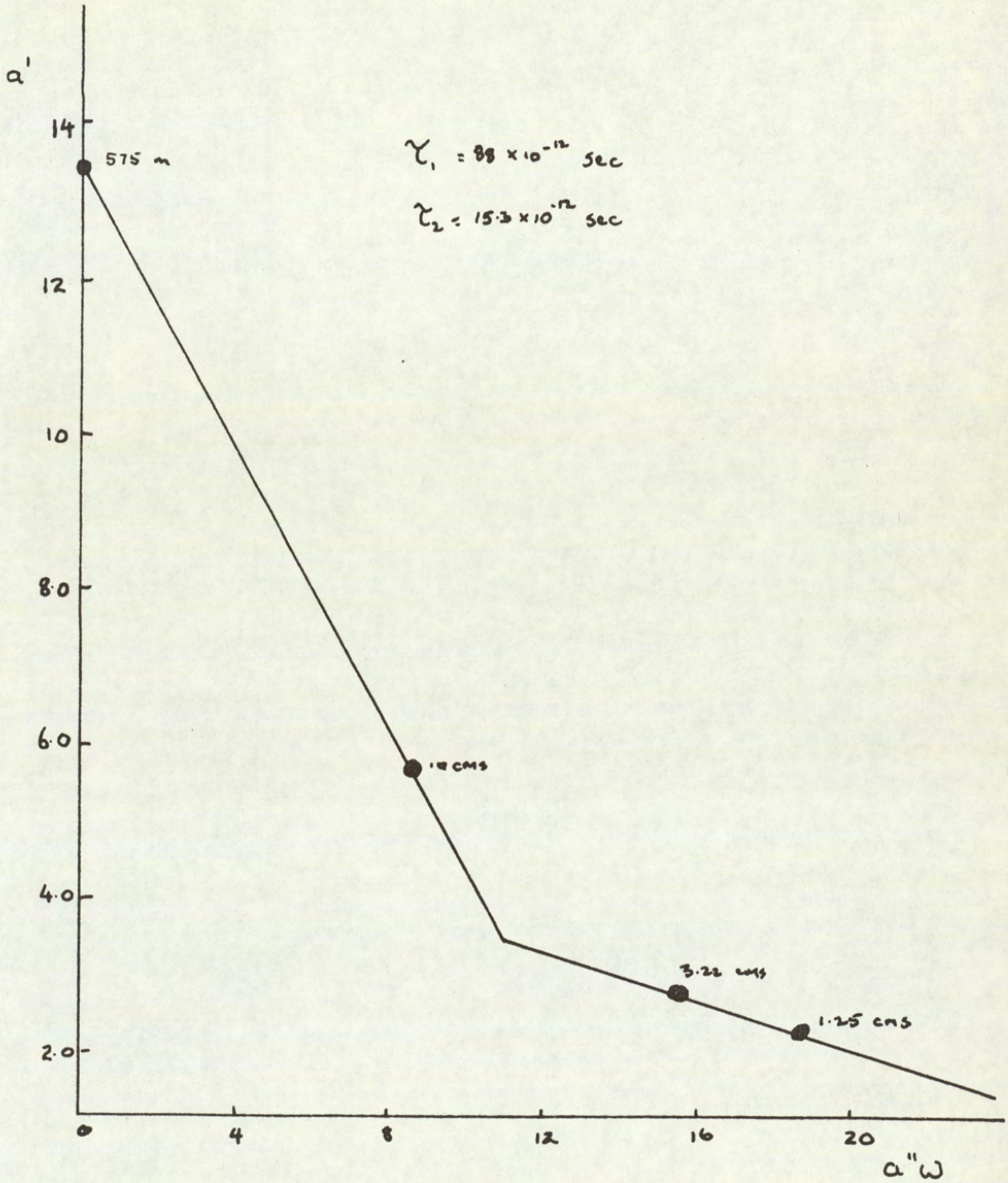


FIG 2:6 PLOT OF a' VS a"ω FOR 4-ACETYL-O-TERPHENYL AT 30°C AS REPORTED BY SMYTH.[10]

small number of microwave frequencies used, especially at the low wave length range where this distortion is to be expected.

Hufnagel and Kilp (60) have reported a relaxation time for 9-bromophenanthrene of 44 x 10^{-12} sec at 20°C in cyclohexane. Although 9-acetylphenanthrene is a larger molecule and the value in p-xylene will be slightly higher, a τ_o of 40.7 x 10^{-12} sec at 25°C for this compound indicates a relatively large contribution from molecular reorientation. This may also be seen on comparing the Cole-Cole plot to those in Fig. 2:4. A τ_1 of 50.4 x 10^{-12} sec at 25°C appears to be of a correct magnitude on comparison with the bromo derivative, yet the intramolecular process (5.9 x 10^{-12} sec) appears abnormally low even with a low weighting. The dipole moment of the 9-acetylphenanthrene is also low when it is compared with that of the other two phenanthrenes, having a similar value to that of acetophenone ($\mu \sim 2.8D$). Initially it may be inferred from the dielectric results that the acetyl group is as freely rotating in 9-acetylphenanthrene as in acetophenone, with no increase in the barrier to rotation arising from resonance energy. The comparitively low moment of the 9-Phenanthrenes, however, is surprising since Fukui and his co-workers (67) have postulated the 9 and 10 positions to be the positions of largest frontier electron density and Pauling has assigned an 80% double bond character to this 9, 10 bond (68). The infra-red carbonyl stretching frequency (Table 2:5) would also suggest increased conjugation between the acetyl group and the C^9 of the phenanthrene nucleus. Thus, from previous results given in this chapter, 9-acetylphenanthrene would be expected to have a larger intramolecular relaxation time and dipole moment than observed.

This discrepancy may be somewhat tentatively explained by the $\varepsilon_\infty - n_D^2$ value. The difference is slightly higher than that normally obtained (17) and, indeed, as shown by the other acetylphenanthrenes. As has been stated earlier $\varepsilon\infty$ may differ from n_D^2 due to enhanced atomic polarization, and a large atomic polarization has been used as evidence to indicate a high frequency absorption region. (69) Yet the enhancement of atomic polarization by the presence of a librating polar group is not very large (13) and so, the acetyl group in 9-acetylphenanthrene may undergo some form of libration in comparison to the rotation observed in other acetyl derivatives. The former motion would have a lower relaxation time than the latter and would also cause a low dipole moment. (70)

Examination of the Courtald model of 9-acetylphenanthrene shows that the acetyl group is slightly hindered to rotation by the hydrogen atom on the 14 carbon. Thus, this molecule is analogous to 1-acetonaphthone measured by Smyth(13) and may be assigned the same form of librational motion. This sort of oscillation is not normally observed so far into the microwave region being so fast that absorption occurs in the far infrared up to 2 mm wavelength. Here the double bond character of the 9, 10 bond of the phenanthrene molecule is so great that the acetyl group is still quite strongly conjugated, although it is slightly out of plane of the parent nucleus. The conjugation lengthens the librational motion so it is detected by the microwave bridge frequencies. Hunsberger(84) and his co-workers,(39) who measured the carbonyl stretching frequency of this molecule could not understand why the absorption was not lower than observed, the above suggestion may well be the reason. In fact ^{13}C N.M.R. measurements(85) show the acetyl group in 1-acetonaphthone and 9-acetylphenanthrene to be ∿25° out of plane, this would also tend to decrease the dipole moment. Smyth has measured the moment of 1-acetylnaphthone by the Guggenheim method(66) (using n_D^2 and not ε_∞ for the calculation) and obtained 2.93D in benzene.(12) The difference between this and 3.1D of 2-acetonaphthone will be due to the twist angle of ∿25° in the 1 substituted compound. While the difference between 2.93D and that obtained for 9-acetylphenanthrene from the Cole-Cole plot (2.80D) may be due to libration. Unfortunately, insufficient high frequencies were used by Smyth to detect this sort of motion in 1-acetonaphthone. Further studies, however, of both these compounds at 2 mm and far infra-red frequencies may confirm the suggested libration.

It is interesting to note that plots of ε" vs log f for 9-acetylphenanthrene, gave asymmetrical peaks with no indication of a second relaxation process, the inference being that the two relaxation times must completely separate before they are detectable by this method.

The following summary may be made of the results presented in this section:

(i) 2-acetyl, 3-acetyl and 9-acetylphenanthrenes appeared to have large weightings to molecular rotation.

(ii) Due to (i) and the size of k in 2-acetyl and 3-acetylphenanthrene, no distortion of the Cole-Cole plot was observed. The τ_2 values of these compounds were therefore subjected to large errors, yet appeared to be of the same order as in other conjugated acetyl compounds.

(iii) A distortion of the Cole-Cole plot was found in 9-acetylphenanthrene, however, the intra-molecular relaxation time, which resulted was lower than has been previously observed for aromatic acetyl molecules. Chemical evidence predicts a similar degree of acetyl conjugation in this compound as in

2-acetonaphthone; librational motion due to steric hindrance of the acetyl group by the hydrogen on the 14 carbon, has been suggested for the intra-molecular process.

(d) Studies in Viscous Solutions

Much literature has been published on the poor correlation of relaxation time with the viscosity of the medium. The arguments for and against the dependence of τ on solvent viscosity are not within the scope of this thesis and will therefore not be discussed in any great detail. As mentioned previously, a more distinct separation of relaxation times in a non-rigid molecule may be obtained by increasing the solvent viscosity. It has been found by Meakins(21) and Smyth(75) that increases in viscosity also magnify the molecular relaxation time, yet the process of group rotation is roughly of the same magnitude as that observed in less viscous solutions. A more viscous solvent in effect, therefore, increases the size of k (τ_1/τ_2).

In rigid compounds the increase in τ with viscosity (η) has been found to depend on the shape of the molecule. The more spherical the molecule, the smaller the dependence of τ on η. This may be explained by considering the medium to initially consist of spheres in which there is some kind of freedom of motion. The concept of "holes" in a liquid has been introduced to account for this characteristic. The energy required to make "holes" in the activation process is considered to be closely associated with viscosity(74). Consequently, rotation of a spherical molecule need not make new "holes" in the solvent, in contrast to a non-spherical molecule where rotation will require displacement of surrounding molecules. This latter process will obviously depend more on viscosity than the former.

By analogy to this, intramolecular rotation will be relatively independent of η, as this process can function in a solvent "hole"; the volume being swept out by the group being so small. In practice viscous solvents are not spherical but this does not nullify the basic concept of group rotation in solvent "holes", but only complicates the solvent/solute relationship.

Smyth and his co-workers have measured a series of non-rigid methoxy and ethoxy molecules in decalin and nujol; the relaxation parameters he obtained, together with the results of other workers are presented in Table 2:3:b. Studies of anisole have all indicated that the observed relaxation time is too short to be attributed solely to molecular relaxation. In fact, the C_2 value has been reported to be 0.75 ± 0.1(78)(79). The results in table 2:3:b show that there is very little change in intramolecular relaxation time with increasing solvent viscosity. Smyth did not determine τos from his methoxy/nujol data, as the dielectric results produced poor Cole-Cole plots. When τos are shown for these compounds, they have been determined by computer. The accuracy of these parameters is dubious, as it is difficult to assign an $\alpha\infty$ value to the data, and the same inadequacies have also been found in computer analyses of viscous solutions, as were encountered in section (c) for 9-acetylphenanthrene. The magnitudes of the τos, however, suggest that when the C_1 is low, the size of the mean relaxation time is not increased greatly with increasing solvent viscosity. This has also been observed for diphenylether for which Farmer suggested a $C_1 < 0.1$.(1) Thus, if for the p-haloacetophenones, C_1 is also less than 0.1, (as indicated by Group Moment Calculations), studies in viscous solutions should produce τos comparable to those already obtained in section (a).

Acetophenone, 4-acetylpyridine, 4-bromoacetophenone and 3-acetylphenanthrene were measured in varying viscous solvents, (comprising of nujol, nujol/p-xylene and nujol/cyclohexane) at 25°C. The solvent mixtures, nujol/p-xylene and nujol/cyclohexane, were used for two reasons. Firstly, to reduce the solvent viscosity, as was the case with 4-bromoacetophenone, and secondly, owing to the insolubility of the solute in nujol, as was the case with 4-acetylpyridine and 3-acetylphenanthrene. The dielectric data obtained provided good Cole-Cole plots, as shown in Fig.2:7a for acetophenone in nujol, no distortion being detectable. Nor did a plot of ε'' vs log f show any indication of a separation of two relaxation times. This was surprising as k was expected to be large enough for this type of behaviour to be apparent. It may well have been that there were insufficient frequencies measured at the site of distortion, for a separation to be recognised. ε' vs $\varepsilon''\omega$ plots however, do show two distinct relaxation processes, similar to those observed for 9-acetylphenanthrene. The behaviour of the compounds studied in viscous solvents was also analogous to that of the 9 substituted phenanthrene, in that the computer could not fit the data to the Cole-Cole or Budo equations. This is due to the fact that for most solutes nujol gives rise to a distribution of relaxation times for over all rotation, and therefore these equations should not be used. Nujol's behaviour has been reported by Smyth(73)(76) who employed the α' vs $\alpha''\omega$ plot to obtain τ_2 and then calculated a loss-log frequency curve corresponding to this relaxation time value. The loss due to the molecular process was then determined by subtraction of this curve from the experimentally observed curve. The latter process has not been contemplated for these results, as two distinct slopes resulted from our ε' vs $\varepsilon''\omega$ plots in comparison with the curve observed by Smyth in plotting α' against $\alpha''\omega$. Moreover the τ_1 values obtained using the former plot were quite adequate, as it must be remembered that this parameter is rather meaningless, since it will vary according to the chemical content of the nujol. A log v/u against log ω calculation was employed to obtain the mean relaxation time.

A τ_o for p-bromoacetophenone in nujol of 194×10^{-12} sec and a large α of 0.2 shows conclusively thatits $C_1 \nless 0.1$. Even when the solvent viscosity has been reduced by almost two-thirds, the τ_o still remains high.

Unfortunately, owing to practical difficulties, insufficient microwave frequencies were measured to ensure an accurate calculation of the τ_1 and τ_2 values for this compound. Although separation of two relaxation times was observed in the ε' against $\varepsilon''\omega$ plot for the more viscous solvent, it was found necessary to have at least three microwave bridge points to determine τ_2 with sufficient accuracy.

Farmer(1) measured 4-acetylpyridine in p-xylene and decalin, with a fourfold increase in solvent viscosity and observed no apparent change in the mean relaxation times (Table 2:3:a). He therefore concluded that only intramolecular rotation was present in this molecule, The solvent used in this study has a viscosity 90 times higher than that of p-xylene, and the mean relaxation time (43.9×10^{-12} sec) would not appear to substantiate Farmer's conclusions. A τ of this size indicates the presence of some molecular process. It may well be that $\tau_1 \approx \tau_2$ in 4-acetylpyridine, since it is a smaller molecule than acetophenone, and therefore no lowering of the τ_o (14.2×10^{-12} sec at 25^{o}C) would be detectable. The τ_2, obtained from the viscous study of 15×10^{-12} sec is comparable with the latter. The infra-red carbonyl stretching ($1706 cm^{-1}$) suggests that there is less conjugation in this compound than in acetophenone. Thus a smaller intramolecular relaxation time would be expected, although the reverse is observed. An interaction of the pyridine nucleus with the Π electron system of the p-xylene solvent molecule has previously been suggested to account for the larger τ values in p-xylene in comparison with those in cyclohexane. Possibly such an interaction complex would hinder the rotation of the acetyl group to such an extent that the τ_2 value would be increased. This hypothesis could be tested if a saturated solvent could be found in which 4-acetylpyridine was soluble.

The nujol solution of acetophenone, on the other hand, gives a τ_2 value of 8.5×10^{-12} sec which is lower than Farmer assigned to acetophenone in p-xylene (9.7×10^{-12} sec) using a $C_1 = 0.33$(1). However, this value for molecular weighting, calculated from group moments must now be held in doubt, as C_1s calculated by this method have inadequately described the behaviour of the p-halo and p-methylacetophenones as well as the large acetyl molecules.

Only a weak solution of 3-acetylphenanthrene could be measured owing to its insolubility in nujol. The τ_2 of 15×10^{-12} sec confirms the longer relaxation time on account of increased acetyl conjugation observed in the previous sections.

The mean relaxation time of p-bromoacetophenone is three times greater than that of acetophenone, yet this does not mean that C_1 x-$\phi COCH_3 > C_1$ ϕ-$COCH_3$. It is well known that a poor correlation exists between relaxation time (τ) and viscosity (η), even the concept of internal or macroscopic viscosity does not improve the correlation to any great extent(80). Higasi has developed a relationship between log τ and log η which is described by the following equation:

$$\log \tau = A + X \log \eta$$

where A and X are constants relating to the substance alone under a given temperature. Higasi has shown that X depends mainly on molecular shape and is smallest for spherical type molecules, increasing with molecular size. The value of X may also be depressed for molecules having high intramolecular weightings, such as diphenyl ether.

By the use of this relationship $\tau_o \alpha \eta^X$, X values for the acetophenones have been determined for both solvent and solution viscosities and are shown in Table 2:8. As the solution viscosity (η_{AB}) of other workers was not known, X_{AB} was calculated by a comparison of the three compounds:

$$\frac{\tau_{o(1)}}{\tau_{o(2)}} = \frac{\eta_1^{X_1}}{\eta_2 X^2}$$

This relationship is not strictly true, but the values compare well with the XA values. The latter were determined by plotting log τ against log η (Fig.2:7). The X values are seen to be more dependent on molecular size than on C_1, acetophenone having the same value as 4-acetylpyridine ($X = 0.3/0.4$), while p-bromoacetophenone exhibits a larger value of 0.5/0.6, although the latter must have a much lower C_1 value than acetophenone. The size of X was found to be larger than measurements determined by Higasi for similar sized molecules$^{(74)}$. It would appear therefore, that further measurements of non-rigid molecules are necessary before any real significance can be attached to the τo s determined in varying viscous solvents. The low τo s which a computer analysis gave for Smyth's anisole results have not been verified by this study, where the C_1 values for p-bromoacetophenone and 4-acetylpyridine should be of the same order as those postulated for anisole and p-methylanisole. However, measurements in viscous solutions are of value for determining whether $C_1 = o$ (as with diphenylether) and for providing further evidence of the size of an intramolecular relaxation time. It must be emphasised that for an accurate assessment of τ in this type of study (especially for large molecules), it is necessary to employ the largest microwave frequency range possible. The bridge frequencies P, X and C, together with those of the Grant cell 2.5Gc/s - 0.8Gc/s, fulfil this requirement well.

TABLE 2:8

ACETOPHENONES IN SOLVENTS OF VARYING VISCOSITY AT 25°C

Compound	Solvent	Solvent Viscosity η_A c.p.s.	Solution Viscosity η_{AB} c.p.s.	τo	XA	XAB
Acetophenone	p-xylene	0.6	-	12.8		
	Decalin	1.94	-	17.5		
	Nujol	166	115.7	65.0	0.3	0.35
4-Acetylpyridine	p-xylene	0.6	-	14.2		
	Nujol + p-xylene	53.7	43	43.9	0.3	0.35
4-bromo-acetophenone	Cyclohexane	∿1	-	14.0		
	Nujol + Cyc.	62	50	103.0	0.51	0.56
	Nujol	166	115	194.0		

Thus, in conclusion, it has been shown that the size of C_1 for 4-bromoacteophenone and 4-acetylpyridine is greater than 0.1, and the maximum values of intramolecular relaxation at 25°C for acetophenone, 4-acetylpyridine and 3-acetylphenanthrene are 8.5×10^{-12}, 15×10^{-12} and 15×10^{-12} sec respectively.

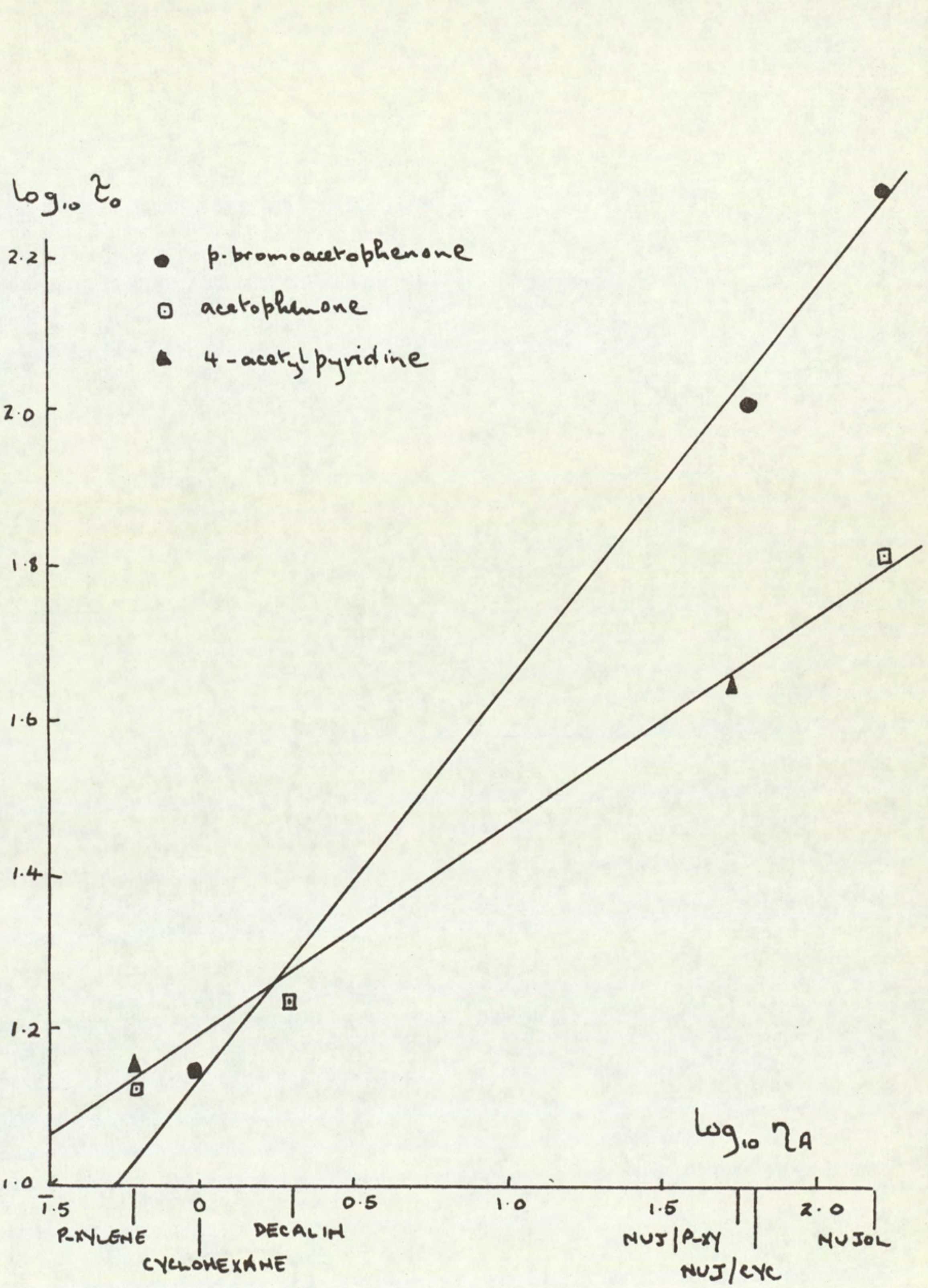


FIG. 2:7 PLOT OF $\log \tau_0$[74] vs $\log \eta_A$ AS PROPOSED BY HIGASI.

(e) Conclusions and Summary

1. C_1 values

The following C_1 values were predicted by group moment and bond moment calculations

	Group Moments	Bond Moments
Acetophenone	0.33	0.52
4-acetylpyridine	0	0
p-alkylacetophenones	0.45	0.61
p-haloacetophenones	0.001	0.25

(i) 4-Haloacetophenones: Although the mean relaxation time of the 4-haloacetophenones in p-xylene and cyclohexane solutions were found to be much lower than analogous rigid molecules, the τ_0 values did vary slightly with size. In section (d) the C_1 of the 4-halo compounds was seen clearly to be not equal to zero.

(ii) 4-Alkylacetophenones: Straightforward $\tau_1 \tau_2$ analysis of these compounds produced C_1 values which were compatible to those predicted by bond moment calculations.

(iii) 2-Acetonaphthone and other large acetyl molecules: Analysis of the dielectric results of 2-acetonaphthone produced a $C_1 = 0.75$ ($\pm$ 0.1), C_1 s of the same magnitude were also obtained for the acetyl substituted phenanthrenes. Smyth(10)(11) observed similar C_1 values for the former compound, p-phenylacetophenone and 4-acetyl-o-terphenyl. The infra-red carbonyl stretching frequencies of the large acetyl molecules studied in this thesis, indicated that the acetyl group was conjugated to a greater extent than in acetophenone. However, a C_1 change from 0.3 for acetophenone to 0.8 for 2-acetonaphthone was much too large to be explained merely by increased conjugation. The value predicted by bond moments for acetophenone would appear to be more appropriate.

(iv) 4-Acetylpyridine: Both methods of calculation suggest for this compound a $C_1 \sim 0$. This was shown to be incorrect by measurements in viscous solution. Thus, it was suggested that an interaction complex was being formed between solute and solvent that hindered acetyl rotation.

In the light of these conclusions, it was decided to fix the C_1 of p-haloacetophenones and acetophenone to the values predicted by bond moment calculations. The increase of C_1 with conjugation may then be explained by taking the C_1 of acetophenone to be 0.55, an additional moment of 0.4D in the p-alkylacetophenones would increase the C_1 to 0.65, larger acetyl molecules with a higher degree of conjugation having a $C_1 = 0.75$. As weighting factors are only accurate to ± 0.1, a lower limit for 2-acetonaphthone would be equivalent to the C_1 of p-methylacetophenone. Although there would be a small variation of C_1 amongst the p-haloacetophenones, it would be within the above error limits and therefore a common value has been given to the series. The $\tau_1\tau_2$ analyses of the p-haloacetophenones are given in Table 2:1 and those of acetophenone are presented in Table 2:9. The latter table also includes the function A for these analyses and for those where $C_1 = 0.33$. 'A' being given by

$$A = \Sigma \ (\varepsilon''\text{obs} - \varepsilon''\text{calc}) \ + \ \Sigma \ \frac{(\varepsilon'\text{obs} - \varepsilon'\text{calc})^2}{4}$$

The magnitude of A is therefore a criterion of how the dielectric data is fitting to the Budo equations, the size of A will also depend

TABLE 2:9

τ_1 ,τ_2 and A values for acetophenone with a fixed C_1= 0.55, together with A values for a fixed C_1= 0.33.

SOLVENT	TEMP.	τ_1	τ_2	A(c_1=0.55)	A(c_1=0.33)	NUMBER OF MICROWAVE FREQUENCIES
	°C	$x10^{12}$ sec		$x10^{8}$		
Cyclohexane	15	15.9	7.8	3247	3060	6
	25	14.8	6.4	2997	2927	6
	40	10.8	5.5	3061	3151	6
	50	9.3	5.2	3172	3148	6
p-xylene	15	19.5	9.8	944	1035	5
	25	18.5	8.6	3256	3118	5
	40	13.0	7.6	1703	1732	5
	50	11.4	6.4	743	833	5
	60	9.3	6.2	841	858	5
Decalin	15	26.1	14.7	783	839	5
	25	23.1	12.2	1235	1412	5
	40	16.6	9.9	1224	1253	5
	50	14.6	9.2	260	260	5
	60	12.5	7.7	610	634	5

on the microwave frequencies used in the determination. Comparison of the A values for $C_1 = 0.55$ and $C_1 = 0.33$ in Table 2:9, shows that a C_1 of the former magnitude mathematically fits the acetophenone data just as well, if not better than a C_1 value of 0.33. Similar reasonable A values were also obtained for the p-haloacetophenones using a $C_1 = 0.25$.

2. Intramolecular Relaxation Times τ_2

1-Acetylcyclohexene in section (b) gave a much higher τ_0 than acetylcyclohexane, although the latter is a slightly larger molecule. It was concluded that the lengthening was due to a higher intramolecular relaxation time in the former molecule caused by increased conjugation.

Relaxation times of acetyl group rotation and the weighting factors for this process are listed in Table 2:10 for p-xylene and cyclohexane solvents at 25°C.

Magee(81) has shown that errors in analysed relaxation times are no worse than about 20%. A τ_2 with a $C_2 = 0.8$ would probably have an error of ∿12%, while one with a $C_2 = 0.2$ would be expected to have an error slightly greater than 20%. If this is the case, results in Table 2:10 do show that the acetyl group does not have the same relaxation time when placed in different electronic conditions.

TABLE 2:10

INTRAMOLECULAR RELAXATION TIMES AND WEIGHTING FACTORS FOR ACETYL COMPOUNDS AT 25^{o}C

Compound	Cyclohexane		p-xylene	
	τ_2	C_2	τ_2	C_2
Acetylcyclohexane			8.2	0.8
Acetophenone	6.4	0.45	8.6	0.4^{5}
p-Methylacetophenone	8.7	0.45	9.9	0.45
p-Ethylacetophenone	7.7	0.31	9.8	0.29
p-Fluoroacetophenone	8.7	0.75	12.1	0.75
p-Chloroacetophenone	10.7	0.75	-	-
p-Bromoacetophenone	10.8	0.75	-	-
p-Iodoacetophenone	11.6	0.75	12.7	0.75
2-Acetonaphthalene	9.7	0.2	14.8	0.22
3-Acetylphenanthrene	-	-	13.5	0.15
1-Acetylcyclohexene	-	-	12.6	0.8

The 4-alkylacetophenones have a slightly higher τ_2 than acetophenone, suggesting an increased barrier to rotation arising from a larger resonance energy. The same explanation has also been attributed to the p-haloacetophen~~o~~ones which show a larger τ_2 than acetophenone. That the relaxation time of the halogen compounds are longer than those of the alkyl derivatives may not have any meaning, taking the extreme errors attached to the C_2 values gives approximately equal relaxation times for both types of compounds. Similarly the very small lengthening of τ_2 within the p-halo series may be assigned to experimental error or increasing conjugation, as suggested by infra-red intensity measurements (Table 2:6).

3. Molecular Relaxation Times τ_1

Comparison of the τ_1 value of a non-rigid molecule with that of a similar sized rigid compound has been used throughout this chapter as verification of the analysis. It therefore only remains to discuss the τ_1 values of acetophenone and the p-haloacetophenones.

Antony and Smyth have measured 2-hydroxyacetophenone in cyclohexane at several temperatures(28). They found it behaved as a rigid molecule due to an intramolecular hydrogen bond formed between the acetyl and hydroxyl groups. An extrapolated relaxation time for this molecule at 15°C is 17.2×10^{-12} sec, being slightly longer than that of acetophenone (15.9×10^{-12} sec) under the same conditions. That the relaxation times should be in this order has been recently shown by measurements of ortho-substituted halobenzenes (Chapter 6). Ortho-chloroiodobenzene in p-xylene was found to have a $\tau = 11.0 \times 10^{-12}$ sec at 60°C which is larger than that of iodobenzene (9.2×10^{-12} sec) at the same temperature(29). Further confirmation of the accuracy of acetophenones τ_1 may be derived by comparing the value obtained in p-xylene at 15°C (19.5×10^{-12} sec) with that of iodobenzene (18×10^{-12} sec), iodobenzene being the slightly smaller molecule.

With a $C_1 = 0.25$ the τ_1 values for the p-haloacetophenones will not be as accurate as those of acetophenone. The magnitude of the error can be seen to be ~20% viz: τ_1 of p-bromoacetophenone in p-xylene at 40°C is 17.6×10^{-12} sec, while in cyclohexane 26.1×10^{-12} sec. However, some rough comparisons have been made below to give the analyses credibility. To reduce the error somewhat, a mean τ_1 of p-xylene and cyclohexane at 40°C has been taken p-fluoroacetophenone 14.5×10^{-12}

p-chloroacetophenone 16.2×10^{-12}

p-bromoacetophenone 21.9×10^{-12}

p-iodoacetophenone 28.6×10^{-12}

p-chlorotoluene 13.6×10^{-12} (Ref.17)

p-bromotoluene 16.8×10^{-12} (Ref.17)

p-methylacetophenone $\sim 21.9 \times 10^{-12}$
(By extrapolation $C_1 = 0.6$)

p-bromoanisole $\sim 25 \times 10^{-12}$ ($C_1 = 0.8$
Ref.1)

p-ethylacetophenone $\sim 26 \times 10^{-12}$
($C_1 = 0.7$. By extrapolation)

4. Energy Barriers to Relaxation

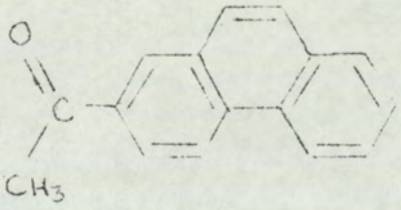
Now the weighting factors have been successfully assigned the energy barriers to molecular and group rotation may be calculated. The $\Delta G^{\ddagger}$ $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the intramolecular process are given in Table 2:2a, while those for the molecular process are presented in Table 2:2b. When the weighting factors of these processes are $\geqslant 0.45$, the linearity of the log τT against $1/T$ plots were good. As the weighting factors decreased from this value and the errors in τ became larger, the linearity naturally became poorer. It should be pointed out, however that this linearity cannot be used to justify or establish the parameters τ_1, τ_2 and C_1. Since if a plot of log $\tau_0 T$ vs $1/T$ is linear, the relaxation time with the higher weighting factor will automatically give a linear plot. This is due to the relationship

$$\tau_0 = C_1\tau_1 + C_2\tau_2$$

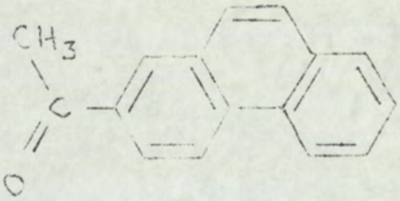
But the log $\tau_0 T$ vs $1/T$ plot may show the accuracy of assigned ε_∞ of individual measurements. Sample log τT vs $1/T$ plots are shown in Fig. 2:8. The second decimal place quoted for $\Delta G^{\ddagger}$ values has no absolute significance, but has been retained as possibly showing trends with temperature. The enthalpies of activation with a high weighting factor are considered to be accurate within ± 20%, while those with a low C value should have an error of ∿± 30%. These errors will also depend on the number of temperatures measured.

Courtauld models show little steric hindrance of the acetyl group rotation in the aromatic acetyl compounds studied in this chapter. Maximum resonance will be achieved in these molecules when the plane of the acetyl group is in the plane of the aromatic nucleus. When the acetyl group is in such a position it is normally regarded as being in an equilibrium position$^{(10)}$. There will be two such equilibrium positions, having equal probability and are shown below for 2-acetylphenanthrene (an unsymetrical molecule).

I



II



These two positions are separated by an energy barrier, the height of which is equal to the resonance energy contribution by the acetyl group to the molecule. The free energy parameter $\Delta G^{\ddagger}$ will therefore be the total energy change of a molecule in going from an initial to an activated state. This energy is expended in changing the $H^{\ddagger}$ and $S^{\ddagger}$ terms

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

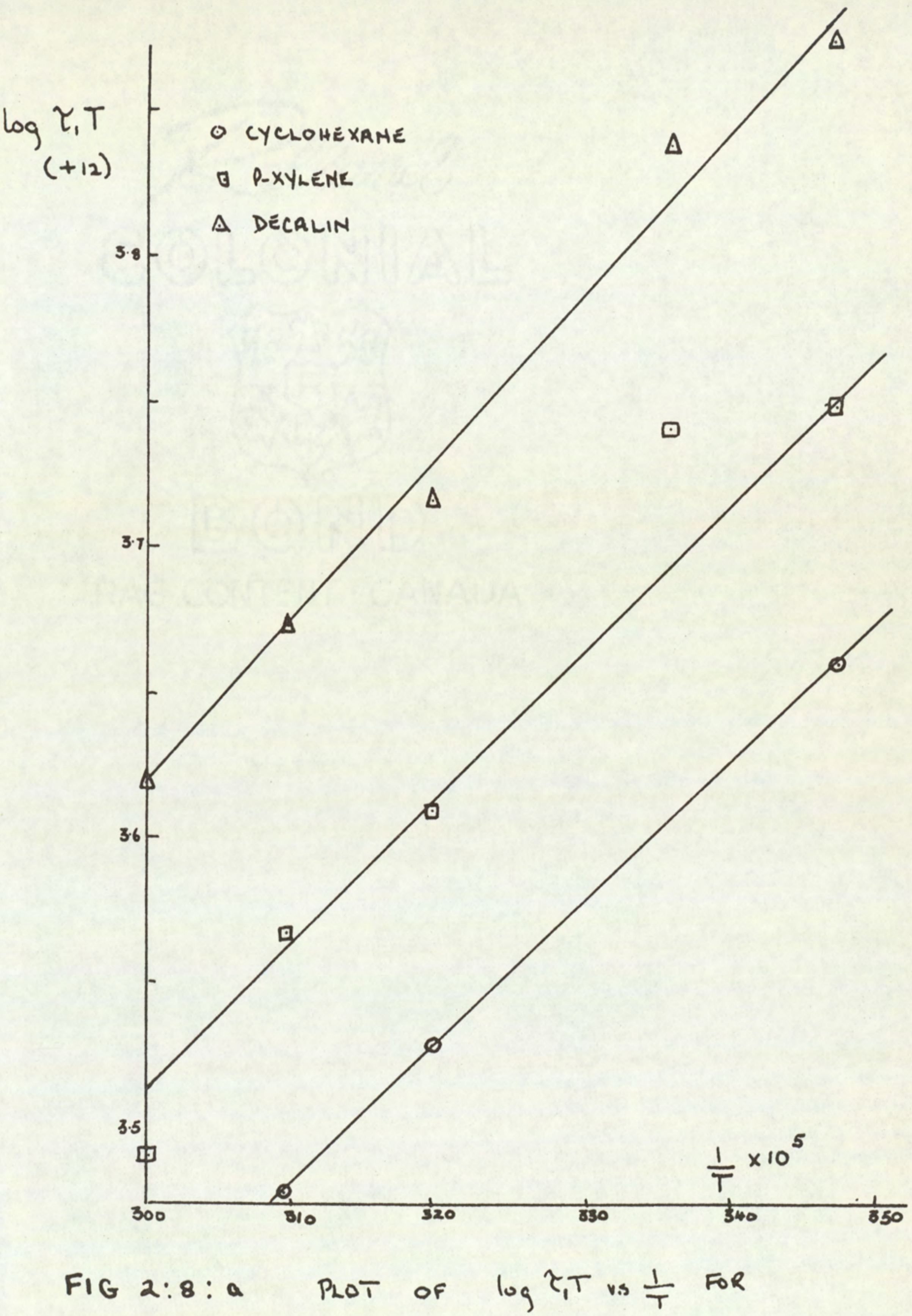


FIG 2:8:a PLOT OF $\log \tau_1 T$ vs $\frac{1}{T}$ FOR ACETOPHENONE $C_1 = 0.55$

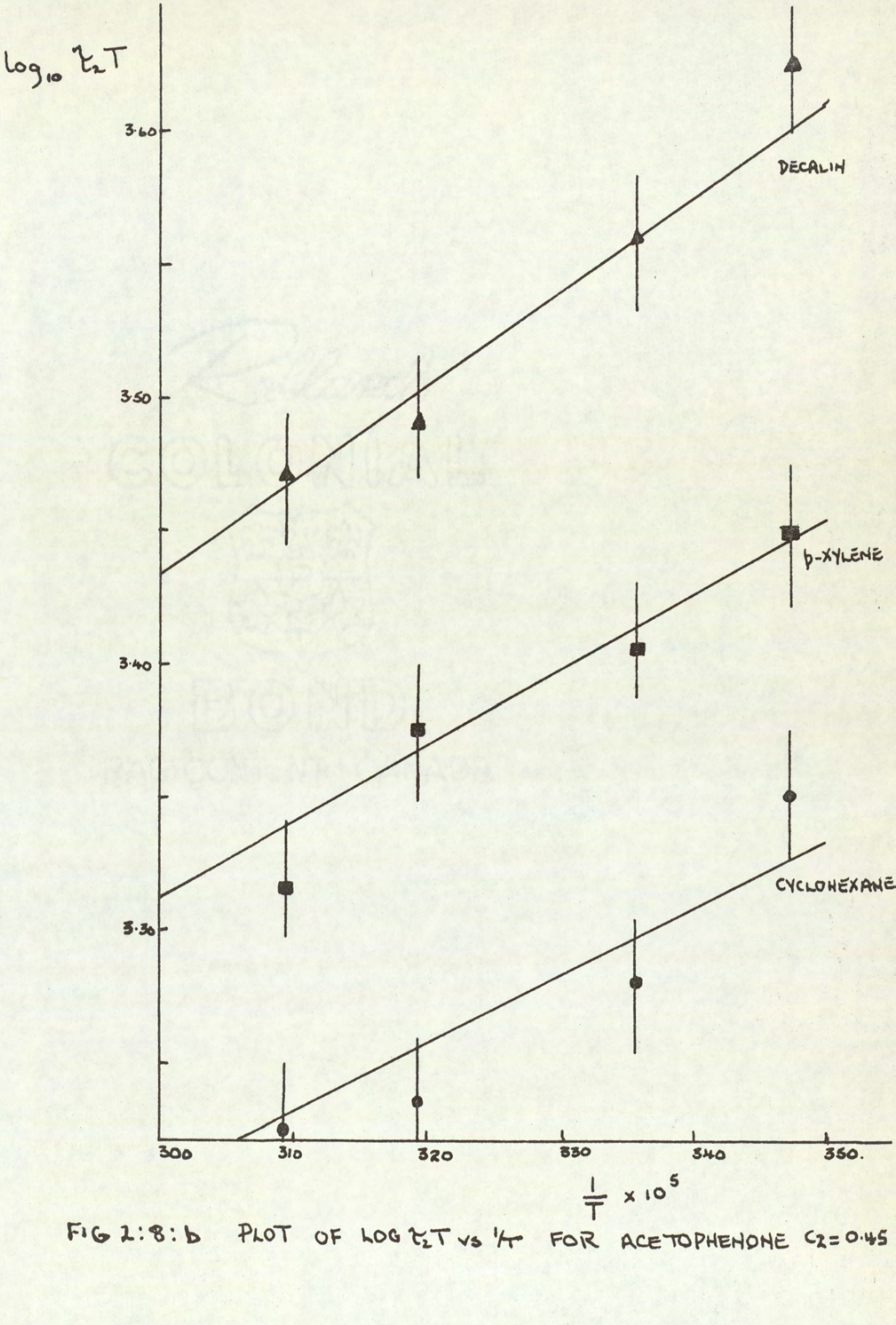


FIG 2:8:b PLOT OF LOG $\tau_2 T$ vs $1/T$ FOR ACETOPHENONE $C_2 = 0.45$

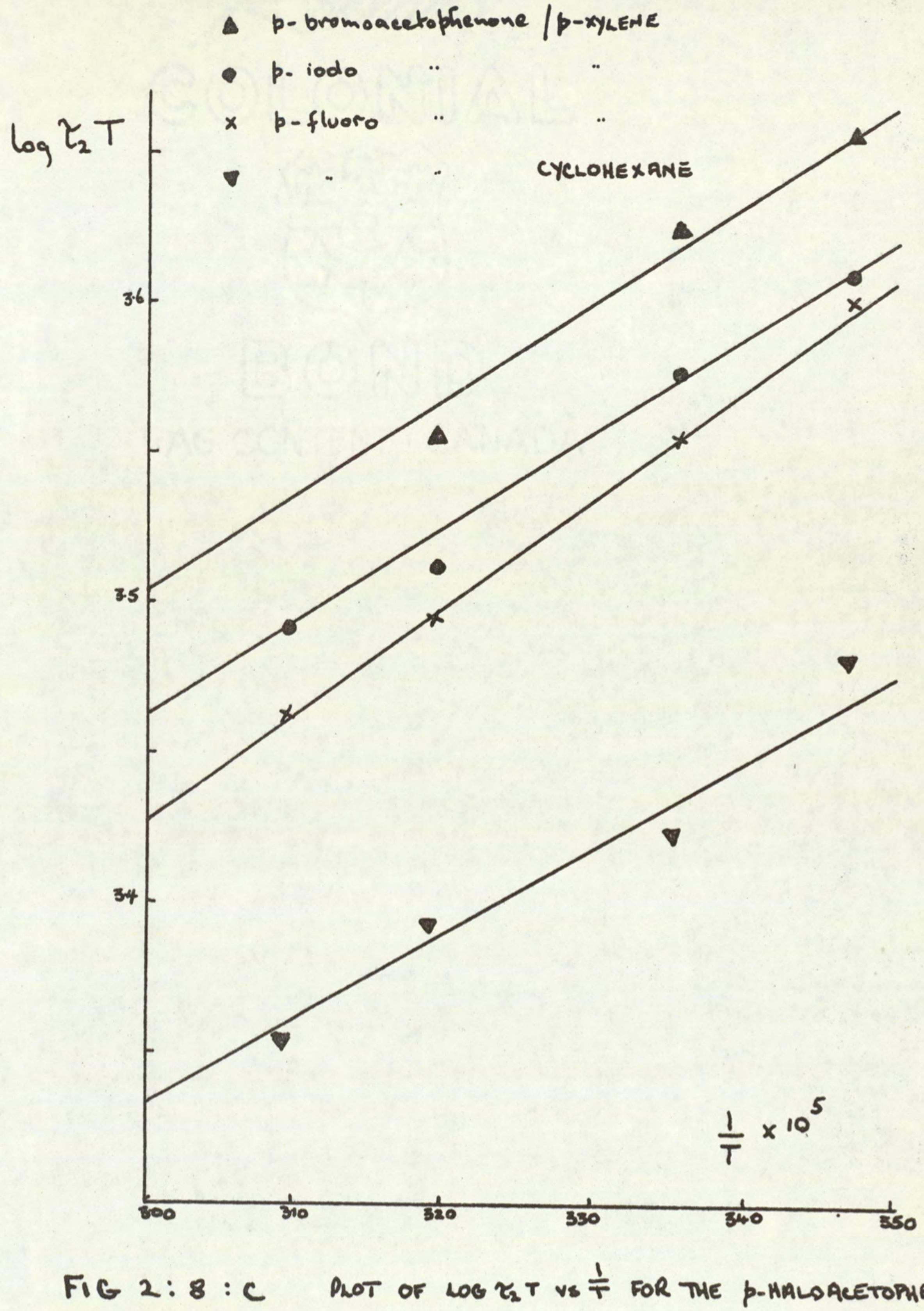


FIG 2:8:C PLOT OF LOG $\tau_2 T$ vs $\frac{1}{T}$ FOR THE p-HALOACETOPHENONES

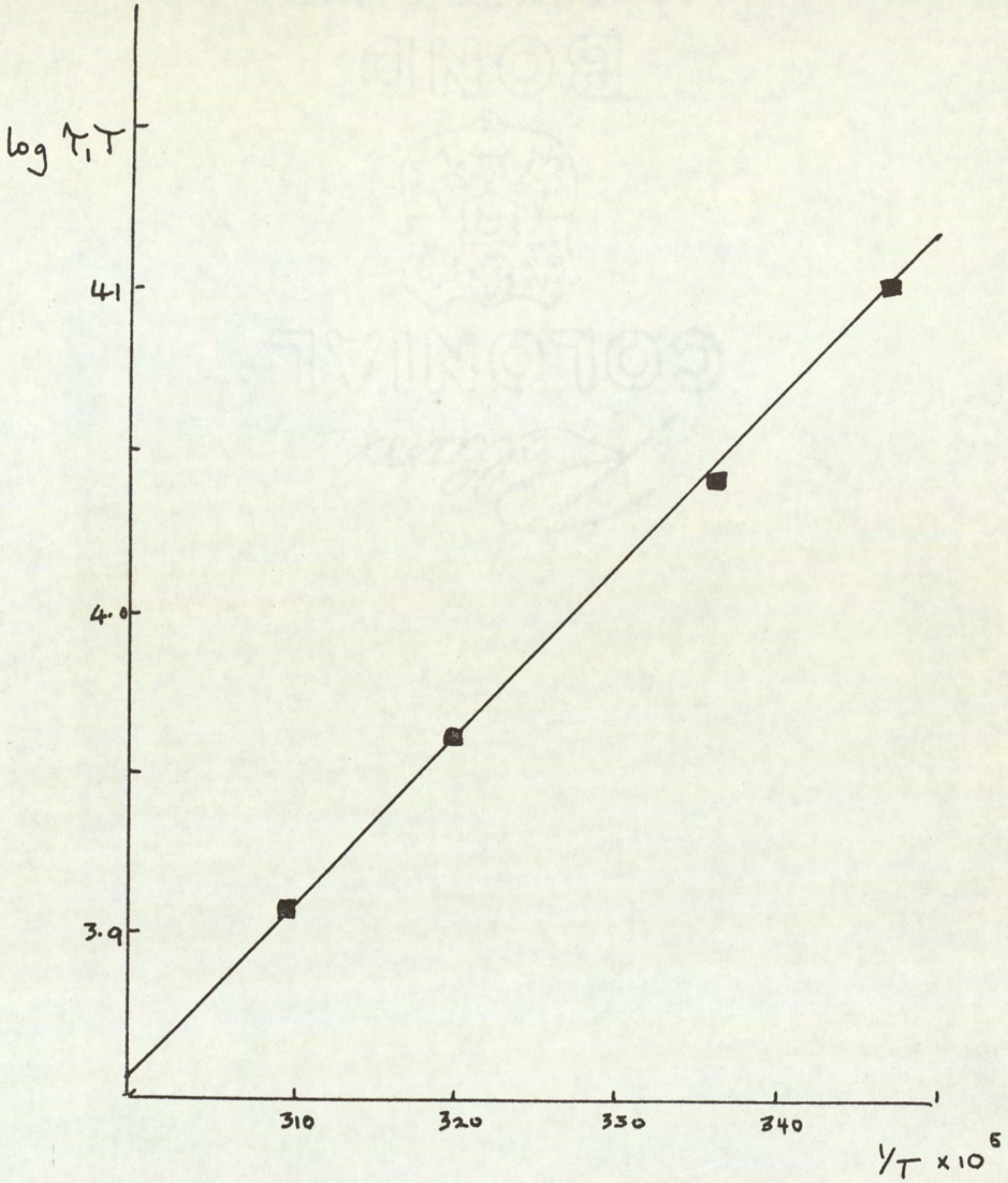


FIG 2 : 8 : d PLOT OF LOG $\tau_1 T$ VS $\frac{1}{T}$ FOR 2-ACETONAPHTHONE IN p-XYLENE

The enthalpy of activation ($\Delta H_2^{\ddagger}$) being the actual potential barrier the acetyl group encounters as it rotates.

The $\Delta H_2^{\ddagger}$ values in Table 2:2a show only small trends which may well be within the experimental error. For example, Farmer's acetophenone results in p-xylene and cyclohexane solvents give a $\Delta H_2^{\ddagger}$ of the order of 1.25 kcal/mole, while in decalin a value of 1.6 kcal/mole is obtained. The discrepancy is most probably due to experimental error, although closer examination of the decalin results shows that $\tau_{2\text{decalin}} > \tau_{2\text{nujol}}$. Obviously in this case further viscous solution studies are required. The $\Delta H_2^{\ddagger}$ value of 1.25 kcal/mole is indistinguishable (within the error limits) from the value for the resonance energy contribution of 1 kcal to the acetophenone molecule by the acetyl group determined calorimetrically$^{(82)}$.

2-Acetonaphthone, in comparison, was found to have a $\Delta H_2^{\ddagger}$ = 1.8 kcal/mole. Although there will be a larger error in 2-acetonaphthone with a $C_2 = 0.2$, an increased enthalpy over that of acetophenone would be expected. Since, as the double bond character of the R-$COCH_3$ increases, so also would the potential energy barrier to rotation. Previously this has been reflected in the larger τ_2 value, and as $\Delta G_2^{\ddagger}$ is obtained directly from this parameter, it is not surprising that $\Delta G_2^{\ddagger}$ is also found to increase with conjugation. 2-acetonaphthone, as well as 1-acetylcyclohexene, have $\Delta G_2^{\ddagger} \simeq 2.6$ kcal/mole, while acetophenone has a value of 2.3 kcal/mole (the error on $\Delta G^{\ddagger}$ being $\sim \pm 0.1$ kcal/mole). Smyth$^{(10)}$ on the other hand obtained a similar $\Delta G_2^{\ddagger}$ and $\Delta H_2^{\ddagger}$ for 2-acetonaphthone as acetophenone. Apart from the error caused by the low C_2, measurements in this study incorporate more high frequency points than in those reported by Smyth. The total dielectric loss from the group relaxation process should predominate in this region and therefore a greater accuracy should be achieved in the derivation of the $\Delta G_2^{\ddagger}$ and $\Delta H_2^{\ddagger}$ values.

The p-haloacetophenones exhibit larger enthalpies of activation to acetyl rotation (mean $\Delta H_2^{\ddagger} = 1.6$ kcal/mole) than acetophenone. Once again this may be attributed to experimental error or increased acetyl conjugation. The error is obviously large in the p-alkylacetophenone results, only two temperature measurements were made and a relatively low weighting factor to acetyl rotation (∿0.35) was observed. Therefore no real comparisons can be made with these results, where the error is most probably greater than 0.5 kcal/mole.

It is, indeed unfortunate that the errors are such in the dielectric method, that the $\Delta H_2^{\ddagger}$ values of molecules, such as 1-acetylcyclohexene and 2-acetonaphthone, can only tentatively confirm the suggestions obtained by other physical methods. The accuracy of the thermodynamic parameters could be enhanced by increasing the temperature range to below 0^{o}C.

Similar errors are present in the energy barrier parameters opposing molecular relaxation which are shown in Table 2:2:b. For this reason only two sample values of the p-haloacetophenones ($C_1 = 0.25$) have been included. As would be expected, a definite trend may be seen in the $\Delta G_1^{\ddagger}$ values with increasing molecular size, however a corresponding trend in the $\Delta H_1^{\ddagger}$ value is not so obvious. The $\Delta H_1^{\ddagger}$ obtained for acetophenone in p-xylene (2.3 kcal/mole) being indistinguishable from the $\Delta H_1^{\ddagger}$ value obtained for 2-acetonaphthone in the same solvent (2.4 kcal/mole). The large $\Delta H_1^{\ddagger}$ exhibited by p-fluoroacetophenone (3.6 kcal/mole) has no physical significance, nor has the positive entropy accompanying it, $\Delta S^{\ddagger}$ automatically assuming a positive value when $\Delta H^{\ddagger}$ is above 3.2 kcal$^{(80)}$. All that can be conclusively said about the enthalpy of activation for molecular rotation is that it is greater than that of the intramolecular process. The same interpretation may be made about the $\Delta S^{\ddagger}$ difference between the two processes. When the dipole reorientates in the dielectric field there are two entropy changes, a $-\Delta S^{\ddagger}$ which accompanies the dipoles moving from a random state to one of more order and a $+\Delta S^{\ddagger}$ evolved from the solvent molecules being displaced to a more chaotic state. In an intramolecular process, the former change would be expected to predominate, this is seen to be true for the acetyl compounds $\Delta S_2^{\ddagger} \sim -3 \rightarrow -5$e.u., ΔS_1 assuming a more positive value ($-1 \rightarrow -3$e.u.) owing to the solvent change becoming more important in the molecular process.

Thus in conclusion the free energies $\Delta G^{\ddagger}$, heats $\Delta H^{\ddagger}$ and entropies $\Delta S^{\ddagger}$ of activation for the acetyl compounds have been calculated. The barrier to acetyl rotation was found to be of the order of 1.5 kcal/mole in comparison to the barrier opposing the molecular process of 2.3 kcal/mole. The degree of error in the dielectric method is such that only tentative conclusions could be drawn from the small trends within the compounds.

5. Summary.

The dielectric absorption of the following compounds has been measured at several microwave frequencies in p-xylene and cyclohexane solvents at several temperatures: the p-haloacetophenones, two p-alkylacetophenones, 2-acetonaphthanone, 2-acetyl, 3-acetyl and 9-acetylphenanthrenes, and 1-acetylcyclohexene. All compounds showed a lowering of the mean relaxation time which has been attributed to an acetyl intramolecular process. A small tendency for the relaxation time of this process (τ_2) and the molecular weighting factor (C_1) to increase with increasing conjugation of the acetyl group was observed. Infra-red evidence was used to justify the nature of this trend. Measurement in a viscous solvent (incorporating nujol) was also used to assist in the establishment of τ_2 and C_1 values for acetophenone 4-acetylpyridine, 4-bromoacetophenone and 3-acetylphenanthrene. To obtain convincing analyses of dielectric data into contributions from two relaxation times it was found necessary to employ several frequencies and carry out measurements at several temperatures to establish consistent behaviour. Measurement of a variety of molecules with varying C_2 contributions was also found to be desirable.

CHAPTER 3

RELAXATION PROCESSES OF SOME STERICALLY HINDERED ACETOPHENONES.

Introduction

Placing substituents in the ortho positions of acetophenone might be expected to hinder the reorientation process of the acetyl group. Dipole moment studies have suggested that the acetyl group adopts preferred conformations which very much depend on the type of substituted group.(86) Similar conclusions have also been drawn from spectroscopic measurements.(35)(87) 2-chloroacetophenone, 2.5-dichloroacetophenone, and 2,4,6-trimethylacetophenone were measured dielectrically in p-xylene at several tempteratures, to determine whether similar effects were also present in the microwave region. 9-Acetylanthracene was measured and included in this chapter as another example of hindered acetyl rotation, similar to that observed for 9-acetylphenanthrene previously. In contrast with the latter, the acetyl group in the anthryl molecule should be hindered by two hydrogens (on the 1 and 8 carbons) and, therefore, very little intramolecular motion would be expected. The dielectric results are presented in Table 3:1.

Discussion of Results

The low mean relaxation times obtained for 2-chloro and 2, 5-dichloroacetophenones indicate that an intramolecular process is present in these compounds. An extrapolated τ_0 for 2-chloro

TABLE 3:1: a DIELECTRIC PARAMETERS OF SOME ORTHO SUBSTITUTED ACETOPHENONES AND 9-ACETYLANTHRACENE IN P-XYLENE

COMPOUND	TEMP.	τ_o	τ_1	τ_2	C_1	α	μ	$\varepsilon_\infty - n_D^2$	$\Delta H_o^\dagger$
	°C	$\times 10^{12}$ sec					D		kcal mole^{-1}
2-Chloro	15	11.5	17.3	5.1	0.66	0.08	2.97		
Acetophenone	25	10.5	16.2	5.8	0.59	0.06	2.94	0.034	1.0
	40	9.2	11.9	5.4	0.66	0.03	2.90		
2.5-Dichloro	15	11.3	17.4	6.7	0.59	0.06	2.54		1.8
Acetophenone	25	9.9	15.6	5.4	0.57	0.05	2.54	0.035	
	40	7.9	11.9	4.1	0.6	0.05	2.53		
	50	6.9	9.8	4.6	0.53	0.02	2.50		
2,4,6-Trimethyl	25	29.7				0	2.66	0.046	2.4
Acetophenone	50	20.0				0	2.64	0.033	
9-Acetyl	25	54.5				0.06	2.70	0.038	2.9
Anthracene	50	34.0				0.02	2.60	0.035	

TABLE 3:1 (b) INFRA-RED CARBONYL STRETCHING FREQUENCIES OF HINDERED ACETYL COMPOUNDS MEASURED IN CARBON TETRACHLORIDE

	$\nu c=o\ cm^{-1}$	Ref.
2-methylacetophenone	1690	
Acetophenone	1691	
2-fluoroacetophenone	1692	35
2-Chloroacetophenone	1702 1694	
2-Bromoacetophenone	1706 1702	
2,3,5,6-Tetramethylacetophenone	1704	
9-Acetylanthracene	1702	†

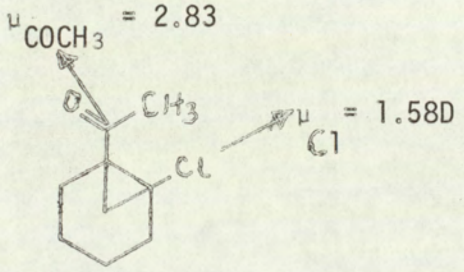
† This study

acetophenone at 60°C ($\sim 7.8 \times 10^{-12}$ sec) is much lower than that obtained for 2-chloroiodobenzene of 11.0×10^{-12} sec. The τ_0 of the dihalo compound would be expected to be even larger, because of the additional substituent, yet if anything, it is shorter, viz at 60°C $\sim 6.1 \times 10^{-12}$ sec. In fact, the τ_0 s of both compounds are shorter than acetophenone itself; the times obtained for 2-chloroacetophenone, 2.5 dichloroacetophenone and acetophenone at 15°C being 11.5, 11.3 and 14.3×10^{-12} sec, respectively. Analysis into two relaxation times give weighting factors of the same order, as predicted by both Group Moment and Bond Moment calculations. In ortho substituted acetophenones, the molecular component of the moment no longer lies along the axis of group rotation. The contributing moments are now resolved into three components, a molecular moment (μ_1) along the major symmetry axis; another rigid moment (μ_3) at right angles to this and the rotating group moment (μ_2), again at right angles to the main symmetry axis. The dipole moment corresponding to overall molecular rotation is now the resultant of two rigid moments, which meet at right angles in the benzene ring. The molecular weighting factor is therefore given by:

$$C_1 = \frac{\mu_1^2 + \mu_3^2}{\mu_1^2 + \mu_2^2 + \mu_3^2}$$

FIG. 3:1 CALCULATION OF WEIGHT FACTORS FOR 2-CHLOROACETOPHENONE FROM GROUP MOMENTS (a) AND BOND MOMENTS (b).

(a)



$$\mu_1 = 1.56 \text{ Cos } 60 + 2.83 \text{ Cos } 54$$

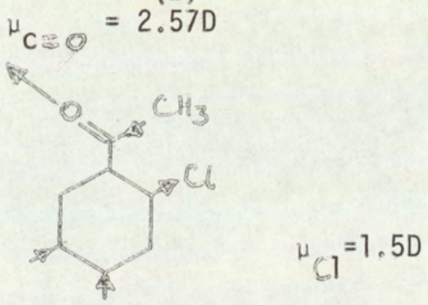
$$\mu_2 = 2.83 \text{ Sin } 54 \text{ (Mobile)}$$

$$\mu_3 = 1.56 \text{ Sin } 60 \text{ (FIXED)}$$

$$C_1 = \frac{\mu_1^2 + \mu_3^2}{\mu_1^2 + \mu_2^2 + \mu_3^2}$$

$$C_1 = 0.6$$

(b)



$$\mu_1 = 1.5 \text{ Cos}60 + 0.4 + 2.57 \text{ Cos}60$$

$$\mu_2 = 2.57 \text{ Sin}60 + 0.45 \text{ Sin}60 \text{ (MOBILE)}$$

$$\mu_3 = 1.5 \text{ Sin}60 + 0.4 \text{ Sin}60 \text{(FIXED)}$$

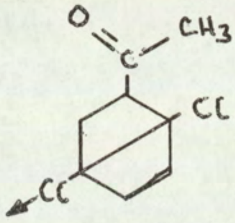
$$C_1 = \frac{\mu_1^2 + \mu_2^2}{\mu_1^2 + \mu_2^2 + \mu_3^2} = 0.58$$

Calculations by both methods are shown in Fig. 3:1 and surprisingly good agrement between them is observed ($C_1 \sim 0.6$). The weight factors of 2.5-dichloroacetophenone should, of course, be the same as those of acetophenone, the moments of the halogen atoms effectively cancelling one another.

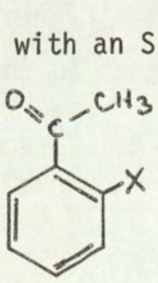
That the $\tau_1 = 17.3 \times 10^{-12}$ sec for 2-chloroacetophenone is analogous to an extrapolated τ for the rigid 2-hydroxyacetophenone measured by Smyth (28) gives the analysis credibility, whether it explains this compound's behaviour correctly, remains to be determined. Klages and Knobloch (14) have measured both these compounds in benzene at 20°C, their analyses into two relaxation times are similar to those given here. For the 2-substituted compound they obtained $\tau_1 = 14.3$, $\tau_2 = 2.4$, $C = 0.7$, while for the 2,5 subsituted acetophenone, $\tau_1 = 12.5$, $\tau_2 = 2.6$ and $C_1 = 0.7$. The τ values are smaller than those determined in this study, yet the general trends are the same i.e. τ_1 2,5-dichloroacetophene $< \tau_1$ 2-chloroacetophenone and τ_2 of both these compounds is less than that observed for acetophenone. Klages and his co-worker explained the latter fact by arguing that the ortho chlorine decreased the mesomeric moment between the acetyl group and the benzene ring and, therefore, the CH_3CO was more mobile than in acetophenone.

The dipole moment they observed for 2.5-dichloroacetophenone which should theoretically have the same moment as acetophenone, was 2.62D, slightly higher than that obtained here (2.54D). This reduction in comparison with that of acetophenone (2.83D) cannot be due to a librational motion, as was observed with 9-acetylphenanthrene, since $\varepsilon_\infty - n_D^2$ is of normal proportions (0.037), and therefore may well be attributed to the lack of a mesomeric moment (0.4 Cosθ) in this compound.

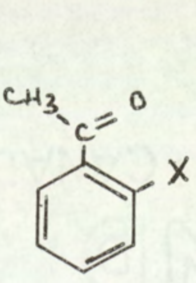
Dipole moment workers, Baliah and Aparajithan(4) preferred to account for the reduction by a mutual induction effect between the halogen atom and the acetyl group, together with a small moment acting along the C_2C_5 axis, as shown below:



These workers also proposed that the configuration of ortho substituted haloacetophenones was a s-trans one, as the observed dipole moments were closer to those calculated for this configuration in contrast with an S-cis



s-trans



s-cis

This suggestion that the acetyl group is in a fixed position, although credible from the dipole moment viewpoint, is not borne out by the dielectric results, which show clearly that the acetyl group is mobile. Nor has the dipole moment been found to increase with temperature in this study as reported by Baliah and Aparajithan, indicating that there are no alternative forms with varying population distributions.(88)

An alternative explanation of the results is that the acetyl group is out of the plane of the aromatic ring, due to steric and electrostatic effects, and therefore assumes an aliphatic moment (acetylcylohexane μ=2.58D, Table 2:3). The acetyl group could rotate between two out-of-plane equilibrium positions, the carbonyl oxygen not approaching the halogen atom too closely because of electrostatic repulsion. This would change the weighting to rotation from that calculated on a planar basis, since the angle between the acetyl moment and the halogen moment would be altered. Dhami and Stothers have calculated a twist angle of 26° for 2-chloroacetophenone from ^{13}C N.M.R. measurements.(87) Thus, the lowering of the τ_0, relative to that of acetophenone, could be explained by an increased weighting to the intramolecular process instead of a shorter τ_2. The longer αs observed for these compounds relative to acetophenone would be expected by either explanation.

The infra-red carbonyl stretching frequencies of 2-haloacetophenones (in carbon tetrachloride) as reported by Jones and his co-workers are given below:

	νco cm^{-1}
acetophenone	1691
2-fluoroacetophenone	1692
2-chloro "	1702,1694
2-bromo "	1706,1702

The increase in stretching frequency for 2-chloro and 2-bromoacetophenone relative to those of the respective 4-haloacetophenones could be caused by less conjugation in the acetyl group, as it twists out of plane of the aromatic ring. However, other direct field effects, such as dipole-dipole interaction, will also lengthen the carbonyl frequency,(89) so that the evidence in this case is not clearly defined. For the 2-chloro and 2-bromo derivatives, Jones found two maxima in the carbonyl region, and in the latter case the proportions of the maxima were observed to vary with temperature. This was attributed to varying distributions of quasi s-cis and quasi s-trans structures.

It would seem likely, therefore, that the acetyl groups' behaviour in these compounds could be described by a hybrid of the two possible explanations. In that, the mobile group encounters a relatively weak steric hindrance to coplanarity and assumes equilibrium positions at a small twist angle. The intramolecular process which occurs is shortened relative to acetophenone, owing to a decreased mesomeric moment between ring and group, and this nonplanarity also produces a larger C_2. Varying degrees of this, in 2-chloroacetophenone and 2,5-dichloroacetophenone, enables them to exhibit similar mean relaxation times. It is considered unlikely that the carbonyl group will rotate past the ortho chlorine atom.

In contrast to these results, the τ_o (29.7×10^{-12} sec at 25°C), of 2,4,6-trimethylacetophenone or acetylmesitylene, does not show a sufficient shortening to warrant the presence of an intramolecular process. Attempted computer analysis into two relaxation times produced a very high C_1 of 0.95 and, as the dielectric parameters would not have any physical significance, they have not been presented. Purcell, Fish and Smyth also obtained a single large relaxation time for a similar molecule, bis-(chloromethyl)-durene, of 43.5×10^{-12} sec in benzene at 20°C,[(90)] indicating that the CH_2Cl group is hindered in rotation and only molecular orientation was observed. The difference in τ between the durene and mesitylene molecules is obviously due to the increased length of the former which is 1,4 disubstituted. Williams (105) maintains that an internal process should occur in the durene molecule, but the steric hindrance of the methyl groups reduces its rate to such an extent that it is not observed dynamically. This sort of explanation could also be applied to 2,4,6 trimethylacetophenone.

Observation of the acetyl methyl shieldings of acetylmesitylene in ^{13}C.N.M.R. studies, led Dhami and Stothers to conclude that the mobile group was twisted out of coplanarity with the benzene ring by 51°. (87) This evidence is further borne out by measurements using other spectroscopic techniques. Jones and his co-workers found that the carbonyl stretching frequency for 2,3,5,6-tetramethylacetophenone was at 1704 cm^{-1} in contrast with 1690 cm^{-1} for 2-methylacetophenone. (35) The non-planar configuration of the acetyl group was attributed to strong Van der Waals' repulsions between the ortho methyl groups and the acetyl methyl; the position of minimum potential energy probably being close to perpendicular to the plane of the ring, since the νcco is near that of an aliphatic ketone. A similar high Raman C-O stretching frequency of 1699 cm^{-1} observed by Saunders, (91) and low U.V. intensities observed by Brande (92) for acetylmesitylene, led these authors to the same conclusions. The dipole moments obtained in this study (2.66D) are lower than for acetophenone, yet higher than those calculated for 2.5-dichloroacetophenone for most probably similar reasons. The mesomeric effects in the latter would not be depressed so much as in acetylmesitylene (owing to the different twist angles), yet the chlorine atoms may be expected to exert inductive effects which will reduce the moment. Smith, however, preferred to explain the difference in moments between ortho substituted halo and alkylacetophenones, by non-bonding interactions e.g. dipole-dipole repulsions of the C=O and C-Br bonds, (which would be stronger in the former compounds), as inductive effects in 2,4,6-tribromobenzonitrile did not change the moment of this molecule relative to benzonitrile.(94) Le Fevre and his co-workers observed the same difference between the dipole moments of acetylmesitylene and acetophenone, and calculated the twist angle for the former compound to be 90° from molar Kerr constants calculations.(93) They also obtained a τ for this molecule of 23×10^{-12} sec in benzene at 22°C, which is slightly low in comparison with our value, and explained the increase in relaxation time, relative to acetophenone, by the larger volume swept out by the rigid anti-planar configuration of acetylmesitylene. The $\varepsilon_\infty - n_D^2$ (0.046) determined for this compound, although slightly larger than is normally observed, is not sufficiently significant for a librational motion. Therefore, all the dielectric evidence clearly points to a rigid behaviour for 2,4,6 trimethylacetophenone.

Since a methyl group is of similar size to a chlorine atom, it may be suggested from a steric viewpoint that when one group of this size is placed in the ortho position of acetophenone, the intramolecular process is not depressed, but accelerated, owing to a decrease in the mesomeric moment, yet insertion of two groups into the ortho positions prevents motion of the CH_3CO completely. Measurement of 2-methylacetophenone would indicate whether this generalisation depended upon the electronic nature of the substituent.

A similar situation arises in 9-acetylanthracene where the Courtald model suggests hindrance of the acetyl group by the two hydrogens on the 1 and 8 carbon atoms. Unfortunately, no dielectric results on rigid 9-substituted anthracenes have been reported in the literature, yet comparison of the τ_o of 54.5×10^{-12} sec obtained at 25°C with the τ of 44×10^{-12} sec, reported by Hufnagel and Kilp(60) for 9-bromophenanthrene in cyclohexane at 20°C, shows that there is little possibility of acetyl rotation in 9-acetylanthracene. The dipole moment is similarly depressed as in acetylmesitylene and unlike 9-acetylphenanthrene and 1-acetonaphthone, there is no librational motion detectable with an $\varepsilon_\infty - n_D^2 = 0.038$. Infra-red measurement produced a $\nu_{C=O}$ = $1702 cm^{-1}$ and N.M.R. studies gave an acetyl twist angle of 49°.(85)

Both these results are again comparable with those of acetylmesitylene and it would appear that 9-acetylanthracene behaves as a rigid molecule. The α=0.06 obtained at 25°C in this case, cannot be used as evidence of an intramolecular process; Cavell and Knight (95) have shown that too much importance cannot be attached to α without proper consideration of the other dielectric parameters and Smyth (79) does not attach any physical significance to an α= of 0.04. The α in this case may arise from a small distribution of molecular relaxation times. A molecule has two symmetry axes, perpendicular to the molecular component moment, about which it can rotate. In small molecules, the two volumes swept out about these axes are comparable, and no distinction can be observed. As the molecular size increases, however, one volume may become slightly larger than the other and an inseparable distribution occurs. This has also been observed in this laboratory in the dielectric measurement of rigid steroids, where the resultant moment is at an angle to the symmetry axes. (97) On inspecting the τ_os in the series, acetophenone, 1-acetonaphthone and 9-acetylanthracene, a large increase is observed between the last two compounds, for example at 25°C the τ_os are: 12.8, $\sim$23.5, 54.5×10^{-12} sec. The increase is further emphasised when the τ_1 of acetophenone (18.5×10^{-12} at 25°C)is considered. This increase tentatively confirms the lowering of 1-acetonapthone's τ_o by the type of intramolecular motion observed in 9-acetylphenanthrene, although it may also be explained by the increased non-planarity of the acetyl group in 9-acetylanthracene. It is unlikely, however, that the latter would affect the relaxation time to this extent.

Only $\Delta H^{\ddagger}_{o}$ has been calculated for the compounds in this chapter, owing to the uncertainty of the τ_1 and τ_2 values of the halogen derivatives, and, of course, acetylmesitylene and 9-acetylanthracene have been found to be rigid. ΔHo has no physical meaning for the former compounds, being determined from the mean of relaxation times, yet the low value of 1.0 kcal/mole for 2-chloroacetophenone once again emphasises the mobility of the acetyl group in this molecule. For the rigid derivatives, as only two temperature measurements were made, $\Delta H^{\ddagger}_{o}$ will be an approximate potential energy barrier to molecular rotation.

Thus in conclusion, evidence of an intramolecular process has been found in 2-chloroacetophenone and 2,5-dichloracetophenone, while 2,4,6-trimethylacetophenone and 9-acetylanthracene were observed to behave as rigid molecules.

CHAPTER 4

DIELECTRIC STUDIES OF SOME AROMATIC ETHERS AND A STEROIDAL ETHER

INTRODUCTION

Many dielectric studies have been carried out on anisole and its derivatives, all the evidence suggests that the methoxy group has a high degree of mobility. Anisole, p-methylanisole and p-dimethoxybenzene for example, have all been found to relax predominantly by methoxy group rotation(1), while the latter compound's τ_0 has been discovered to vary little with increasing solvent viscosity(73) in contrast to the acetyl molecules reported in Chapter 2. The work in the preceding chapter has shown that the acetyl group's mobility is enhanced when a single **substituent** is placed ortho to it, but a further ortho substitunet prevents motion of this group completely. It is, therefore, of interest to examine the effects of similar substitution in the analogous methoxy compounds and for this reason ortho substituted fluoro, bromo and iodoanisoles, together with 2,6-dimethyl and 2,4,6-tribromoanisoles have been measured in p-xylene at two temperatures. 2-Bromoethoxybenzene has similarly been studied, and to ensure that the behaviour of the ethoxy group was the same as that of the methoxy, the relaxation parameters of ethoxybenzene(phenetole) and 2-ethoxynaphthalene have been determined at 25°C.

Finally, in a further effort to obtain a distinct separation of molecular and intramolecular relaxation times by studying a large non-rigid molecule, where $\tau_1 >> \tau_2$ (cf. Chapter 2:c), cholesteryl methyl ether was measured in p-xylene and cyclohexane at 25°C. The molecular relaxation time of this steroid should be of the order of $100 - 200 \times 10^{-12}$ sec(2)(21), while the intramolecular process should be

TABLE 4:1:a DIELECTRIC PARAMETERS AND ENERGY BARRIERS (TO MEAN RELAXATION) OF SUBSTITUTED AROMATIC ETHERS. THE SOLVENT USED WAS P-XYLENE.

Compound	Temp. °C	τ_0 x 10^{12} sec	α	μ D	$\varepsilon_\infty - n_D^2$	$\Delta G_0^\ddagger$ kcal/mole	$\Delta H_0^\ddagger$ kcal/mole	$\Delta S_0^\ddagger$ e.u.
2-Fluoroanisole	25	11.1	0.04	2.26	0.048	2.51	2.3	-0.7
	50	7.6	0.02	2.25	0.032	2.52	2.3	-0.7
2-Bromoanisole	15	21.9	0.02	2.48	0.040	2.79	1.8	-3.4
	50	14.0	0	2.46	0.033	2.92	1.8	-3.5
2-Iodoanisole	15	26.3	0.03	2.36	0.041	2.90	1.8	-3.8
	50	16.8	0	2.34	0.034	3.03	1.8	-3.8
2,6-Dimethylanisole	25	20.5	0	1.20	0.042	2.87	2.1	-2.6
	50	14.3	0	1.20	0.034	2.93	2.1	-2.6
2,4,6-Tribromo-	25	35.1	0.01	1.43	0.041	3.19	2.8	-1.3
anisole	50	22.5	0.01	1.42	0.037	3.22	2.8	-1.3

TABLE 4:1:a DIELECTRIC PARAMETERS AND ENERGY BARRIERS (TO MEAN RELAXATION) OF SUBSTITUTED AROMATIC ETHERS. THE SOLVENT USED WAS P-XYLENE.

Compound	Temp.	τ_o	α	μ	$\varepsilon_\infty - n_D^2$	$\Delta G_o^\ddagger$	$\Delta H_o^\ddagger$	$\Delta S_o^\ddagger$
2-Bromoethoxybenzene	15	27.7	0.03	2.54	0.046	2.92	2.5	-1.4
	25	22.8	0.04	2.48	0.044	2.93	2.5	-1.4
	37.5	19.0	0	2.44		2.95	2.5	-1.4
	50	15.6	0	2.44	0.023	2.94	2.5	-1.4

TABLE 4:1:b DIELECTRIC PARAMETERS FOR UNHINDERED ETHER COMPOUNDS AT 25°C

Compound	Solvent	τ_o	τ_1	τ_2	C_1	α	μ	$\varepsilon_\infty - n_D^2$
Phenetole	P-xylene	11.9	44.5	9.5	0.24	0.09	1.28	0.056
2-ethoxynaphthalene		24.5	47.4	11.3	0.59	0.14	1.26	0.039
Cholesteryl-methyl			193*	6.0*			1.35	0.035
ether	cyclohexane		200*	6.3*			1.34	

* Calculated from ε' vs ε"ω and log ω vs ε" plots.

TABLE 4:2 DIELECTRIC PARAMETERS OF AROMATIC ETHERS AND RELATED COMPOUNDS REPORTED IN THE LITERATURE.

Compound	Solvent	Temp.	τ_o	τ_1	τ_2	C_1	μ	Ref.
		°C	$\times 10^{12}$ sec				D	
Anisole	p-xylene	15	10.8	79.	9.6	0.15	1.19	
		25	9.0	40	8.0	0.15	1.19	
		50	6.7	11	5.8	0.15	1.13	
2-Chloroanisole	Benzene	20	12.3	15.0(calc.)			2.44	136
2-Bromoanisole		20	18.7*	19.7	1.3	0.94	2.48	14
2-Nitroanisole		20	20.8				4.80	14
2,4-Dinitroanisole		33.5	21.1				3.83	139
2,4-Dichloroanisole		20	25.4*	26.6	2	0.95	2.77	14
2,5-Dichloranisole		20	22*	24.8	1.5	0.88	1.35	14
2,5-Dinitroanisole		20	29.7*	33.5	2.1	0.88	1.58	14

TABLE 4:2 DIELECTRIC PARAMETERS OF AROMATIC ETHERS AND RELATED COMPOUNDS REPORTED IN THE LITERATURE.

Compound	Solvent	Temp.	τ_o	τ_1	τ_2	C_1	μ	Ref.
		°C		$\times 10^{12}$ sec				
2,6-Dimethylanisole		20	25	14	40	0.52	1.28	12
		40	20	11	25	0.56	1.28	
		60	15.1	8	17	0.61	1.28	
2,6-Dichloroanisole		20	19.9	19.1 (calc.)			2.63	136
3,5-Dimethylanisole		20	16	18	4.5	0.28	1.26	12
2,4,6-Trimethylanisole		20	15.9	22.7	0.8	0.69	1.26	135
2,4,6-Trichloroanisole		20	12.0	22.5 (calc)			1.40	136
		20	24.1*	27.2	1.5	0.88	1.42	14
		18	20.9				1.40	25+137

TABLE 4:2 DIELECTRIC PARAMETERS OF AROMATIC ETHERS AND RELATED COMPOUNDS REPORTED IN THE LITERATURE.

Compound	Solvent	Temp.	τ_o	τ_1	τ_2	C_1	μ	Ref.
		°C		x 10^{12} sec			D	
2,4,6-Tribromoanisole		20	23.4				1.39	
2.4-Dinitrophenetole		33.5	22.8				4.08	139
1-Methoxynaphthalene	Benzene	20	22.5*	24.3	1.7	0.93	1.24	14
	liquid	20		136	2.3	0.87		138
		20	140				0.97	96
	Decalin	20	55.2	79.4	27.5	0.6		73
	Nujol	20	347	640	27.5	0.7		
1-Ethoxynaphthalene	Decalin	20	105	110	36.3	0.82		
	Nujol	20	1050	1100	33.1	0.92		
2-Methoxynaphthalene	p-xylene	25	20.3	50	10.3	0.5	1.21	1

TABLE 4:2 DIELECTRIC PARAMETERS OF AROMATIC ETHERS AND RELATED COMPOUNDS REPORTED IN THE LITERATURE.

Compound	Solvent	Temp.	τ_o	τ_1	τ_2	C_1	μ	Ref.
		°C		x 10^{12} sec			D	
	Benzene	20	16*	19.7	1.1	0.80	1.17	14
	Liquid	80		14.9	1.0	0.8		138
		80	147				0.95	96
	Decalin	20	33.1	94	15.8	0.49		73
	Nujol			912	20.0	0.58		
2-Ethoxynaphthalene	Decalin	20	56.2	122	24.5	0.45		
	Nujol	20	290	1212	24.5	0.60		
Benzylchloride	P-xylene	15	13.0	15.8	2.6	0.81	1.71	1
		25	11.2	15.4	4.7	0.7	1.70	
		50	8.5	11.4	3.6	0.71	1.67	

TABLE 4:2 DIELECTRIC PARAMETERS OF AROMATIC ETHERS AND RELATED COMPOUNDS REPORTED IN THE LITERATURE.

Compound	Solvent	Temp.	τ_o	τ_1	τ_2	C_1	μ	Ref.
		°C		$\times 10^{12}$ sec				
1-Chloromethyl-naphthalene	Benzene	20	26					78

* τ_o not reported, but has been calculated from the approximate relationship : $\tau_o = C_1\tau_1 + C_2\tau_2$

shorter than that observed in anisole ($\sim 7 \times 10^{-12}$ sec at $25^{o}C$)(1), since there is no mesomeric moment to hinder the methoxy rotation. A τ_2 obtained for this molecule would, therefore, give a minimum value for the aromatic process and may clarify the molecular weighting factors for these compounds since there has been a large variance of C_1 values for anisole reported in the literature(73)(78)(79)(135).

DISCUSSION

Previous dielectric work on possible sterically hindered aromatic ethers has produced conflicting conclusions on the mobility of the methoxy or ethoxy group. Maier(136) measured dilute benzene solutions at $20^{o}C$ of 2 -chloro, 2,6-dichloro and 2,4,6-trichloroanisole obtaining τ_0s of 12.3, 19.9 and 12.0×10^{-12} sec respectively. By comparing these values with a theoretical τ, calculated from molecular dimensions assuming the molecule to be rigid, this author concluded that the methoxy rotation was not hindered at all by the chlorine atoms. Although the relationship between τ and molecular volume has been found to be only of approximate nature (Chapter 6) and should not be used for axially asymmetric molecules(114) an intramolecular process would certainly appear to occur in these compounds, especially in the tri-substituted derivative. The larger τ_0 obtained for the di-substituted molecule was explained by an increased fixed component of the dipole moment and, therefore, a higher C_1, while the C—Cl dipoles in trichloroanisole compensate one another, giving a C_1 similar to that of anisole.

Le Fèvre and his co-workers(25), however, on measuring 2,4,6-trichloroanisole in benzene at $18^{o}C$ found a larger τ_0 of

20.9×10^{-12} sec which was much longer than that of the equivalent phenol. This suggested to them that the methoxy group encountered a high barrier to rotation and calculation of the molar Kerr constant indicated that the O—Me was 90^0 out of plane of the aromatic nucleus(137). Klages and Zenteck reported an approximate mean relaxation time of 15.9×10^{-12} sec for 2,4,6-trimethylanisole in benzene at 20^0C with $\tau_1 = 22.7$ $\tau_2 = 0.8 \times 10^{-12}$ sec and $C_1 = 0.7$(135). Since the methyl group is of similar size to a chlorine atom this result conflicts with that of Le Fèvre. In a later, more detailed paper, however, including 2;2,5, and 2,4,6 substituted acetophenones and anisoles Klages and Knoblich found that the intramolecular process in the 2 and 2,5-substituted anisoles had lengthened in comparison with the parent compound whereas substitution of the same groups in acetophenone appeared to increase the mobility of the acetyl group(14). 2,5-Dichloroacetophenone, for example, gave an $\tau_0 \approx 10 \times 10^{-12}$ sec while 2,5-dichloroanisole, the smaller molecule was found to have a $\tau_0 \approx 22 \times 10^{-12}$ sec. The different behaviour between the acetyl and methoxy compounds was especially noticeable in the 1-substituted naphthalenes (where the hydrogen on the 8 carbon atom is a possible hindrance to group rotation), with 1-acetonaphthone's $\tau_0 \approx 17 \times 10^{-12}$ in contrast to that of 1-methoxynaphthalene which was found to be $\sim 23 \times 10^{-12}$ sec. These results indicate a large hindrance to methoxy rotation, although the authors do not appear to consider the molecules rigid since the results are analysed into two relaxation times. Grubb and Smyth studying viscous solutions of naphthalene ethers observed that the τ_0 of the 1-substituted naphthalenes was larger than that of the 2-substituted derivative (in rigid halonaphthalenes the reverse is true) and also concluded that the ether group in the 1 position was being sterically hindered(73). Vaughan and his co-workers, however, disagree with these conclusions, maintaining that their measurements on the liquid methoxy naphthalenes, show that internal rotation is not restricted in either 1 or 2-methoxy naphthalenes, the τ_2 and C_2 values being comparable in both cases(138). Their analysis, however, appears to be at fault when the molecular relaxation times of the two molecules are compared, at 80°C 2-methoxynaphthalene's $\tau_1 = 14.9 \times 10^{-12}$ sec while an extrapolated value for the 1 substituted derivative is 30.6×10^{-12}, normally 2-substituted naphthalenes have the longer relaxation times(10)

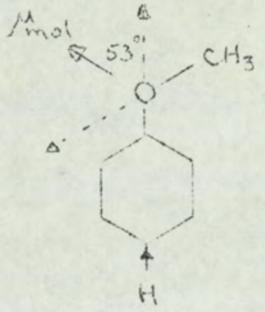
Fong and Smyth(12) found that analysis into two relaxation times of the dielectric data of 2,6-dimethylanisole in benzene, gave rather meaningless τ values and this was attributed to the very high potential energy barrier to methoxy rotation by the presence of the two neighbouring methyl groups. The τ_0 of this molecule is also larger than the equivalent sized 3,5-dimethylanisole, although part of this increase can be accounted for by a smaller molecular component moment in the latter. Farmer suggested that the C_1 for p-methyanisole, which will have the same component moments as the 3,5-substituted derivative, was virtually zero(1) in the 2,6-dimethylanisole,the resultant methyl moment (0.4D) is in the reverse direction and can be expected to decrease the C_2 slightly.

The principal area of dielectric study of aromatic ethers has been with anisole derivatives and if the methoxy group rotation is hindered by ortho substitutents, this effect could be expected to increase in the ethoxy compounds. Mehrotra and his co-workers measuring 2,4-dinitro substituted derivatives of phenol, anisole and phenetole, found that the relaxation times increased with the size of the mobile group and the τ of 2,4-dinitrophenetole (22.8×10^{-12} sec at $33.5^{\circ}C$) was larger than that of p-nitrophenetole (18.6×10^{-12} sec) under the same conditions. Although the latter difference is most probably within the experimental error and no allowance was made for the varying C_1s in these compounds, they concluded that the increased τ of the 2,4-dinitrophenetole was due to steric hindrance of the OEt group.

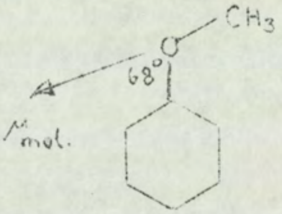
It can, therefore be seen that a certain amount of controversy exists in the literature concerning the mobility of the ether groups when there is a possible steric interaction between the movable group and a neighbouring substituent. No extensive survey of this problem has been carried out and comparing relaxation times obtained by different methods has the disadvantage that varying errors will occur, depending on the number of frequencies and temperatures measured. Comparison of the mean relaxation times of ortho substituted aromatic ethers with those of the analogous dihalobenzenes (reported in Chapter 6) should, therefore, be a more sensitive approach for detecting such processes.

Courtauld models(22) and Edward's atomic volume method(19) suggest that anisole is intermediate in size between that of bromo and iodobenzene, and slightly smaller than benzyl chloride; fluorine being such a small substituent should not increase the τ_0 of 2-fluoroanisole much above that of anisole and is most probably comparable to that of benzyl chloride.

Anisole would be expected to have a molecular relaxation time in p-xylene at 25^{0}C, of $\sim 13 \times 10^{-12}$ sec, while benzyl chloride one of 15.4×10^{-12} sec(1), comparing these with that of 2-fluoroanisole (11.1×10^{-12}) at the same temperature shows that rotation of the methoxy group is occurring in this molecule. Conducting a survey of anisoles, Farmer found that bond moment and group moment calculations predicted different directions for the molecular dipole, the former method giving an angle of 53^{0} to the main symmetry axis, away from the benzene ring, while the other gave an angle of 68^{0} directed towards the aromatic nucleus as shown below:(1)



BOND MOMENT

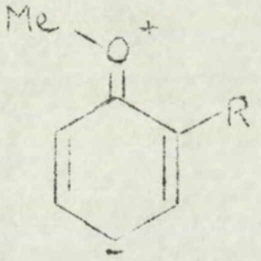


GROUP MOMENT

Dipole moment evidence coupled with the τ_0s of p-methylanisole and p-bromoanisole, led this worker to the conclusion that the group moment calculations predicted the correct direction of anisole's molecular moment. Taking, then, an angle of 68^{0} and a methoxy group moment of 1.19D(1), together with the usual halo group moments(29) produces a C_1 value for the 2-haloanisoles (calculated as in Chapter 3) of $\sim$0.6, this, of course, assumes that the methoxy group is freely rotating and no interaction occurs between it and the halogen atom. Analysis of the 2-fluoroanisole dielectric data into two relaxation times gives the following results at 25^{0}C, τ_1 = 17.2, τ_2 = 5.4, C_1 = 0.61 and at 50^{0}C τ_1 = 11.1, τ_2 = 3.7, C_1 = 0.6, the molecular relaxation is slightly larger and the intramolecular relaxation slightly smaller than would be expected from the analogous results of anisole. Here, as with 2-chloroacetophenone it is difficult to assess the applicability of the analyses and it would most probably be unwise to attach too much significance to them. Until further studies determine the extent of the interaction between the neighbouring groups, all that can be safely concluded is that some form of intramolecular relaxation is present in this compound.

In contrast to 2-fluoroanisole the τ_0s of 2-bromo and 2-iodoanisole when compared with the corresponding halobenzenes do not show any depression. Extrapolated τ_0 values at 60^{0}C for 2-bromo and 2-iodoanisole are 12.5 x 10^{-12} and 14.9 x 10^{-12} sec respectively,while τ_0s at this temperature for 2-chloro, 2 bromo and 2-iodo iodobenzene are 11.0 x 10^{-12}, 12.0 x 10^{-12} and 14.6 x 10^{-12} sec respectively. The molecular relaxation time for 2-bromoanisole would be expected to be just shorter than that of 2-bromoiodobenzene and similarly 2-iodoanisole's slightly shorter than that of 2-diiodoanisole, in fact, the τ_0s of the two sets of compounds are found to be the same and, therefore, only molecular relaxation is apparent in these ethers at this temperature. Intramolecular processes are easier to detect at lower temperatures, yet at 15^{0}C the τ_0s of the ortho iodo substituted anisole and iodobenzene are comparable (26.3 x 10^{-12} and 27 x 10^{-12} sec respectively) and as the $\Delta H^{\ddagger}$s (1.9 ± 0.1 kcal/mole) of these two types of compounds are the same, i.e. equivalent log τT vs $^{1}/T$ slopes, the τ_0s of the ortho bromo derivatives will also be compatible. If the C_1 value for the ethers is of the magnitude predicted by group moment calculations (bond moments suggest higher C_1s) the methoxy group then appears to be completely sterically hindered to rotation.

The increased dipole moments of anisoles with a single ortho alkyl substituent over those calculated on the basis of free rotation of the methoxy group, led Baliah and Uma(140) to suggest that this was due to enhanced resonance caused by the preferred orientation of the OMe away from the substituent, viz:



R = alkyl group

I

Such a preferred orientation, claimed these workers, would restrict the rotation of the ether group and the probability of its attaining planarity with the benzene ring would increase. Dhami and Strothers(141), however, repudiated this increase in resonance, stating that Baliah and his co-worker had neglected in their calculations the contribution of an ortho substituent to the total dipole moment of the molecule. The results of ^{13}C.N.M.R measurements indicated to them that the conjugative interaction of the methoxyl group with the aromatic ring is operative in the mono-ortho derivatives, although probably there will only be one planar conformation (I) in which this interaction is appreciable. The methoxyl carbon shieldings were similar for all the mono-substituted compounds (meta, para, and ortho) and, therefore, no exaltation of conjugation could be detected in the o-alkylanisoles.

One of the more usual approaches to an investigation of steric hindrance to conjugative interactions is an examination of the electronic spectra. The question of steric inhibition of resonance in substituted anisoles has been studied by a number of workers by using ultraviolet spectroscopy and a marked decrease in the molar extinction coefficient (ε_{max}) of the absorption near 260-270mμ has been attributed to a steric effect. Burawoy and Chamberlain(142) reporting the U.V. spectra of anisoles substituted by Me, Cl, Br or I observed only a small displacement and change of intensity for the absorption of the anisole derivatives with only one ortho substituent in comparison with the corresponding phenol, and as with the C^{13}N.M.R. studies, the effect was also the same for meta and para derivatives. Later Dearden and Forbes(144) found that the ε_{max} values of ortho-fluoro and ortho-chloro compounds, were smaller for the phenols than for the anisoles, but for the ortho-bromo compound, the ε_{max} value of the ortho-substituted phenol was greater than that of the anisole. Although even for bulky ortho-substituents, the maximal bond absorption still occurs close to 220mμ it may be inferred from these latter results that the behaviour of the methoxy group changes as the size of the ortho-substituted halogen is increased.

A recent study by P.M.R. spectroscopy of ortho substituted anisoles tends to confirm this view. Crecely and his co-workers suggest that long range coupling constants (J_{lr}) may be associated with the mobility of the OMe group, for 2-chloro, bromo and iodoanisole the J_{1r} values were found to be much larger than that of the fluoro derivative, the increase being attributed to restricted rotation$^{(143)}$.

The dielectric data presented in this chapter also show a marked difference between the fluoro and the two larger substituents, the reason why no intramolecular process is detected in these anisoles in contrast to the acetophenones may be explained by any of the following:

(i) the molecular weighting factor is too high

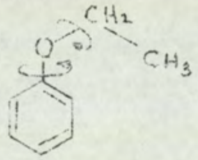
(ii) the OMe group as well as being smaller than the CH_3CO group, has shorter bond lengths which would bring it closer in rotation to the ortho substituent

(iii) all the physical measurements discussed above indicate that the preferred orientation of the OMe is as in I and in all probability it is more coplanar to the benzene ring than the acetyl group under similar conditions. This, together with the larger repulsive forces of the neighbouring halogen atom caused by (ii) may be expected to increase the height of the energy barrier to rotation. The $\varepsilon_\infty - n_D^2$ term is of normal proportions and it is unlikely that any librational motion can be attributed to the methoxy group.

Physical measurements show a marked change in the MeO parameters when two methyl groups are substituted ortho to it. In the U.V. there is a large displacement of the absorption to shorter wavelengths and in particular, a reduction of the intensity$^{(142)}$, while in the N.M.R. large differences in the methoxyl carbon shieldings, in comparison with anisole, are observed, indicative of a major change in the electronic nature of the methoxyl oxygen(141). The dipole moment of 2,6-dimethylanisole, however, is similar to that of anisole, Fong and Smyth also observed the same dipole moment for the former compound as that of 3,5-dimethylanisole and suggested that the methoxy group was forced out of coplanarity with the benzene ring by the two neighbouring methyls in the 2,6 derivative(12). This is verified by the U.V. and N.M.R. studies and the methoxy in such a position would have a higher dipole moment (the mesomeric moment being reduced), which would be counteracted by the resultant methyl moment acting in the reverse direction to produce a dipole moment of 1.2D. The τ_0 of this compound (20.5×10^{-12} sec at 25°C) is the same, within the error limits, as that reported by Smyth(12) and similar to the value obtained by Maier for 2,6-dichloroanisole(136). No equivalent sized rigid molecule has been dielectrically measured in dilute solution for comparison of the τ_0, but in view of the spectroscopic evidence, the zero distribution coefficient and the normal $\varepsilon\infty - n_D{}^2$ term, it is considered unlikely that any motion of the methoxy group occurs. Further confirmation of this was given by an attempted analysis into the two relaxation times, a molecular weighting factor of unity being produced.

Neither can an intramolecular process be expected for 2,4,6-tribromoanisole by the same reasoning. The τ_0 of 35.1×10^{-12} sec at 25°C is higher than that obtained for 2,4,6-trimethylacetophenone (29.7×10^{-12} sec) which has already been assigned a single relaxation mechanism (Chapter 2). In the tribromoanisole the methoxy group is probably further out of the plane of the benzene ring than in the dimethyl derivative(142), and this is reflected in the dipole moment of 1.43D comparable with those obtained for 2,4,6-trichloroanisole (Table 4:2). Here, the methoxy moment appears to be assuming an aliphatic character (cholesteryl methylether μ = 1.35D) where the moment is directed away from the aromatic nucleus and although the halogen resultant moment should be theoretically zero, they also appear to be exerting some influence since the dipole moment of 2,4,6-trimethylanisole (1.26D) is lower than that of the trichloro derivative (1.40D).

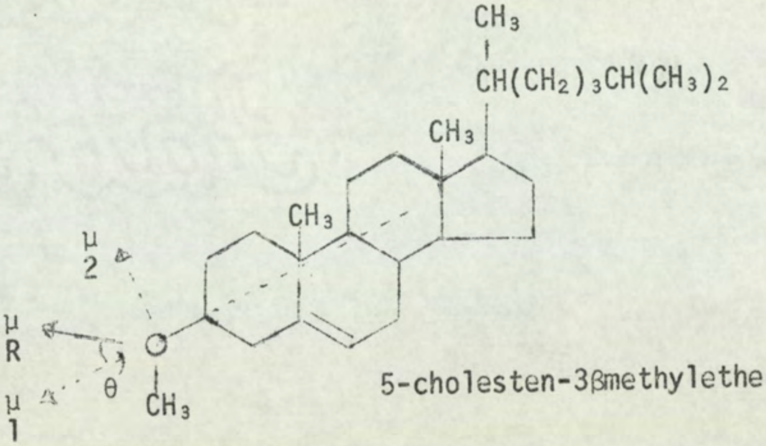
The behaviour of the ethoxy group in penetole can be seen to be very similar to that shown by the CH_3O in anisole. The addition of a CH_2 unit increases the τ_0 of phenetole (11.9×10^{-12} at 25°C) only a small amount above that of anisole (9×10^{-12} sec), and a τ_0 depression in the former compound can be easily observed when comparing it with the extrapolated relaxation times of ethylbenzene ($\tau_1 \approx 16 \times 10^{-12}$) and iodobenzene ($\tau_0 \approx 15.5 \times 10^{-12}$) obtained under the same conditions - both these molecules being smaller in size than phenetole. Budo analysis of the dielectric data also gives analogous values to those obtained by Farmer for anisole(1) with τ_1 = 44.5, τ_2 = 9.5 and C_1 = 0.24, the latter parameter is the same as the accepted C_1 value of 0.25 ± 0.1(73)(78)(79) for the methoxy derivative and the intramolecular relaxation time has lengthened only a small amount. Both ethers give larger τ_1s than can be attributed to molecular rotation and this is most probably due to the low weighting factor involved. An intramolecular process may be observed too in 2-ethoxynaphthalene where the τ_0 of 24.5×10^{-12} sec at 25°C is much lower than that of 43×10^{-12}sec obtained for 2-iodonaphthalene (Chapter 6). On analysis into two relaxation times τ_1 = 47.4, τ_2 = 11.3 C_1 = 0.59, the molecular relaxation time is very close to that of the iodine derivative, while the increase in C_1 over that of phenetole is probably due to the increased conjugation of the mobile group with the naphthalene nucleus, as was observed for the analogous acetyl compounds (Chapter 2). The small lengthening of the τ_2 may also be attributed to this, although the difference is within the error limits; a similar effect has also been reported for the methoxy derivatives(1). The ethoxy group is approximately comparable in size to $COCH_3$ and the τ values obtained for both groups are found to be very similar e.g. τ_2 acetophenone = 8.6×10^{-12} sec in p-xylene at 25°C, which gives further confirmation of the results. Thus, it would appear that the dielectric behaviour of the ethoxy molecules is the same as that already observed for the anisoles, although it may be suggested that part of the τ_0 lowering is due to an additional movement within the ethyl fragment



no such motion, however, can be detected in 2-bromophenetole. The volume of 2-bromophenetole is similar to that of 2-diiodobenzene which has a relaxation time in p-xylene at 15°C of 27×10^{-12} sec and, therefore, as with the ortho substituted anisoles, no intramolecular process is observable in the 2-bromophenetole's τ_0 of 27.7×10^{-12}. Nor do negligible distribution coefficients and the normal $\varepsilon'_\infty - n_D^2$ terms give any indication of an internal motion; the reasons for the lack of movement of the ethoxy group are most probably the same as those previously suggested for the anisoles. A $CH_2 \circlearrowright CH_3$ relaxation should not be hindered, since the OCH_2CH_3 is likely to be away from the bromine atom and as long as the C_1 is not approaching unity such a rotation should be observed if it is occurring.

Thus, in conclusion, similar relaxation processes have been observed for methoxy and ethoxy aromatic molecules, of the ortho substituted derivatives studied an intramolecular relaxation mechanism was only detected in 2-fluoroanisole, the remaining molecules having similar τ_0s as analogous rigid compounds.

As has been seen in this and the preceding chapters an accurate knowledge of the weighting factors are advisable before any real conclusions may be made about the behaviour of a molecule in which two relaxation processes may occur. Although a weighting factor for anisole in dilute solution of 0.25 ± 0.1 is fairly well established, there is a small discrepancy between the τ_2 value of 6.5×10^{-12} sec obtained by Smyth in benzene at 20°C(79) and 8.5×10^{-12} sec reported by Farmer in p-xylene at 25°C(1). By measuring a large methoxy molecule where $\frac{\tau_1}{\tau_2} = k>8$, it is hoped to clarify these parameters by obtaining a distinct separation of the two dispersion regions, one being due to the molecular absorption, the other to the intramolecular. As was mentioned in Chapter 2:c, this type of separation has already been observed(21)(49)(56)(57)(58) and in a recent paper Smyth and his co-workers obtained a flattening of the Cole-Cole plot for alkyl ethers in heptane attributed to two distinct relaxation processes(145). In this study cholesterylmethylether (chemical structure shown below) was measured in cyclohexane and p-xylene at 25°C using both bridge and grant frequencies.



5-cholesten-3βmethylether

Cooke in this laboratory has measured several rigid keto steroidal molecules and has found that their relaxation times are dependent on the direction of the resultant moment$^{(97)}$. 5α-Cholestan-3-one has this moment along its major axis having a relaxation time in p-xylene at 25°C of 2.6×10^{-12} sec, the similar sized cholesterylmethylether being a non-rigid molecule will also have its molecular component μ_1 along this axis and, therefore, k for the latter compound can be expected to be of the order of 30. With such a high k, complete separation of the two absorptions should occur and this, in fact, is found to be the case, as can be seen in Figs. 4:1 and 4:2, with the bridge frequencies falling on the plot due to intramolecular relaxation, while the grant frequencies appear on that due to overall molecular relaxation. As has been mentioned previously (Chapter 2, sections c and d), it is considered unwise to calculate the relaxation parameters for this type of system using the computer, $\tau_1\tau_2$ has, therefore, been determined from ε' vs $\varepsilon''\omega$ plots (Figs. 4:1:b and 4:2:b) and the values obtained verified from ε'' vs log ω plots (Figs. 4:3 and 4:4). In the latter instance the

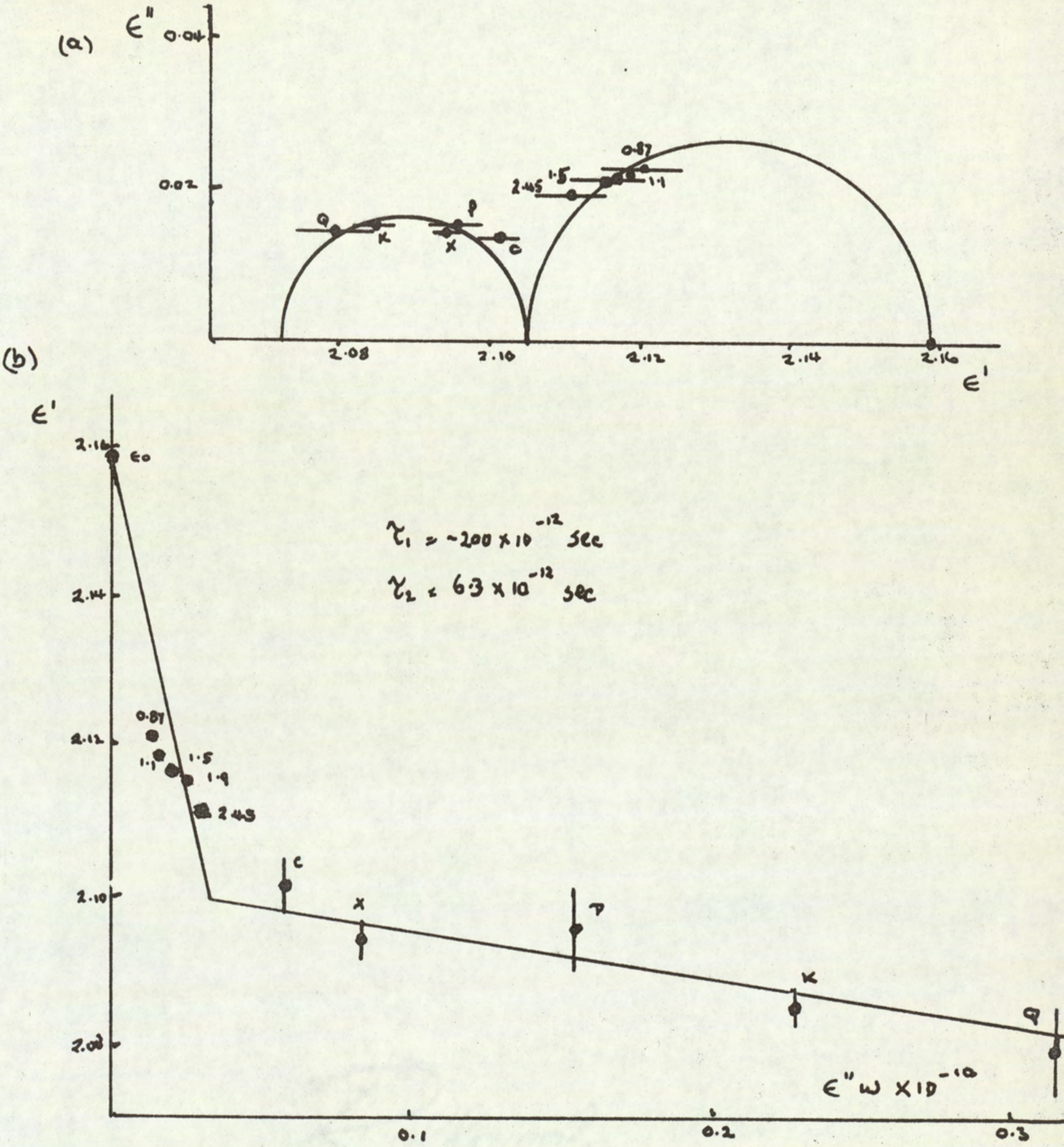


FIG 4 : 1 SEPERATION OF TWO RELAXATION TIMES IN CHOLESTERYL METHYL ETHER /CYC AT 25°C (a) COLE - COLE PLOT

(b) ϵ' vs $\epsilon''\omega$ ''

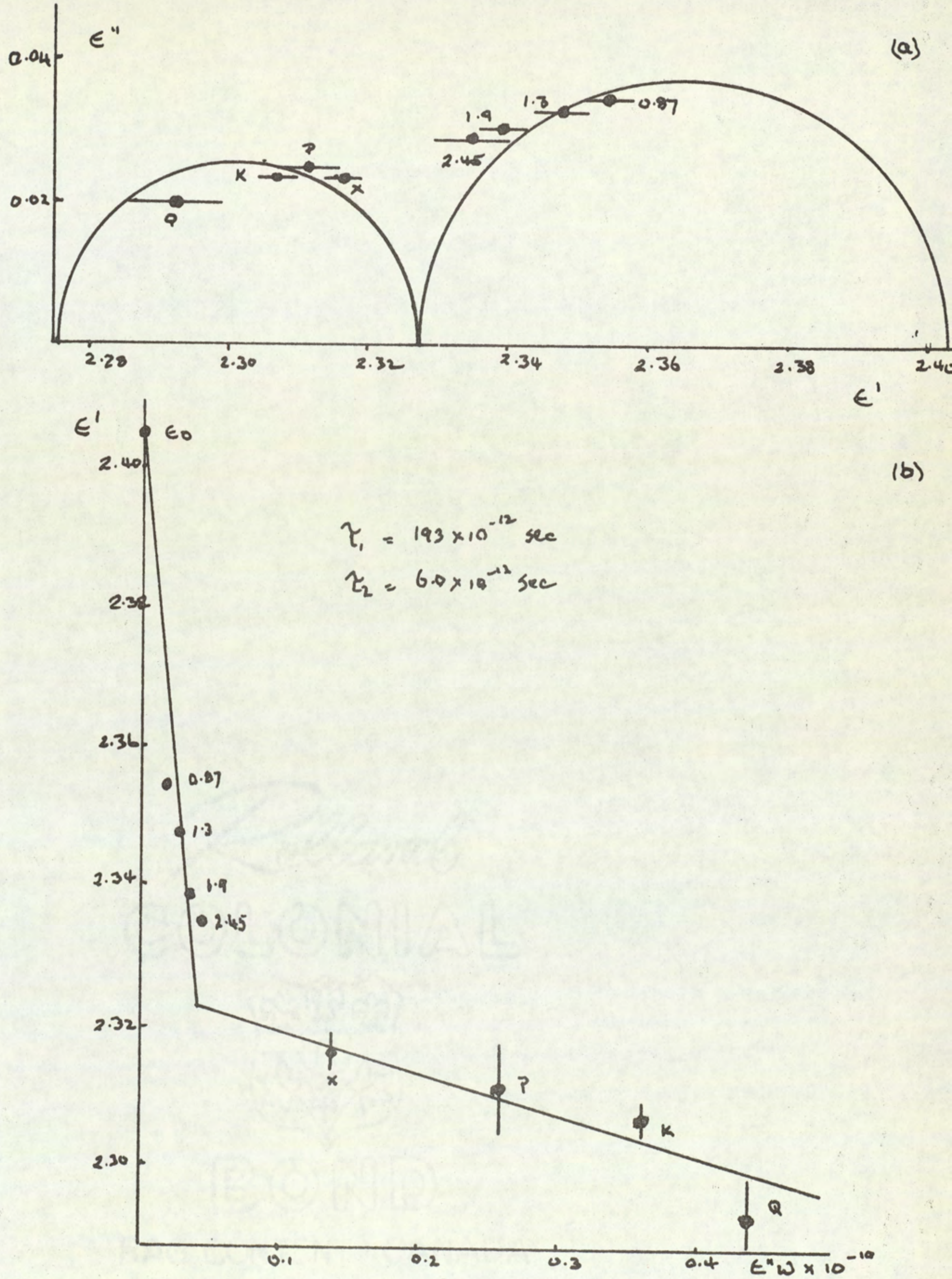


FIG 4:2 SEPERATION OF TWO RELAXATION TIMES IN CHOLESTERYL
METHYL ETHER | P-XY AT 25°C (a) COLE-COLE PLOT
(b) ϵ' vs $\epsilon''\omega$ PLOT

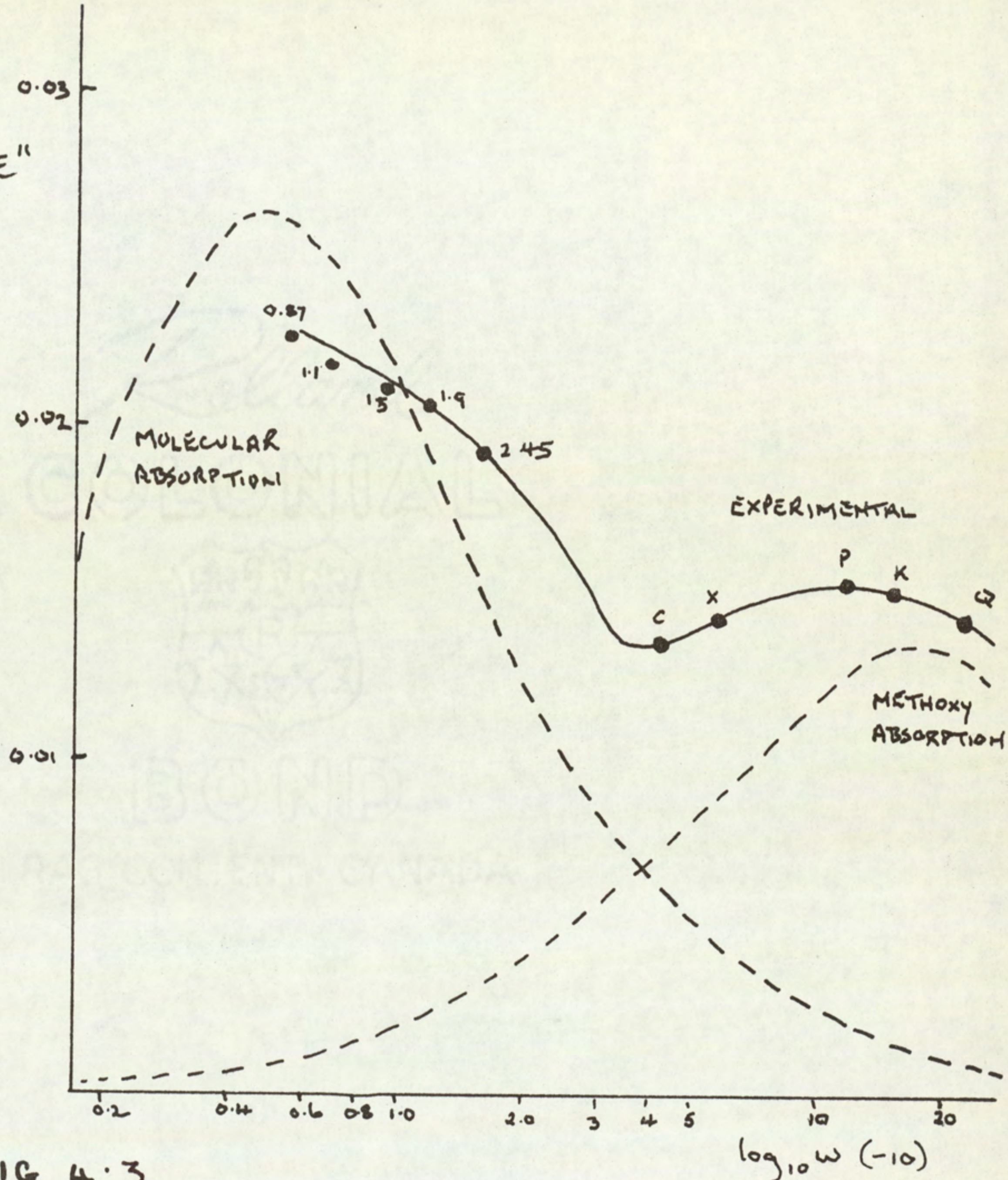


FIG 4:3

DIELECTRIC ABSORPTION FOR CHOLESTERYL METHYL ETHER IN CYCLOHEXANE AT 25 °C.

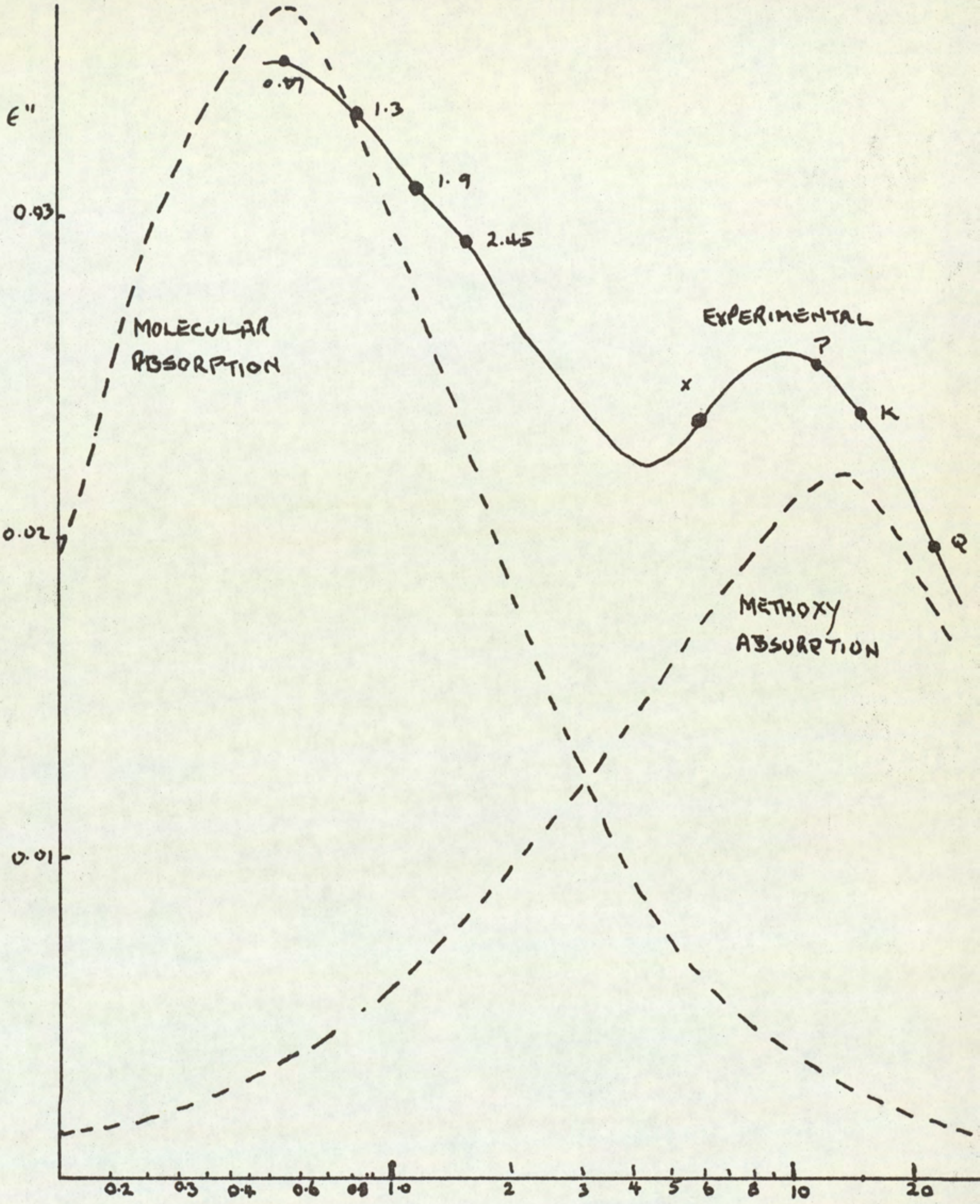


FIG 4:4 PLOT OF ε'' vs log ω FOR CHOLESTERYL METHYL ETHER
P-XYLENE AT 25°C

theoretical Debye curve corresponding to the molecular relaxation has been calculated and the loss due to this mechanism subtracted from those observed at the bridge wavelengths, to obtain the intramolecular loss curve. The molecular Debye loss curve does not fit exactly over the Grant experimental points this being due to the low loss ($\varepsilon''_{max} = 0.035$), the deviation however, is well within the experimental limits of the Grant cell and also it is just as likely that the intramolecular absorptions affects the molecular loss as vice-versa. The τ_1s of 193×10^{-12} sec in p-xylene and 200×10^{-12} sec in cyclohexane are in excellent agreement with Cooke's value for 5α-cholestan-3-one and further verify the results. The intramolecular relaxation times obtained from the ε' vs $\varepsilon''\omega$ and corrected ε' vs log ω plots of the two solvent measurements, are in the region of $6.0 - 6.5 \times 10^{-12}$ sec. Considering that complete separation of relaxation processes has been observed, these values should provide a reliable standard for methoxy rotation in other compounds. For example, the τ_2 of anisole in these solvents should be $> 6 \times 10^{-12}$ sec at 25°C, the mesomeric moment would be expected to increase the relaxation time in the aromatic derivative, as was observed with the acetyl compounds (Chapter 2). Therefore, Farmer's τ_2 value for anisole in p-xylene at 25°C of 8.5×10^{-12} sec may be preferred to Smyth's value of 6.5×10^{-12} sec in benzene at 20°C(79). For dodecylmethylether in heptane, Smyth and his co-workers obtained intramolecular relaxation times of 4.4×10^{-12} sec at 12°C and 3.7×10^{-12} sec at 30°C(145), the k for this compound was found to be 10.5 and only a flattening of the Cole-Cole plot was observed in contrast to the distinct separation

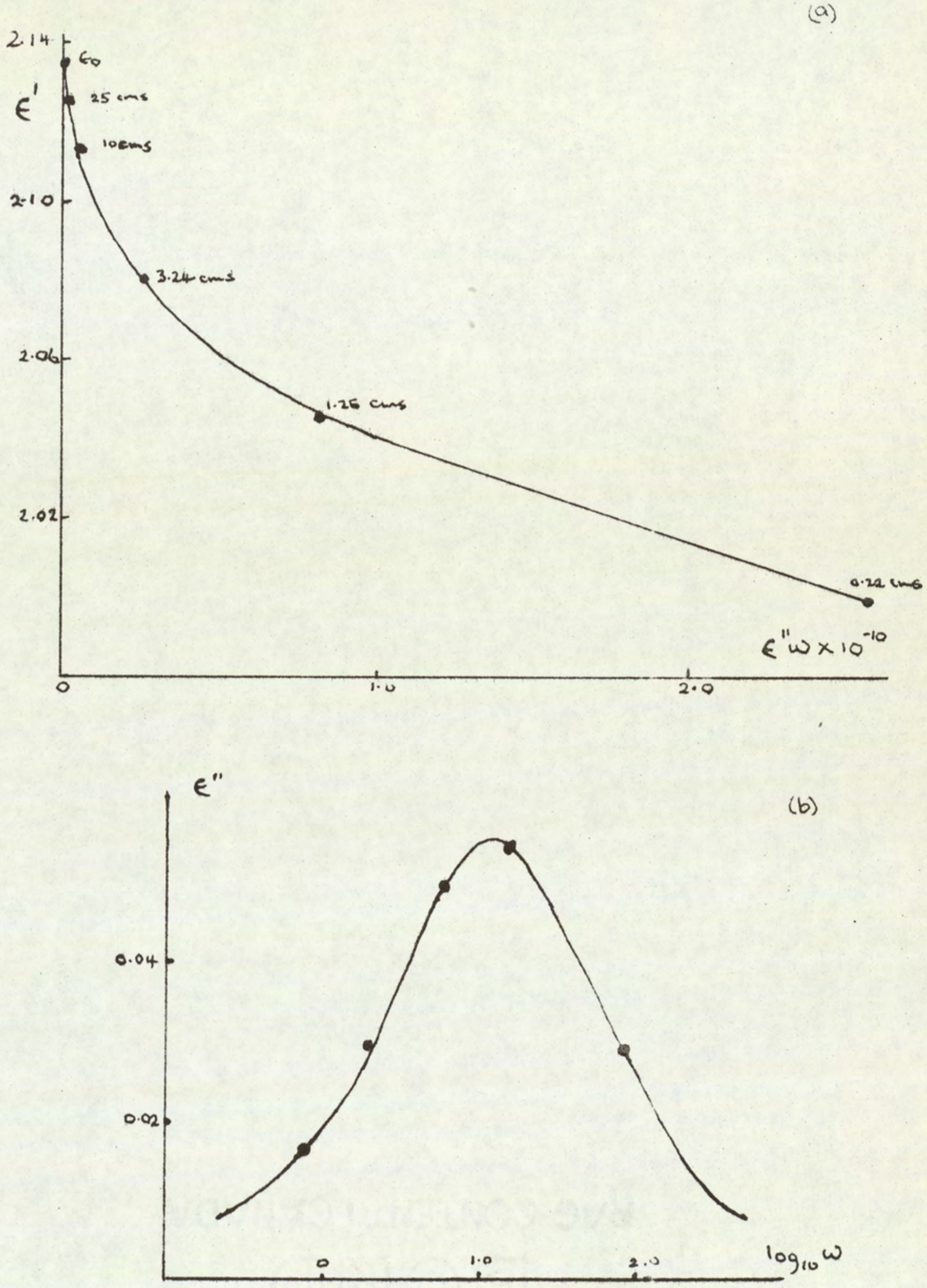


FIG 4:5 (a) ϵ' VS $\epsilon''\omega$ PLOT } FOR DODECYLMETHYL ETHER IN HEPTANE SOLUTION
(b) ϵ'' VS $\log_{10}\omega$ " } AT 30°C, AS REPORTED BY SMYTH.[145]

detected for the cholesteryl derivative, no separation, for example, can be seen in the ε" vs log ω plot (Fig. 4:5:b) and the ε' vs ε"ω plot (Fig.4:5:a) is in the form of an arc. It is thus felt that the τ of $\sim 6 \times 10^{-12}$ sec at 25°C is the more accurate value of aliphatic methoxy relaxation, especially on considering the complications which will occur with flexible dodecyl chain.

Taking the extreme ε_0, ε_∞ values of cholesteryl methylether yields the resultant dipole moment (using the equation for concentrated solutions) of 1.34(5)D which differs from those of analogous aliphatic ethers in the literature by no more than their probable errors (viz. cyclohexylmethylether-vapour 1.3D)(15)(104). As complete separation of the two absorption processes has occurred, the component moment corresponding to each mechanism may be calculated, the $\varepsilon_0 - \varepsilon_\infty$ terms may be estimated directly from the two Cole-Cole semi-circles in the usual manner or from the corrected ε" vs logωplot, where it is assumed that $\varepsilon''_{max} = \frac{1}{2}(\varepsilon_0 - \varepsilon_\infty)$. Both methods should, of course, give the same results and this is found to be the case, the component values from four determinations involving the two solvent measurements all agreeing within the experimental error. The mean values being

Molecular component, $\mu_1 = 1.03$

Intramolecular component, $\mu_2 = 0.85$ (where

$$w_{2OMe} = w_{2ROMe} \times \frac{M_{OMe}}{M_{ROMe}} \quad)$$

The molecular weight factor evolving from these figures for cholesterylmethylether of ∿0.6, is larger than that reported for anisole due to the lack of a mesomeric moment in the former compound. The resultant moment of the aliphatic ether will be in a direction away from the steroid nucleus (Fig. 4:6:a) at an angle θ to the major axis where $\tan \theta = {}^{\mu_2}/_{\mu_1}$, thus $\theta \approx 40^{\circ}$. Since the only difference between the dipole moments of the aliphatic and aromatic ethers should theoretically be the mesomeric moment, if a vector diagram is drawn as in Fig.4:6:b, where AB is the resultant aliphatic moment (1.35D) inclined at 40° to the major axis AY, the resultant moment of anisole (1.19)$^{(1)}$ should lie at either AC or AD, depending on the magnitude of the mesomeric moment, BC or BD.

The resulting angle of inclination for the anisole moment (θ_2) is found from the vector diagram to be 48° ($\sin \theta_2 = \frac{1.35 \sin 40}{1.19}$), a value close to that predicted by bond moment calculations as reported earlier$^{(1)}$, in which the moment is directed away from the benzene ring. In this position, the mesomeric moment BC is found to be 0.24D, a value much lower than has previously been reported (0.6 - 0.8D)$^{(78)(73)}$. Also there exists much dipole moment evidence to support the view that the resultant moment is directed towards the benzene ring$^{(1)(3)}$, which suggests that BD is the true mesomeric moment. The magnitude of BD which emerges from the vector diagram of 1.8D, however, appears equally unrealistic and it would, therefore, appear that the basic assumption of this calculation, regarding the positions of the major symmetry axes of the aliphatic and aromatic ethers to be the same, is incorrect, i.e. unlike anisole the major axis of cholesterylmethylether does not symmetrically bisect the substituted aliphatic ring, due to the geometry of the steroid and so

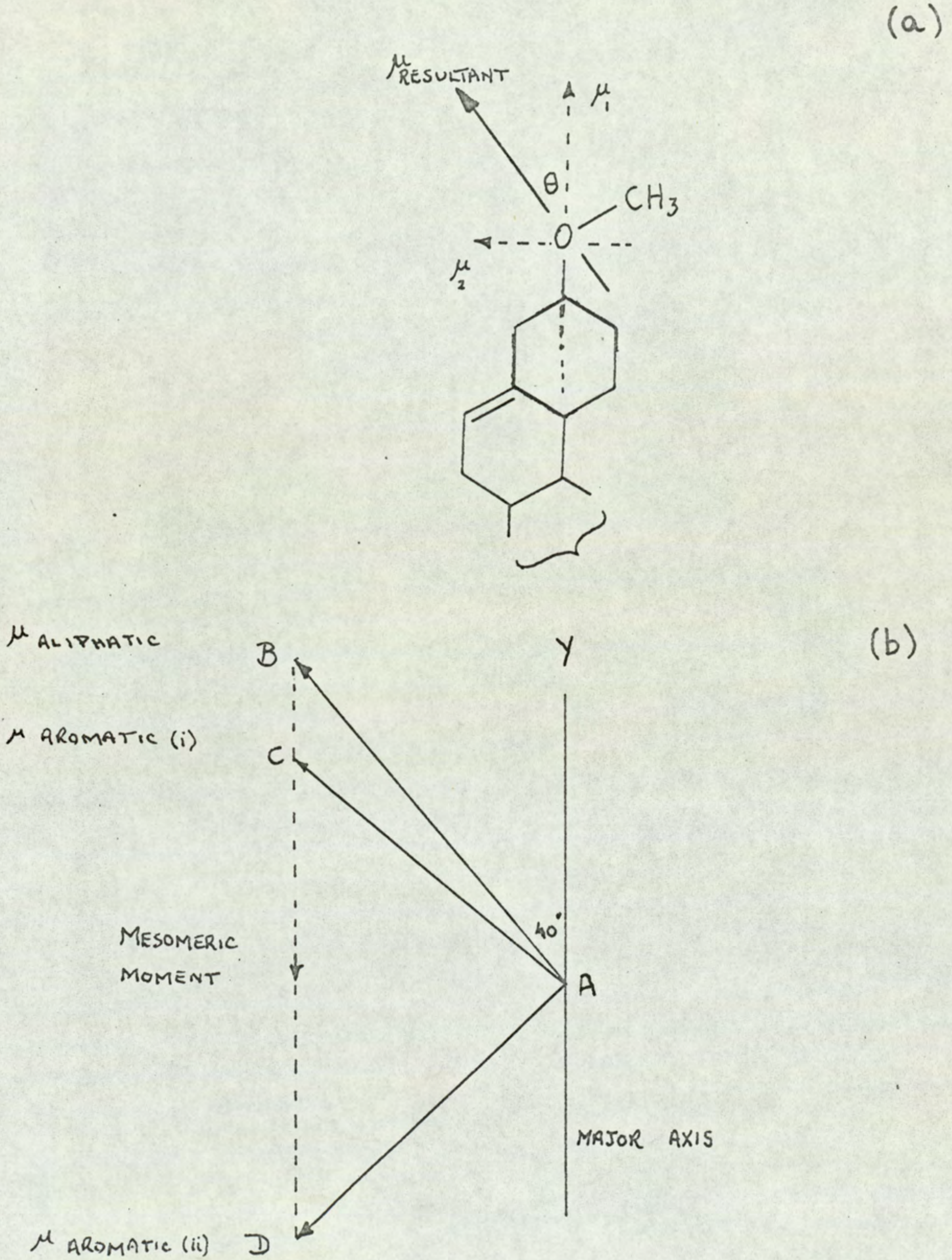


FIG 4:6 THE RESULTANT DIPOLE MOMENT OF CHOLESTERYLMETHYLETHER, (a) AND THE POSSIBLE DIFFERENCE BETWEEN THIS AND THE AROMATIC MOMENT IN ANISOLE, SHOWN VECTORIALLY, (b).

θ for an aliphatic ether, such as cyclohexylmethylether, would be expected to be larger than 40^0. The calculation and experimental errors, themselves are not of sufficient magnitude to produce a sizeable variation in the angle θ, since to obtain $\theta > 45^0$ requires $\mu_2 > \mu_1$ and as

$$\frac{\mu_1}{\mu_2} \quad \alpha \quad \left[\frac{(\varepsilon_0 - \varepsilon_{\infty 1})}{(\varepsilon_{\infty 1} - \varepsilon_{\infty 2})}\right]^{\frac{1}{2}}$$

this would necessitate the intramolecular absorption to be greater than the molecular. Even with an angle of inclination of 48^0, which must be the minimum θ_2 possible for anisole, the resulting C_1 is only 0.44 ($C_1 = \cos^2\theta$) and therefore, a $C_1 = 0.6 \rightarrow 0.9$ as reported by Vaughan and his co-workers recently for varying concentrated solutions of anisole in benzene(146) cannot be justified from a dipole moment point of view. Similarly, from the intramolecular relaxation time obtained for cholestryl-methylether, the τ_2 of $0.8 - 4 \times 10^{-12}$ sec at 20^0C reported by these authors appears equally incorrect, but may be due to the high weighting factor used in their analyses.

Thus, in conclusion, measurement of a large molecule which includes a small mobile group, so that $k >> 10$, provides a useful method for observing directly the intramolecular process and also study of a symmetrical molecule promises to be a useful technique to determine the mesomeric moment and weighting factors of the analogous benzene derivative.

CHAPTER 5

RELAXATION PROCESSES OF SOME ALDEHYDO COMPOUNDS

INTRODUCTION

Fischer$^{(124)}$ originally examined benzaldehyde dielectrically together with acetophenone in benzene, determining the mean relaxation times of these molecules to be indistinguishable from the τ_1 values obtained theoretically using an expanded version of the Debye equation (Eqn. 6:1). Acetophenone gave a relaxation time of 12.2×10^{-12} sec at 23^{o}C, while the calculated τ_1 value was only 11.3×10^{-12}, a lowering of this magnitude, Fisher concluded, was insufficient to indicate the presence of an intramolecular process in these compounds. As will be discussed in Chapter 6 the equation developed by this worker, for predicting molecular relaxation times, has not been found to hold quantitatively, especially for axially asymmetric molecules. The latter fact is most probably due to the assumptions involved in the original Debye equation, as this requires only one process leading to the equilibrium and all the dipoles having equivalent positions$^{(114)}$. Practically, it has been found that relaxation times of similar sized molecules, under the same solvent conditions, are comparable and this method has been used in Chapter 2 to show that the τ_1 calculated by Fischer for acetophenone was, in fact, too short and, therefore, an intramolecular process did occur in this compound. Since benzaldehyde is structurally similar to acetophenone and Fischer's dielectric results of these two compounds did show a strong compatability, it would be interesting to determine whether internal rotation also occurred in the benzaldehydes.

An investigation (parallel to that of the ketones) of the relaxation processes of: benzaldehyde, crotonaldehyde and 2-naphthaldehyde together with the following *para* substituted benzaldehydes

TABLE 5:1 DIELECTRIC PARAMETERS FOR THE ALDEHYDES REPORTED IN THIS CHAPTER

Compound	Solvent	Temp.	τ_o	τ_1	τ_2	C_1	α	μ
		°C		× 10^{12} sec				D
Benzaldehyde	p-xylene	15	13.3	14.3	2.4	0.9	0.05	2.9
		25	11.8	12.5	2.1	0.9	0.04	2.9
		40	9.6	10.4	8.3	0.7	0	2.9
		60	7.7	8.6	4.9	0.8	0	2.9
	cyclohexane	15	9.0	11.5	5.9	0.63	0.04	2.95
		25	8.3	10.8	5.2	0.61	0.02	2.95
		40	6.5	8.0	4.7	0.6	0.01	2.95
Crotonaldehyde	p-xylene	15	13.0	23.5	12.8	0.03	0	3.30
		50	8.4	18.2	7.0	0.18	0.03	3.28
	cyclohexane	15	8.4	37.7	6.7	0.23	0.1	3.34
		40	6.3	87	5.9	0.09	0.05	3.29

TABLE 5:1 DIELECTRIC PARAMETERS FOR THE ALDEHYDES REPORTED IN THIS CHAPTER

Compound	Solvent	Temp.	τ_o	τ_1	τ_2	C_1	α	μ
		°C		x 10^{12} sec				D
2-Naphthaldehyde	p-xylene	15	36.7	50.8	20.7	0.66	0.05	3.24
		25	31.1	41.0	17.1	0.7	0.05	3.25
		40	24.1	27.4	19.0	0.66	0.01	3.20
		50	21.7	24.7	17.0	0.67	0.01	3.18
	cyclohexane	25	25.1	27.3	5.0	0.9	0.05	3.22
Terephthaldehyde	p-xylene	25	13.6				0.02	2.21
p-Fluorobenzaldehyde		15	15.9	28.1	11.5	0.4	0.05	1.98
		25	13.3	23.2	9.6	0.4	0.05	1.96
		40	11.2	18.3	8.2	0.4	0.04	1.95
		50	9.7	16.9	6.8	0.4	0.05	1.94

TABLE 5:1 DIELECTRIC PARAMETERS FOR THE ALDEHYDES REPORTED IN THIS CHAPTER

Compound	Solvent	Temp.	τ_o	τ_1	τ_2	C_1	α	μ
		°C		x 10^{12} sec				D
p-Chlorobenzaldehyde	p-xylene	15	18.5	36.2	13.0	0.4	0.07	1.94
		25	15.8	32.9	10.8	0.4	0.08	1.93
		40	12.0	18.4	9.0	0.4	0.03	1.88
		50	11.1	17.4	8.3	0.4	0.03	1.88
		60	9.9	14.1	7.9	0.4	0.02	1.86
	cyclohexane	25	10.0				0	1.88
p-bromobenzaldehyde	p-xylene	15	19.2	36.8	13.3	0.4	0.06	1.94
		25	16.9	33.3	11.8	0.4	0.06	1.95
		40	13.6	20.0	10.8	0.4	0.02	1.92
		50	11.6	14.3	10.2	0.4	0.04	1.90
p-nitrobenzaldehyde	p-xylene	40	15.8	24.4	8.6	0.6	0.07	2.33

aldehydo, fluoro, chloro, bromo and nitro has therefore been carried out - the results are presented in Table 5:1. The principle solvent used in this study was p-xylene, owing to the poor solubility of the solid aldehydes in cyclohexane. As mentioned in Chapter 1, aldehydes are susceptible to auto-oxidation and thus a small amount of catechol (∿ 0.1% of solute) was included in the solutions to act as an inhibitor.

Trial measurements showed that such small concentrations had a negligible effect on the dielectric constant and loss of the solutions; to ensure that no chemical change occurred during individual temperature measurements the static dielectric constant was determined before and after each one.

DISCUSSION

Theoretical calculation of the weight factors for benzaldehydes by the bond moment method is prone to a higher error than the equivalent acetophenone determination for two reasons:

(i) uncertainty of the mesomeric moment

(ii) uncertainty of the magnitude or direction of the aldehydo C–H bond moment.

In regard to the latter it has been found that in methane the C–H bond has a moment of 0.3D in the sense $\overrightarrow{\text{C–H}}$, where the convention adopted is that the arrow points to the negative end of the dipole, while in ethylene a bond moment of 0.4D in the reverse sense, $\overleftarrow{\text{C–H}}$, is observed. Infra-red dispersion studies of acetylene has shown the C–H bond in this molecule has an even higher moment of 1.05D in the same direction as ethylene. A good deal of space has been devoted to this topic, which, of course, affects all bond moment calculations to some extent, and adequate discussions may be found in the texts of Smith(7) and Smyth(15).

The former author concludes from the collected evidence that the C–H moment is not a constant quantity but varies both with the nature of the hybrid orbital used by the carbon atom and with the character of the other atoms linked to this carbon atom. Thus the moment in ethylene is in the reverse direction to that in methane, as the carbon orbitals are trigonally hybridized in the former, in comparison with tetrahedrally in the latter. The direction of the C–H moment is, therefore, reasonably known for the series, alkanes, alkenes and alkynes, however, although the carbon atom of the aldehyde group in benzaldehyde is trigonally hybridized, the effect of the strongly electronegative oxygen is somewhat uncertain. If the moment in this molecule is assumed to be of the same magnitude and direction as in ethylene and the mesomeric moment is assumed to be of similar proportions of that of acetophenone, then bond moment calculations of the type described in Chaper 2 produce an angle θ between the molecular moment and the benzaldehyde main symmetry axis of 57^0. This is the value obtained by Coomber and Partington$^{(125)}$ who also used bond moment calculations, formally neglecting the C–H moment by calculating the C=O moment, from the moments of acetaldehyde (2.25D) and acetone (2.75D), to be 2.25D, claiming that the C–H moment was really included in that of the C=O If the C–H moment of benzaldehyde is taken to be of the same order as that in acetylene (all other parameters remaining the same) an angle $\theta = 66^0$ results, while the reversal of the moment, as in methane, the angle will tend towards the value obtained in the acetophenone bond moment calculations ($\theta = 44^0$).

Group moment determinations of the type previously described in Chapter 2, using the dipole moment values from table 5:1 and those of Hassell$^{(29)}$ produced θ angles for p-fluoro, chloro, bromo and nitro-benzaldehyde of 37.5^0, 38.5^0, 39^0 and 36^0 respectively, the approximate mean of these being 38^0. The molecular weighting factors of this series for various θ values are shown below:

Compound θ	30^0	38^0	55^0	66^0
benzaldehyde	0.75	0.62	0.33	0.17
p-fluoro "	0.37	0.2	0.01	0
p-chloro "	0.3	0.14	0.002	0.004
p-bromo "	0.29	0.13	0	0.006
p-nitro "	0.49	0.46	0.48	0.48

C_1 values for $\theta = 30^0$ are also included in the table, this was the angle Fischer adopted for benzaldehyde and it is only in this case that p-halobenzaldehydes do have significant molecular weighting factors. It would therefore, appear that this type of compound would again be suitable for detecting the possible presence of an intra-molecular process.

Examination of the aldehydes mean relaxation times in Table 5:1 shows that the p-xylene solution values have lengthened considerably in comparison with those determined in cyclohexane. At 25°C the τo of benzaldehyde in p-xylene has increased by 42% over the cyclohexane value, the increase is of the same order for crotonaldehyde, higher for p-chlorobenzaldehyde (58%, although part of this figure may be due to the compounds very poor solubility in cyclohexane) and lower for 2-naphthalaldehyde (24%). The increment in the p-xylene values has previously been attributed to some form of interaction between the solute's polar group and the Π electrons of the xylene ring.
The hydrogen of the CHO group will exhibit a fair degree of protonic nature (H^+) and it is possible that some form of weak hydrogen bonding is being formed between it and the Π electrons of the p-xylene, as was suggested for the large τo for pyrrole in the same solvent(129).

Tucker found that the mean relaxation time of this compound in p-xylene (7.1×10^{-12} sec at 25^{0}C) had increased more than 200% over that in cyclohexane at the same temperature (2.3×10^{-12} sec). This form of interaction would therefore be expected to have a large effect on the molecular relaxation time of the benzaldehydes and also lengthen the intramolecular process to some extent - indeed, the discrepancy between the p-xylene and cyclohexane τos of the aldehydes is far larger than that observed for the equivalent keto compounds. Also the formation of a hydrogen bond between the aldehyde hydrogen and Π electrons would most probably result in a mesomeric shift of charge within the solute and solvent molecules. This shift must be quite small as the p-xylene and cyclohexane dipole moments are comparable, however, such a shift may nullify the C factors previously calculated.

As an intramolecular process would be most apparent in the p-halobenzaldehydes, it would appear profitable to discuss the results of these molecules first. Courtauld models(22) and Edwards(19) atomic volume increments suggest that the volume of the CHO group is intermediate between that of a chlorine atom and a bromine atom, lying closer to the former, while the OCH_3 group is slightly larger than the latter and the $COCH_3$ group is comparable in volume to that of an iodine atom. Bearing these facts in mind the mean relaxation times of the p-halobenzaldehydes may be compared with the analogous acetyl, methoxy and toluyl molecules as in Table 5:2. Although they are smaller molecules the benzaldehydes are seen to have comparable τos to those of the acetophenones, while in comparing them with the toluenes, a reduction in the τo is only noticeable with the bromo derivatives. As mentioned earlier, the solubility of the p-halobenzaldehydes in cyclohexane was poor, only one measurement of p-chlorobenzaldehyde has been made, the weight fraction of which was by necessity small and the resulting maximum loss low ($\sim$0.02)

TABLE 5:2

MEAN RELAXATION TIMES (x 10^{12} SEC) OF PARA SUBSTITUTED BENZALDEHYDES, ACETOPHENONES, TOLUENES AND ANISOLE IN P-XYLENE AT 15° and 40°C

Substituent	Benzaldehyde	Acetophenone	Toluene	Anisole
15°C				
fluoro	15.9	16.5		
chloro	18.5		19.3	
bromo	19.2	18.5	27.2	32.2
40°C				
fluoro	11.2	11.4		
chloro	12.0	12.3	14.0	
bromo	13.6	12.7	17.4	21.9
Reference	—— this study	——	(17)	(1)

and thus, the mean relaxation time will include a larger error than normally observed. However, even with an error of 25% a relaxation time of 1 x 10^{-11} sec for p-chlorobenzaldehyde at 25°C is smaller than 16.4 x 10^{-12} sec exhibited by p-chlorotoluene(17) under the same conditions. Observation of Table 5:2 also shows that the increase of τ_0 with molecular size is more pronounced in the benzaldehyde derivatives than in the corresponding acetophenones. The possible interaction between the aldehyde and p-xylene makes it difficult to assess these results, yet the small depression of the τ_0 in p-xylene and the larger shortening in cyclohexane would indicate that the CHO group is undergoing some form of internal rotation in contrast to the molecules behaving as rigid units. The magnitude of this depression and the larger increase of τo with respect to size in comparison with the acetophenones would suggest that the molecular relaxation time has a larger weighting in the aldehydes. This latter point is further underlined by the larger distribution coefficients observed for the aldehydes in p-xylene ($\alpha = 0.06 \pm 0.01$ at $15^{o}C$ - cf Appendix, Table A:1). It may be argued that the increase in α was due to the distribution of molecular relaxation times caused by the solute-solvent interaction, however, Tucker found that pyrrole's α in p-xylene was much reduced compared to that in cyclohexane(129). Analysis into two relaxation times for the p-halobenzaldehyde results produced varying C_1s from 0.2 to 0.6, the most consistent value being 0.4, the C_1s of these compounds were therefore fixed at this value. The significance of the analyses is questionable as they cannot be verified in the normal manner, the molecular relaxation time at $25^{o}C$ being lengthened by solute-solvent interaction above that of the analogous toluene by ∿70%. The resulting τ_2s vary within the three compounds at any one temperature by about 20%, which is most probably within the error limits of these analyses and at $25^{o}C$ the mean τ_2 of 10.7×10^{-12} sec is comparable to those of the p-haloacetophenones, suggesting that the solute-solvent interaction has also lengthened this parameter. Klages and Knobloch(14) have measured p-chlorobenzaldehyde in benzene at $20^{o}C$ and obtained a $\tau_1 = 20.6 \times 10^{-12}$, $\tau_2 = 3.8 \times 10^{-12}$ sec and a $C_1 = 0.78$, with a C_1 of this magnitude $\tau_1 \approx \tau_o$ and their result is comparable to an extrapolated τo value in p-xylene at this temperature, which indicates that a solvent interaction is lengthening the τ in benzene as well. This, of course, would be expected and is further emphasised by these authors' results of p-chloroacetophenone under the same conditions where $\tau_1 = \tau o = 14.3 \times 10^{-12}$ sec ($C_1 = 0.92$). No explanation is given for the analyses in this paper and as only one measurement has been carried out, our C value would appear to be the more reasonable; however, as they themselves cannot be verified only the enthalpies of activation have been calculated - these parameters are shown in Table 5:3. The appropriate log τT against $1/T$ plots can be seen in Figures 5:1:a and b. It would be unwise to attach too much significance to the actual values, yet discussion of the trends through the p-halobenzaldehyde series it most probably reasonable. The increase of the $\Delta H_1^{\ddagger}$s with molecular size is much larger than has been observed elsewhere in this thesis and may be attributed to the solute-solvent interaction. The trend in the $\Delta H_2^{\ddagger}$ where F>Cl>Br is somewhat surprising, although it has also been observed in the far infra-red.

TABLE 5:3

MOLECULAR ($\Delta H_1^{\ddagger}$) AND INTRAMOLECULAR ($\Delta H_2^{\ddagger}$) ENTHALPIES OF ACTIVATION FOR THE P-HALOBENZALDEHYDES IN KCAL/MOLE

	$\Delta H_1^{\ddagger}$	$\Delta H_2^{\ddagger}$
p-fluorobenzaldehyde	2.0	2.0
p-chlorobenzaldehyde	3.2	1.6
p-bromobenzaldehyde	6.4	0.8

Energy barriers to internal rotation in benzaldehydes have been obtained by measurement of torsional frequencies in the far infra-red. Silver and Wood originally measured liquid benzaldehyde and a nujol mull of p-chlorobenzaldehyde and obtained barrier heights of 6.4 and 4.9 kcal/mole respectively(6). Fateley and his co-workers, however, in two recent papers(126)(127) have shown that barriers obtained in the gaseous state give a more accurate account of the forces within a molecule, obtaining energy barriers for benzaldehyde, p-fluoro, chloro and bromobenzaldehydes of 4.7, 3.6, 2.8 and 2.4 kcal/mole respectively in the gaseous state, in comparison with 6.7, 5.2, 4.6 and 3.7 kcal/mole in the liquid state. They account for the discrepancy between the two states being due to the influence of neighbouring molecules. These values are in contrast with the barrier to internal rotation of 1.15 kcal/mole for acetaldehyde obtained by Kilb and his co-workers using microwave spectroscopy(128), the difference presumably owing to the overlap of the Π orbitals of the benzene ring with those of the carbonyl group. The actual significance of these results in relation to those determined by the dielectric method is questionable, Higasi has already pointed out that barrier heights obtained by other methods are invariably higher than those determined using the Eyring rate expression in dielectrics(80). Indeed Fateley's values for acetophenone, ortho and para fluoroacetophenones in the gaseous state of 3.1, 3.0 and 3.5 kcal/mole respectively(127) are higher than those determined in this thesis, although the lowering of the barrier in the ortho derivative in contrast with acetophenone is discernable in both methods. As stated earlier, similar trends are also observed in the p-halobenzaldehyde's $\Delta H_2^{\ddagger}$ values. Mesomeric moments of the halogens decrease in the order F>Cl>Br(7) and so the additional amount of charge supplied to the ring by fluorine in comparison with a bromine atom may well increase the barrier height to internal rotation in p-fluorobenzaldehyde by increasing the double bond character of the C_{Ar}—C=O bond. No such trend was detected in the p-haloacetophenone's $\Delta H_2^{\ddagger}$s, yet the $\Delta G_2^{\ddagger}$s of these compounds were thought to be greater than that of acetophenone for similar reasons.

The results of p-chloroacetophenone in cyclohexane have not been analysed into two relaxation times, since the low loss obtained in this measurement would produce errors of such magnitude (in contrast to the τ_0 determination) that the resulting parameters would be meaningless.

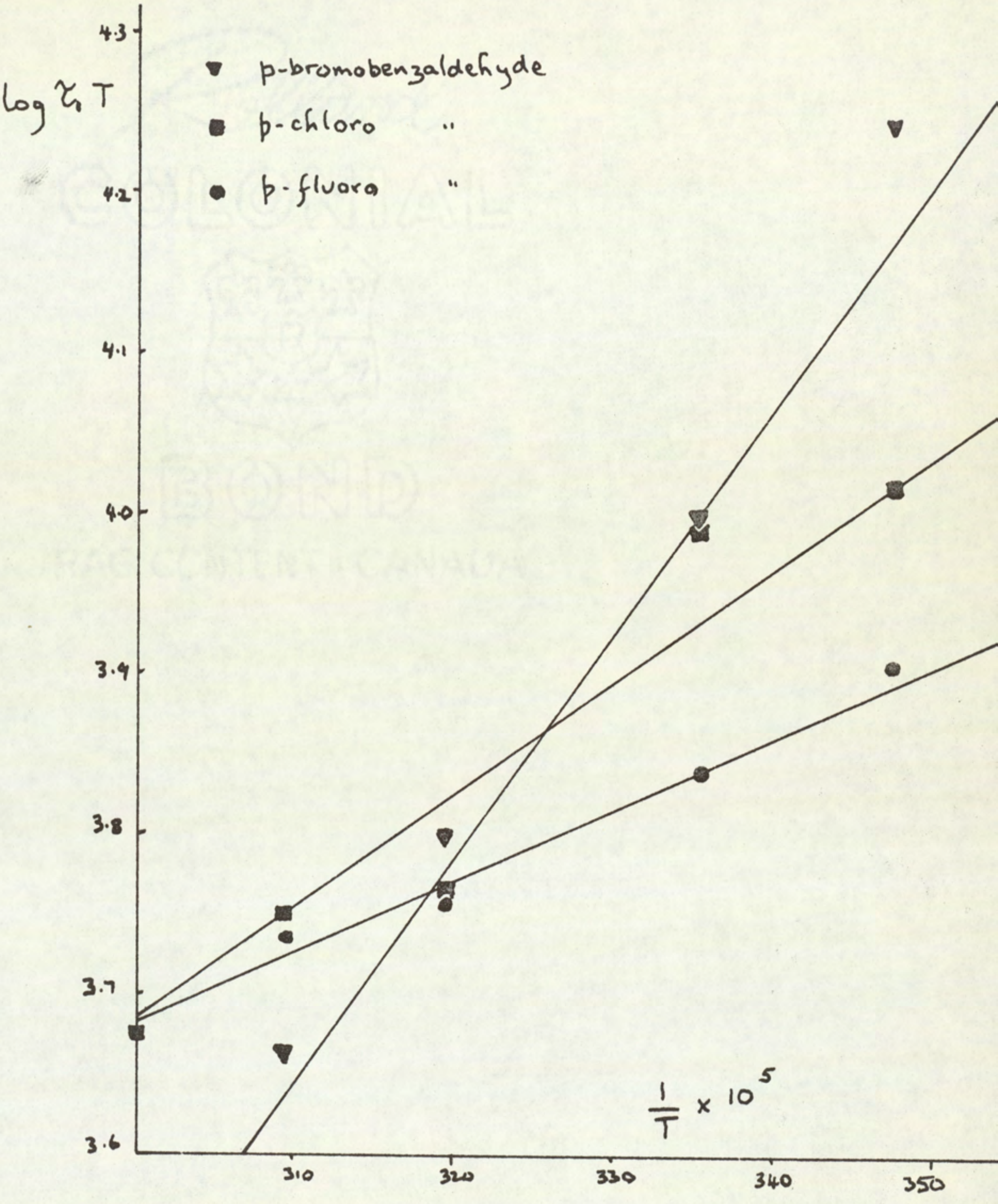


FIG 5:1:a PLOT OF LOG $\tau_1 T$ vs $\frac{1}{T}$ for p-HALOBENZALDEHYDES IN P-XYLENE

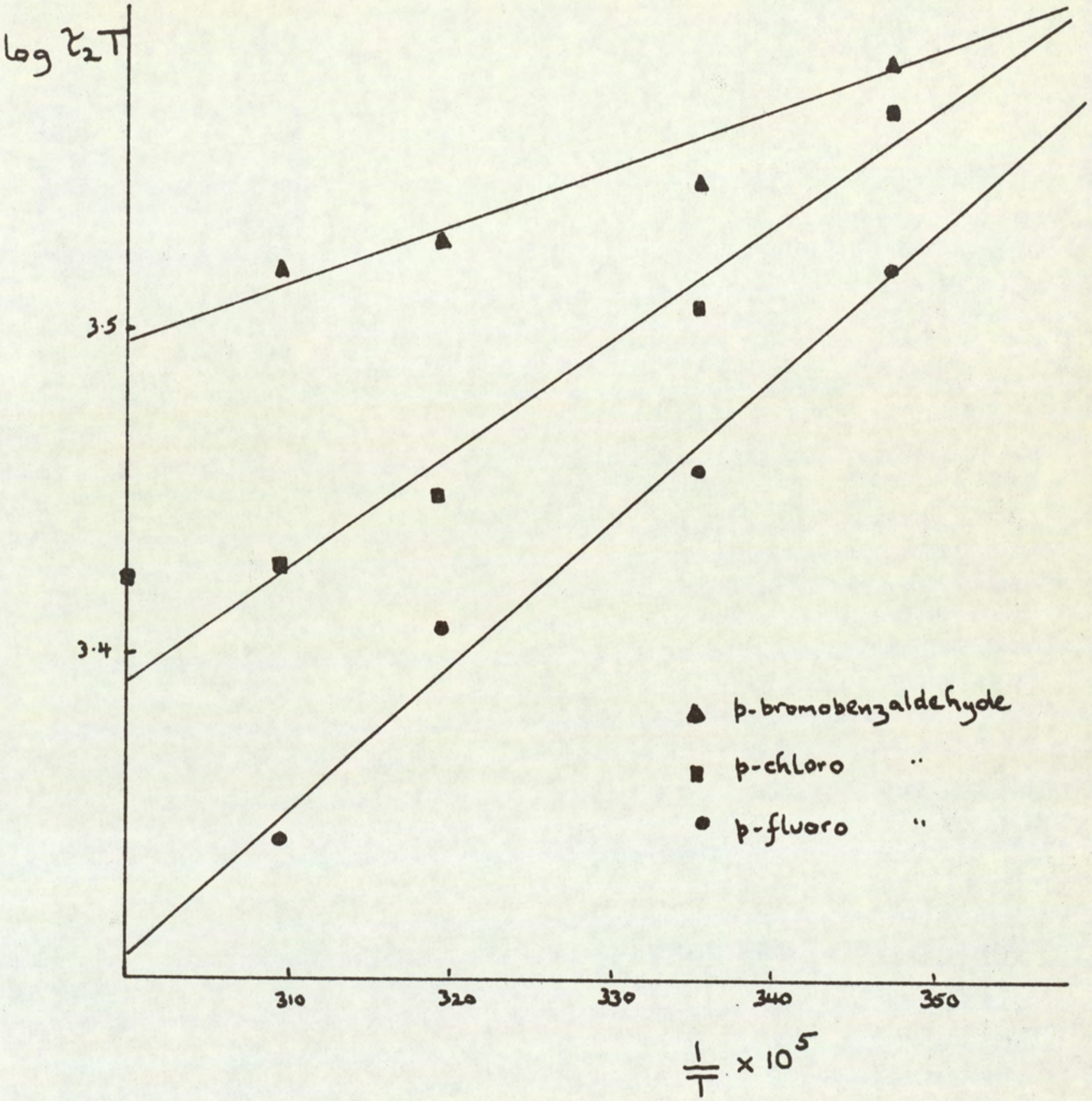


FIG 5:1:b PLOT OF LOG $\tau_2 T$ VS $\frac{1}{T}$ FOR p-HALOBENZALDEHYDES IN P-XYLENE

The mean relaxation time of 15.8×10^{-12} sec for p-nitrobenzaldehyde in p-xylene at $40^{\circ}C$ is slightly lower than the value of 18.8×10^{-12} sec obtained for p-nitrotoluene under the same conditions(17). As the expected C_1 for this molecule is higher than that of the halogen derivatives and Hassell reported that nitrobenzenes possibly form solute aggregates, no further depression of the τ_0 can be expected. Here again analysis into two relaxation times produces a small lengthening in τ_1 and C_1 ($\tau_1 = 24.4$ $\tau_2 = 8.6 \times 10^{-12}$ sec $C_1 = 0.6$), yet the intramolecular relaxation time is the same, within the error limits, to those obtained for the p-halobenzaldehydes and, therefore, it can be concluded that a similar internal motion is present in this molecule.

Now that an internal process has been assigned to the para derivatives the results of the parent molecule, benzaldehyde can be examined, this material being a liquid, has an advantage over the latter compounds in that it is soluble in cyclohexane. In spite of this no significant depression of the τ_0 can be detected in comparison with the halobenzenes. The molecular relaxation time of benzaldehyde would be expected to be slightly larger than that of chlorobenzene which has relaxation times of 10.2 and 6×10^{-12} sec in p-xylene at 15° and $60^{\circ}C$ respectively. As these values would be slightly lower in a cyclohexane solution the relaxation times for benzaldehyde of 9.0 and 5×10^{-12} sec (extrapolated) at these temperatures are comparable with the above. Use of a relationship between the molecule's moment of inertia and relaxation time (Chapter 6) predicts a τ for benzaldehyde in cyclohexane at $25^{\circ}C$ of $\sim 10.5 \times 10^{-12}$ sec, which is again comparable to the τ_0 of 8.3×10^{-12} sec at this temperature. Thus the probable internal process in this molecule cannot be observed which means that if an intramolecular motion is present, the C_1 value is greater than the value determined with a group moment angle $\theta > 55^{o}$, since anisole, a larger molecule, has the same τo value at $25^{o}C$, the C_1 for this latter molecule being approximately $0.25^{(1)}$. Analysis of the cyclohexane results into two relaxation times, gives a $C_1 = 0.6$; this, with the results of the p-halobenzaldehydes suggests that $\theta = 30\text{-}38^{o}$. The analyses appear to be genuine with the τ_1 s being of the expected size, e.g. $\tau_1 = 10.8 \times 10^{-12}$ sec at $25^{o}C$, yet an intramolecular process cannot definitely be attributed to benzaldehyde, as it could be argued that although internal motion was detected in the p-halo derivatives, the barrier height would be expected to be higher in the parent molecule (from far infra-red evidence) and rotation of the CHO group may be prevented. For this reason and the fact that only three temperature measurements were made in cyclohexane no real significance can be attached to the enthalpy values $\Delta H_1^{\ddagger} = 1.7$ $\Delta H_2^{\ddagger} = 0.9$ kcal/mole.

The τo of 11.8×10^{-12} sec at $25^{o}C$ in p-xylene is comparable within the experimental errors, to Fischer's value for benzaldehyde in benzene of 10.9×10^{-12} at $23^{o}C^{(124)}$, the solvent interaction prevents any observation of a secondary process, the τos being larger than those of the comparative halobenzenes. Nor will the quoted $\tau_1\tau_2$ analyses have much meaning, they are mentioned mainly for comparison with the values reported by Knobloch$^{(27)}$ in benzene at $20^{o}C$ ($\tau_1 = 12.2$ $\tau_2 = 0.9 \times 10^{-12}$ sec $C_1 = 0.89$) and also to show the slight increase of C_1 in p-xylene. The latter would explain why a $C_1 = 0.4$ was observed for the p-halobenzaldehydes instead of 0.15- 0.25 as suggested by the resultant moment angle $\theta = 38^{o}$ and a high C_1 of 0.7 (± 0.1) for benzaldehyde coupled with $\tau_2 > \tau_1/_2$ is also a possible explanation for the apparent lack of a depression in this compound's τ_0.

Besides benzaldehyde Knobloch also measured 4-pyridinecarboxaldehyde which like 4-acetylpyridine would be expected to have a low C_1. This author has only reported τ_1, τ_2, C_1 values, but using the approximate equation(2):

$$\tau o = C_1\tau_1 + C_2\tau_2$$

the mean relaxation times in benzene at 20°C for benzaldehyde and the pyridine derivatives are 11.0 and 8.6 x 10^{-12} sec, respectively. Very little lowering of τ can be observed even though the pyridine compound is the smaller molecule; as with 4-acetylpyridine it would appear that if an intramolecular process is occurring in 4-pyridinecarboxaldehyde the $\tau_2 \approx \tau_1$.

Trans-crotonaldehyde is also smaller than benzaldehyde both in width and length, yet the mean relaxation times obtained in cyclohexane and p-xylene are the same as those determined for benzaldehyde at the same temperatures. Smyth and his co-workers explained a large dipole moment for this compound of 3.65D (obtained in the vapour state) by increased resonance, that is the C—CHO bond having a high degree of double bond character(133). The dipole moments obtained in this study (3.3D) are lower than Smyth's value partly because gas moments are normally higher than solution moments and also, the traditional dipole moment method does not adequately allow for the atomic polarization term when equating the atomic and electronic polarization to R_D. The increased conjugation of the carbonyl group can be further seen in the infra-red carbonyl stretching frequencies shown in table 5.4 and thus crotonaldehyde is probably to benzaldehyde as 1-acetylcyclohexene is to acetophenone. It is quite likely that this aliphatic aldehyde is behaving as a rigid molecule owing to this resonance since the $\tau_1\tau_2$ analyses with low C_1 terms could be interpreted as showing only one relaxation process.

TABLE 5:4

I.R. CARBONYL STRETCHING FREQUENCIES ($\gamma_{C=O}$) FOR SOME ALDEHYDES MEASURED IN CARBON TETRACHLORIDE$^{(83)}$.

Compound	$\gamma_{C=O}$ cm^{-1}
acetaldehyde	1733
butyraldehyde	1729
benzaldehyde	1705
2-naphthaldehyde	1698
crotonaldehyde	1696

If this was the case, benzaldehyde, being the larger molecule, could definitely be attributed two relaxation times. However, further studies of aliphatic aldehydes are required as it is equally probable that some form of polymerisation is lengthening crotonaldehyde's relaxation time, which would account for an α of 0.1 in cyclohexane at $15^{o}C$.

The mean relaxation time for 2-naphthaldehyde in cyclohexane at $25^{o}C$ of 25.1×10^{-12} sec gives even less support to a second relaxation time than benzaldehyde, being comparable to that of 2-bromonaphthalene (25.5×10^{-12}) under the same conditions. The usual lengthening of τ is observed in the p-xylene measurements which frustrates any comparisons of the mean relaxation time. As with benzaldehyde, this lack of depression in the τo could be due to a high molecular weighting factor and if an intramolecular process was present, the large τ_2s obtained in p-xylene could be explained by the increased conjugation of the CHO group with the naphthalene nucleus (cf. Table 5:4) as was suggested for 2-acetonaphthene.

Terephthaldehyde (1,4-dialdehydobenzene), although measured in p-xylene, showed a significant reduction in its τo (13.6×10^{-12} sec) at 25^{o}C in comparison to p-chlorobenzaldehyde (15.8×10^{-12} sec) and p-chlorotoluene (17×10^{-12} sec). Several studies have been made on the relaxation behaviour of the analogous molecules p-dimethoxy-benzene(1)(14)(18)(73)(79)(96)(134) and p-diacetylbenzene(1)(14)(73). Measurements of the former molecule under several medium conditions, viz: liquid, dilute solution + viscous solvents all indicate that only intramolecular relaxation is taking place since the τos obtained are approximately the same as the τ_2 observed for anisole. p-Diacetylbenzene's τo (21.9×10^{-12} at 25^{o}C in p-xylene)(1) on the other hand was found to have lengthened considerably in comparison to acetophenone's τ_2 (8.6×10^{-12}) under the same conditions. Unfortunately, this compound's solubility prevented measurements in a viscous solvent, yet Farmer(1) suggested that the lengthening was due to the increased conjugation of the two acetyl groups. Although the evidence in Chapter 2 (Sections B and c) showed that the acetyl relaxation time was dependent on the nature of the R—$COCH_3$ bond, it would appear unlikely that the τ_2 would be magnified to the length observed in p-diacetylbenzene and, therefore, some form of molecular rotation is most probably occurring in this molecule, which could be confirmed by measurement in a nujol/p-xylene mixture. Terephaladehyde's τo is only slightly longer than the τ_2s obtained for the p-halobenzaldehydes and this could be adequately explained by an increased conjugation of the CHO groups with the benzene ring, however, it would be unwise to describe a molecule's behaviour on the basis of a single measurement and thus further studies in varying solvent conditions are required before any definite conclusions can be drawn.

The dipole moment of a para disubstituted non-rigid benzene may be used to calculate the orientation θ of the mobile group's dipole, using the equation:

$$\mu_{obs} = \sqrt{2}\mu_g \, \mathrm{Sin}\, \theta \quad (7)$$

where μ_g will be the dipole moment of benzaldehyde and μ_{obs} that of terephalaldehyde when the CHO group is considered. This equation assumes complete free rotation of the groups which is unlikely to occur in practice and for this reason the angle θ will only be of an approximate nature, for example, it gives a θ value of 76^0 for the OCH_3 group which is larger than would be expected (Chapter 4). Use, however, of a dipole moment for p-diacetylbenzene of 2.75D$^{(1)}$ and acetophenone of 2.83D gives a θ angle of 43.5^0 which is very close to 44^0 finally attributed to the acetophenones when considering their molecular weighting factors. Similarly, using the values in Table 5:1, a θ value of 32.5^0 is produced which, once again, would fit in with the C_1s derived for the benzaldehydes.

Use of the above equation then provides further evidence for employing a $C_1 = 0.7$ for benzaldehyde and it has been suggested that this high C_1 would hinder observation of an intramolecular process. Yet it could also be argued that compounds such as 2-acetonaphthone exhibits such high molecular weighting factors and a depression in this compound's τ_0 is still observable in comparison with that of 2-iodonaphthalene. This argument would apply to 2-naphthaldehyde but, not necessarily, for benzaldehyde, since in the latter the expected τ_1 is so low that the τ_2 would have to be of the order of 1×10^{-12} sec for the depression of τ_0 to be outside the experimental error limits. In the final analysis, however, it is felt that the lack of this depression can only partly be explained by the high C_1 value, a further factor most probably lies in the height of the energy barrier which the CHO group must overcome to rotate. If, for example, in the extreme but unlikely case of $\Delta H_2^{\ddagger} = 6.5$ kcal for 2-naphthaldehyde, by use of the following equations:

$$\Delta G_2^{\ddagger} = \Delta H_2^{\ddagger} - T\Delta S_2^{\ddagger} \quad (\text{where } \Delta S_2^{\ddagger} \propto \Delta H_2^{\ddagger} \text{ (cf Higasi relationship}^{(80)}\text{)})$$

$$\tau_2 = \frac{h}{kT} \cdot e^{\Delta G_2^{\ddagger}/RT}$$

$$f_{max} = \frac{1}{2\Pi\tau_2}$$

the maximum absorption for CHO rotation at 15°C would lie in the frequency range 10^5 - 10^7 c/s. Thus examination of these molecules in the megacycle area would show if the energy barriers derived in the far infra-red applied to their dielectric behaviour. Further studies on ortho substituted benzaldehydes would also be useful as Klages and Knobloch(14) detected a similar lowering of the mesomeric moment in o-chlorobenzaldehyde as was observed with the ortho substituted acetophenones. Thus in conclusion:

(i) Far infra-red and dielectric techniques indicate that the energy barriers and the relaxation times of aromatic aldehydes are very dependent on the medium in which they are measured and this is a disadvantage for detecting the presence of an intramolecular process.

(ii) An internal relaxation process was detected for the para substituted benzaldehydes but not in benzaldehyde or 2-naphthaldehyde, the latter being attributed to

(a) the magnitude of the C_1 values

(b) the barrier height for the CHO rotation ($\Delta H_2^{\ddagger}$) being higher than in the analogous acetyl and methoxy compounds.

(iii) Further areas of research have been suggested which would clarify the preceding points

CHAPTER 6

RELAXATION TIMES OF SOME RIGID MOLECULES

INTRODUCTION

Throughout this thesis the τ_1 parameter analysed for non-rigid molecules has been verified by comparing it with the τ of a similar sized molecule. For ortho substituted acetophenones and anisoles, very few analogous rigid compounds have been reported in the literature, and for this reason the work in this chapter was initiated.

Ortho and meta dichlorobenzenes have been measured by Hassell in p-xylene at 25°C(30), he found that the relaxation times of the two compounds differed very little from one another and were only slightly larger than the mono substituted compound. Crossley suggested that this was due to τ_0 being related to the length of the molecule, more so than with its volume(16). This worker obtained reasonable correlations between molecular volumes (calculated from Courtauld models) and relaxation time for haloethanes, and also for similar plots of molar volumes vs τ for substituted benzenes. In the latter case the ortho and meta dichlorobenzene relaxation times appeared short by comparison with their total volumes.

The dependence of τ on molecular volume originates from a modification of the original Debye dielectric theory for spherical molecules(99), by Perrin(100) and Fischer.(101) The latter author postulated the following equation to account for the behaviour of ellipsoidal molecules having semi-axes a,b,c;

$$\tau = \frac{4\Pi abc\eta^{*}f}{kT} \qquad (6:1)$$

where the volume of the ellipsoid is given by $V = 4\Pi abc/3$

and η^* = microscopic viscosity coefficient

f = a molecular structure factor

k = Boltzman's constant.

This relationship is expected to apply to molecules of similar size and shape, especially when the same solvent and temperature are considered, since η^* and f should then be roughly constant(98)(23). Quantitatively, however, the Fischer equation has been found to be inadequate for polar molecules where both solute and solvent molecules are of similar size(21), and this is borne out by Crossley's plot of τ against volume, which although reasonably linear does not pass through the origin.

There have been several explanations for divergence of the observed relaxation times and those calculated from the Fischer Equation, one being that the original Debye theory did not take into account the moment of inertia of the solute molecule(102)(103). As a fairly accurate knowledge of molecular relaxation time is required to intelligently discuss the behaviour of non-rigid molecules, it was decided to expand the work on ortho dihalobenzenes to include meta substituted benzenes and, therefore, determine whether the relaxation time of these molecules was related to volume, moment of inertia or molecular length. It should also be possible, with the increased amount of relaxation data to estimate if any correlation exists between τ and I.

Ortho and meta-di-iodobenzenes were, therefore, measured at 15^0 and 60^0 in p-xylene, while ortho-bromo and chloro-iodobenzenes together with

TABLE 6:1:a MEAN RELAXATION TIMES, DIPOLE MOMENTS AND ENERGY BARRIERS OF SOME ORTHO AND META SUBSTITUTED IODOBENZENES IN p-XYLENE AND 2-IODONAPHTHALENE IN CYCLOHEXANE.

COMPOUND	TEMP. °C	α	τ_o x10^{12} sec	μ D	μ_{LIT}^{104} D	$\varepsilon_\infty - n_D^2$	$\Delta G^\ddagger$ -kcal	$\Delta H^\ddagger$ mole^{-1}	$\Delta S^\ddagger$ e.u.
o-diiodobenzene	15	0.04	27.0	1.69	1.71	0.037	2.91	2.0	-3.2
	60	0	14.6	1.69		0.028	3.05	2.0	-3.3
o-bromoiodobenzene	60	0	12.0	1.88	1.88	0.028			
o-chloroiodobenzene	60	0	11.0	1.97	1.95	0.028			
m-diiodobenzene	15	0.08	22.8	1.25	1.28	0.034	2.86	1.9	-3.3
	60	0	12.6	1.24		0.022	2.95	1.9	-3.2
m-bromoiodobenzene	60	0	10.3	1.33	1.15	0.028			
2-iodonaphthalene	† 25	0.09	43.1	1.60	1.57	0.018			

† cyclohexane solvent

TABLE 6:1:b

COMPOUND	TEMP. °C	α	τ_o x10^{12} sec	μ_D	μ_{LIT}[104] D	$\varepsilon_\infty - n_D^2$	$\Delta G^{\ddagger}$ -kcal	$\Delta H^{\ddagger}$ mole^{-1}	$\Delta S^{\pm}$ c.u.
fluorobenzene	15	0	6.8	1.39	1.48	0.05	2.2	1.4	-2.4
	60	0	3.2	1.40			2.23	1.4	-2.4
chlorobenzene	15	0	10.2	1.56	1.58	0.046	2.36	1.6	-2.5
	60	0	6.0	1.55			2.47	1.6	-2.5
bromobenzene	15	0	14.0	1.59	1.56	0.039	2.54	2.0	-2.0
	60	0	7.6	1.58			2.63	2.0	-2.0
iodobenzene	15	0	18.0	1.39	1.40	0.041	2.68	2.2	-1.6
	60	0	9.2	1.39			2.75	2.2	-1.6
o-dichlorobenzene	†25	0	9.4	2.27	2.27				
m-dichlorobenzene	†25	0	10.0	1.49	1.49				
2-bromo-	†25	0.08	25.5	1.86	1.73		2.99	2.9	-0.6
naphthalene	50	0	16.1	1.82			3.00	2.9	-0.3

Dielectric Results of Hassel[17] for some aromatic halides

The solvent used was p-xylene except for †

† cyclohexane solvent

meta-bromoiodobenzene were measured just at 60°C. The results of these measurements together with 2-iodonaphthalene in cyclohexane at 25°C are presented in Table 6:1.

DISCUSSION OF RESULTS

A. The disubstituted iodobenzenes were chosen for this study as iodine closely resembles acetyl and methoxy groups in size, also the large volume of the iodine atom should emphasise any significant differences between ortho and meta compounds. The equivalent sized alkylbenzenes were not considered as Hassell and Crossley have suggested that these molecules do not exhibit Debye behaviour(30).

(a) Ortho substituted Iodobenzenes: As the relaxation times of these molecules were to be used as standards, the dielectric parameters were verified by comparing the dipole moments obtained by the microwave technique to those reported in the literature. The two sets of values can be seen to be well within each method's experimental error and thus this supports the extrapolated ε_∞ and the fit of the Cole-Cole plot to the experimental points. Since the dihalobenzenes were measured in relatively concentrated solutions ($\omega_2 \sim 0.15$), the dipole moments were determined using the equation incorporating the solution density (Equation 1:33); they exhibit the usual "ortho effect"(15) shown by benzenes substituted with immobile groups, the effect being a discrepancy between the observed moment and that calculated theoretically using the equation:

$$\mu = \left(\mu_1{}^2 + \mu_2{}^2 + \mu_1\mu_2\right)^{\frac{1}{2}}$$

where μ_1 and μ_2 are the group moments of the two substituents(3).

This discrepancy has been attributed to steric repulsion and mutual induction, the former producing a slight distortion of the substituents in and out of the plane of the benzene ring(15).

It may be suggested that a distribution coefficient of 0.04 obtained for o-diiodobenzene is not significant yet those obtained for m-diiodobenzene and 2-iodonaphthalene obviously are! They probably all arise from a distribution of molecular relaxations similar to that described for 9-acetylanthracene. An equivalent hypothesis has been assigned to this distribution by Hill(102); she claims that if the moments of inertia about different axes of a molecule differ widely, there is a range of relaxation times, associated with rotation about each symmetry axis, which will also have a large difference. The ortho, meta-dihalobenzenes and 2-substituted naphthalenes do have a wide range of moments of inertia, as will be seen later, and therefore, this may well be the case. Smyth has explained a large α of 0.35, obtained for large oblate ellipsoidal molecules, in a similar manner(20). Thus it is preferable to compare τ values at higher temperatures, where the relaxation times about the axes are smaller, the difference between them not so large and this distribution will decrease.

The $\varepsilon_\infty - n_D^2$ term is of normal proportions for these compounds, being comparable to those obtained by Hassell(29) for the halobenzenes. Poley observed a much higher $\varepsilon_\infty - n_D^2$ term (∿0.2 at 20°C) for the latter compounds in the pure liquid state and used this as evidence of a high frequency absorption region in the neighbourhood of 1 mm.(106) Later, Garg and Smyth measured the liquid halobenzenes at 2 mm wavelength and found a smaller $\varepsilon_\infty - n_D^2$ (∿0.03) than Poley, these authors concluded that the magnitude of this term could adequately be explained by normal atomic polarization(50). M.Davies and his co-workers, however, studying these compounds in the far infra-red, discovered they did absorb in the wave number range 30-80 cm^{-1} and suggested that this was the predicted Poley absorption(130). Far infra-red measurements of liquid dihalobenzenes have also been carried out in this laboratory(131), and these molecules, too, have been found to have some type of absorption. It appears that there exists two kinds of absorption, one emerging from molecules diffusing from one position to another, as at microwave frequencies, the other from a faster type of motion, where the molecules may undergo lattice type vibrations which would give a resonance absorption(132). As all molecules appear to absorb to some extent in the far infra-red and at this time the full nature of these absorptions is not fully understood, all that can be said of the $\varepsilon_\infty - n_D{}^2$ of mono and dihalobenzenes in dilute solution is that this term is of normal proportions and does not, itself, indicate any anomalous behaviour in these molecules. The relaxation times presented in Table 6:1:a may, therefore, be taken as accurate assessments of the molecular behaviour of compounds of their size and shape.

Comparison of the relaxation times of o-diiodobenzene (14.6 x 10^{-12} sec) and iodobenzene (9.2 x 10^{-12} sec) at 60°C shows that there has been an increase of over 50%, a difference which cannot be termed slight. This difference becomes progressively smaller as the size of the ortho substituent decreases, till with o-chloroiodobenzene the difference in

τ from iodobenzene is only 20%. The latter increase may be assigned to experimental error, yet the consistent progression through the series would suggest that it is meaningful. It is of interest to note that plots of ε' vs $\varepsilon''\omega$ for these rigid compounds produce τ values which differ very little from those obtained by computer analysis, Fig. 6:1 shows an example of this.

(b) Meta-substituted Iodobenzenes: The dielectric parameters of these molecules may be verified as above. The literature dipole moment for m-bromoiodobenzene would, however, appear to be too low, since it is inconceivable that the moment of this compound is lower than that of m-diiodobenzene. In comparison with the ortho derivatives, the agreement between the calculated and observed moments is much better, the very small differences which have been observed being attributed to small mutual inductive effects, which tend to produce slightly lower observed moments in the case of m-dihalobenzenes(15). As the dipole moment of a meta benzene derivative is given by:

$$\mu \;=\; \left(\mu_1{}^2 + \mu_1{}^2 - \mu_1\mu_2\right)^{\frac{1}{2}} \quad (3)$$

and to counteract this mutual inductive effect the moments of m-dibromobenzene (1.46D)(15) and m-di-iodobenzene (1.25D) are taken for μ_1 and μ_2, the calculated dipole moment for m-bromoiodobenzene is found to be 1.36D; a value similar to the one observed experimentally in this study of 1.33D.

The relaxation time of m-diiodobenzene is to fall in between that of the ortho and mono substituted derivatives, being 12.6 x 10^{-12} sec at

$60^{o}C$. This is in contrast to the results of chlorobenzene, o-dichlorobenzene and m-dichlorobenzene of Kastha and his co-workers who reported relaxation times in benzene at ∿$23^{o}C$ of 11.1, 11.7 and 9.4×10^{-12} sec respectively(107). It is also at odds with Hassell's results, where τm-dichlorobenzene>τo-dichlorobenzene, and indeed, with the theory of τα molecular volume, as the volume of meta substituted compounds is greater than those with ortho substituents. Within the experimental error the relaxation times of the meta compounds may be said to be the same as those of the ortho derivatives. Similarly the enthalpies of activation are also equivalent and show no suggestion of increasing $\Delta H^{\ddagger}$ with larger molecular volume as was observed by Hassell with the mono substituted halobenzenes. Thus it would appear that in view of their size the meta dihalobenzene results are anomalously short and will be discussed further in the next part of this chapter.

(c) 2-Iodonaphthalene: The dipole moment observed for this compound again is consistent with the literature value and the large distribution coefficient obtained at $25^{o}C$ is similar to that observed by Hassell for 2-bromonaphthalene(17). The relaxation time, however, of 43.1×10^{-12} sec is considerably longer than would be expected in comparison with 25.5×10^{-12} sec for the bromo derivative. It is submitted that the result in this study may be more accurate owing to measurement at lower frequencies (1.9 Gc/s), closer to where the maximum absorption occurs, although the disparity may be explained to some extent by rotation of the molecules about their respective centre of masses. Practical difficulties prevented examination of 2-iodonaphthalene at higher temperatures.

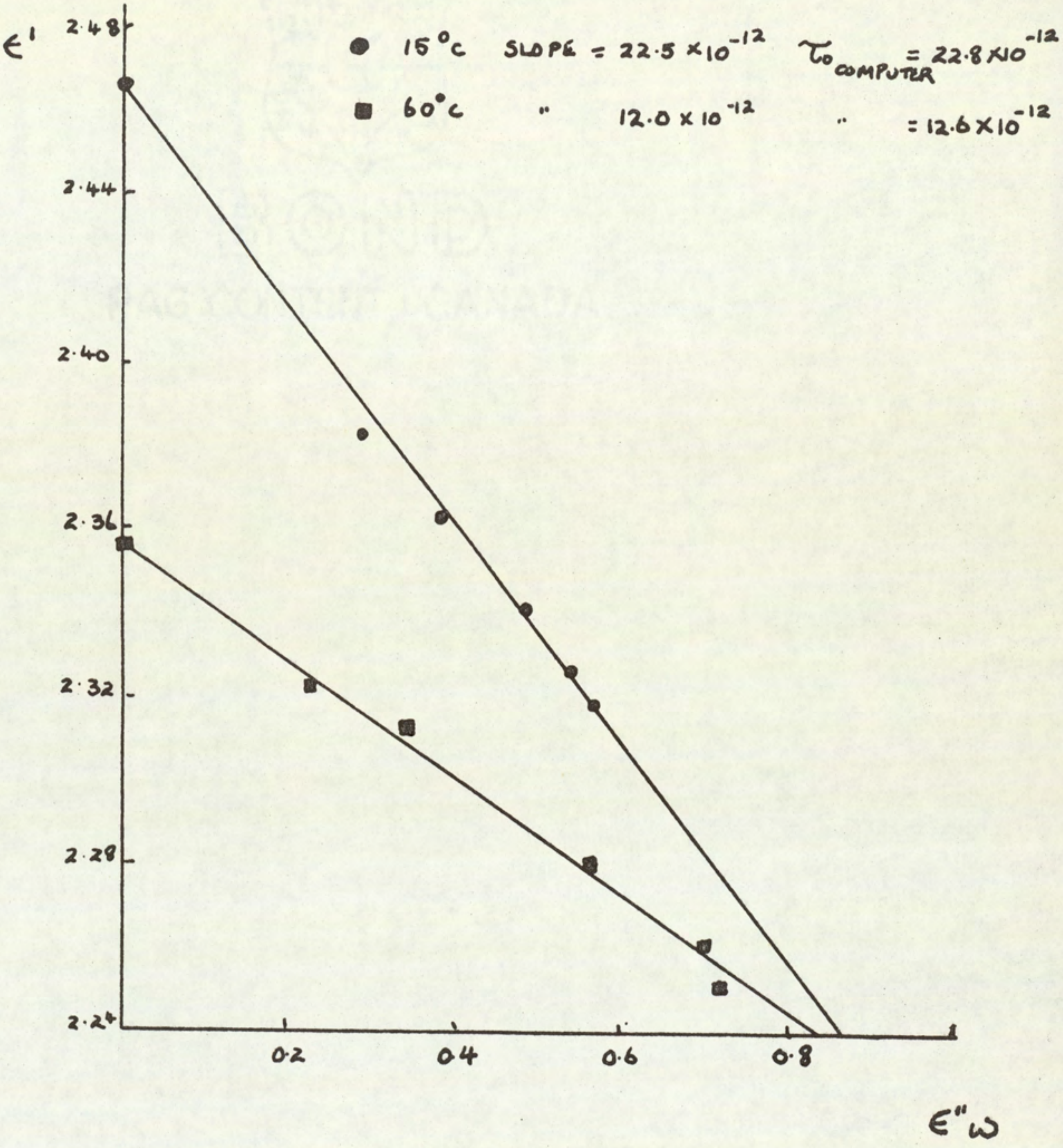


FIG. 6:1 PLOT OF ϵ' VS $\epsilon''\omega$ FOR M-DIIODOBENZENE / P-XYLENE

TABLE 6:2 PRINCIPLE MOMENTS OF INTERTIA, MOLECULAR EFFECTIVE RADII AND MOLECULAR RELAXATION TIMES OF SOME AROMATIC MOLECULES IN P-XYLENE AND CYCLOHEXANE SOLUTIONS.

COMPOUNDS	Ia	Ib	Ic	I	$\sqrt{I}$	Reff	τ@15°	τ@60°	τ@25°	
	$\times 10^{40}$ gcm^2				$\times 10^{20}$ (gcm^2)$^{1/2}$	Å	$\times 10^{12}$ sec p-xylene		cyclohexane	
<u>Mono Benzenes</u>										
Fluoro	149.23	329.09	478.4	403.75	20.09	3.00	6.8	4.2		(17)
Chloro	149.23	541.31	690.6	615.95	24.81	3.45	10.2	6.0		(17)
Bromo	149.23	855.9	1005.1	930.5	30.5	4.15	14.0	7.6		(17)
Iodo	149.23	1079.9	1229.1	1154.5	33.98	4.60	18.0	9.2		(17)
Nitrile	149.23	544.27	693.49	618.87	24.88	3.34	15.0*			(17)
Nitro	207.58	681.0	888.6	784.8	28.01	3.70	15.3	9.0	9.9*	(17)
<u>TOLUENES</u>										
P-Chloro	152.72	835.11	987.83	911.47	30.19	4.15	19.5	11.1	16.4	(17)
P-Bromo	152.72	1270.2	1422.9	1346.6	36.70	4.80	26.6	13.0	19.9	(17)
<u>O-DIBENZENES</u>										
Dimethyl	254.53	383.59	638.13	510.86	22.60	3.05			8.3	(17)

COMPOUNDS	Ia	Ib	Ic	I	$\sqrt{I}$	Reff	τ@15°	τ@60°	τ@25°
	X10^{40} gcm^2			X10^{20} (gcm^2)$^{1/2}$		Å	x10^{12} sec p-xylene-cyclohexane		
Dichloro	412.45	598.85	1011.3	805.07	28.37	3.66			9.4 (17)
Chloroiodo	511.40	1093.5	1604.87	1349.2	36.73	4.53		11.0	
Bromoiodo	917.02	1099.3	20.6.4	1557.8	39.47	4.56		12.0	
Diodo	1010.9	1346.0	2356.8	1851.4	43.03	4.59	27.0	14.6	
<u>M-Dibenzenes</u>									
Dimethyl	226.93	466.40	693.34	460.1	21.45	3.37			9.3* (17)
Dichloro	299.23	997.0	1296.2	797.72	28.24	3.23			10.0 (17)
Bromoiodo	414.96	2911.09	3326.05	1870.5	43.25	3.75		10.3	
Diiodo	438.52	3796.2	4234.7	2336.6	48.3	3.79	22.8*	12.6	
<u>Naphthalenes</u>									
2-Bromo	400.36	21.04.9	2505.0	2304.9	48.0	5.27			25.5* (17)
2-Iodo	446.70	2676.9	3123.6	2900.2	53.85	5.82			43.1*

COMPOUNDS	Ia	Ib	Ic	I	$\sqrt{I}$	Reff	τ@15°	τ@60°	τ@25°	
							$X10^{12}$ sec			
	$X10^{40}$ gcm^2			$X10^{20}$ (gcm^2)		Å	p-xylene-cyclohexane			
Rigid Carbonyls										
Fluorenone	576	1430	2010	1293	35.96		21.5*	11.5*		(120)
Anthrone	536	1960	2420	1478	38.44		27.5*	13.6*		(120)
Phenanthrene-Quinone	708	1510	2450	1579	39.74		34.4*	16.1*		(120)
Non-Rigid Compounds										
ωωωTrifluoroacetophenone	415.26	922.15	1337.4	1229.8	33.61	4.06	24.7*	13.1	19.9	(1)
p-Bromo anisole	183.37	1762.1	1945.5	1853.8	43.06	5.58	32.2*	17.4*		(1)

*$\alpha > 0.04$

B. RELAXATION TIME AND MOMENT OF INERTIA.

Several workers have suggested that the dielectric behaviour of molecules in dilute solution may depend upon their moments of inertia. There are two approaches which have been discussed:

(1) Corrections to the Debye Model(108),

(2) Alternative models to the Debye approach.

(1) Firstly, the Debye approach will be considered, in this, the mean orientation moment of molecules in time dependent fields have been evaluated in terms of orientational diffusion, expressed by a probability function f. The dissipative character of the problem is introduced by a molecular friction constant ζ, relating torque L of the molecular field to the angular velocity $\delta\theta/\delta t$ by $L = \zeta(^{\delta\theta}/\delta t)$; - - - - - - - (6:2)
with a sinusoidal field $F = F_o e^{i\omega t}$ the torque on a molecule of dipole moment μ at θ to this field is $L = -\mu F \mathrm{Sin}\theta$ - - - -- - - - (6:3)
Consideration of the equation of continuity in configuration space and assuming that f reduced to a linearized equilibrium Boltzmann function led Debye to the solution

$$4\Pi f = \frac{1+\mu F_o \mathrm{Cos}\theta}{kT(1+i\omega\tau)} \qquad (6:4)$$

the molecular relaxation time being defined by

$$\tau = \frac{\zeta}{2kT} \qquad (6:5)$$

He interpreted ζ by assuming the molecular dipole to respond to torque as would a rigid sphere of radius "a" turning in a hydrodynamic fluid of microscopic viscosity η. For this model, Stokes' classical calculation gives $\zeta = 8\Pi\eta a^3$, hence

$$\tau = \frac{4\Pi\eta a^3}{kT} \qquad \text{- - - - - - - - - - -} \qquad (6:6)$$

a modification of the latter equation producing the Fischer correlation equation 6:1.

That Debye had neglected to take into account inertia effects in equation 6:2 since he considered them unimportant, was first noted by Rocard(109), referred to by Whiffen(110) and tentatively corrected by Powles(111), so that equation 6:2 became

$$I\frac{d^2\theta}{dt^2} + \zeta\frac{d\theta}{dt} = L \qquad \text{- - - - - - - - - - -} \qquad (6:7)$$

By extending his analysis Powles determined that the effect of molecular inertia for a polar solute in a non-polar solvent was given by

$$\frac{\tan\delta}{\tan\delta_{I=0}} = \frac{\left[1 + (1-\alpha)x\right]\left[1 + (\omega\tau)^2\right]}{\left[1 - x(\omega\tau)^2\right]^2 + (\omega\tau)^2\left[1 + (1-\alpha)x\right]^2} \qquad (6:8)$$

where $\tan\delta$ = loss tangent = $\varepsilon''/\varepsilon'$

α, ω and τ having the normal dielectric meaning and

$$x = \frac{I}{2kT\tau^2} \qquad \text{- - - - - - - - - - -} \qquad (6:9)$$

A graph of τ vs $\sqrt{I}$ for a limited number of relatively small compounds gave Powles a linear plot which bisected the origin of the two axes. This led him to suggest that τ was proportional to some "mean radius" of the molecule and not its volume as suggested by the Debye equations. As the slope of the graph gave a small x value Powles concluded that the effect was not large enough to show promise as a method of estimating moment of inertia values of polar molecules. He also suggested that the greatest effect was to be expected with solvents of low viscosity.

Since Powles, other workers, notably Sack(113) and Gross(112), have approached this problem in greater mathematical detail, dealing with a compressed polar gas in a non-polar gas medium where the interaction between polar molecules could be neglected. Sack, for example, pointed out that in the Debye approximation the relaxation time calculated for molecules whose dipole direction coincide with a principal axis of inertia is independent of the moment of inertia Iz about this axis. This arises from the Debye model being based on a configurational equation (Smoluchowski), whereas these workers maintain that for consistent kinetic treatment the problem must be considered in phase space as well, where both positions and momenta are taken as independent variables, since in all relaxation processes inertial effects will become important at sufficiently high frequencies. However for collision mechanisms which leave the orientation of the dipoles unaltered, both Gross and Sack found that the corrections required by the Debye relaxation formulae were relatively small, being largest for frequencies near the absorption maximum ($\omega\tau \sim 1$). The modified Debye equation that these authors obtained effectively agrees with that of Powles.

Although these theoretical calculations indicate that a molecule's moment of inertia will tend to have only a small effect on its absorption curve, it still remains to be seen whether the experimentally observed τ values do bear any correlation to $\sqrt{I}$.

(2) The Debye approach assumes that the molecules are undergoing some form of Brownian motion, Kauzmann(80), however, has argued that a diffusion model of reorientations is less likely in polar liquids than discrete 'jumps' between stable orientations. Meakins(21) has shown that when a solute molecule is at least three times as large as the solvent molecule, the Debye equations are obeyed. Since the energy for a molecule to go from one equilibrium site to another, is obtained by kinetic collisions with adjacent molecules(114) (in dilute solution the majority of collisions will be of the solute-solvent type) it is possible that small polar molecules will undergo a 'jump' process and as the molecular size increases, the motion will decrease towards that of the Brownian type as observed by Meakins. Hoffmann(115) considering such a 'jump' mechanism found that there was some implication that the pre-exponential term (A) of the Arrhenius expression:

$$\frac{1}{\tau} = A\, e^{-H^{\ddagger}/RT} \qquad \text{(cf Chapter 1)}$$

was of the order:

$$\left(\frac{3}{2\Pi}\right)\left[\frac{kT}{I}\right]^{\frac{1}{2}} \qquad (6:10)$$

In fact earlier Bauer had reported an alternative rate equation to that of Eyring, the A factor of which included a similar moment of inertia term to Hoffman's suggestion., viz:

$$A = \left(\frac{kT}{2\Pi I}\right)^{\frac{1}{2}} \times \left[\frac{1}{\sigma_1} + \frac{1}{\sigma_2}\right] \times L \qquad (6:11)$$

where σ_1 and σ_2 are configuration partition functions corresponding to the two equilibrium positions and L is the effective length of the potential barrier(116). Davies and Clemett have compared the Bauer and Eyring rate expressions and found they gave very similar results(117), although they preferred the former method as it fitted their numerical data better. These results do not necessarily verify the Bauer rate expression, however, they at least give credibility to the relationship $\tau \propto \sqrt{I}$. Similarly Powles, considering a jump mechanism favours an A term, which includes the moment of inertia of the rotating molecule and also calculates the angle θ of the molecular jump by:

$$\theta = \left(\frac{3kT}{I} \right)^{\frac{1}{2}} \tau \qquad (115)$$

In view of the foregoing discussion of the Debye and other models, and the increased dielectric data was now available, it was decided to examine these theoretical correlations further, to determine whether the dependence of τ on the moment of inertia was sufficiently large to be used as a method to predict molecular relaxation times.

THE DETERMINATION OF A MOLECULES MOMENT OF INERTIA

The molecule's centre of mass was calculated in the normal manner

i.e.
$$X_{CM} = \sum_{i=i}^{i=1} \left(M_i X_i \Big/ M_i \right) \qquad (6:12)$$

$$Y_{CM} = \sum_{i=i}^{i=1} \left(M_i Y_i \Big/ M_i \right) \qquad (6:13)$$

where X and Y are the co-ordinates of the individual atoms and M their atomic weights. The atomic spacings were evaluated from spectroscopic and diffraction measurements(118)(119) and the principal moments of inertia (Ia, Ib and Ic) were determined by the use of ordinary mechanics, using the equation

$$Ia = \left[\sum_{i=i}^{i=1} (M_i \, r_i{}^2) \right] \frac{10^{-16}}{N} \text{ g cm}^2 \qquad (6:14)$$

M having the same meaning as before, r_i being the distance in Angstrom units from the a axis to the i th atom and N, the normal notation for Avogadro's Number. The a, b and c axes all meet at the centre of mass and normally axes a or b are placed along the molecule's major symmetry axis. A sample calculation is shown in Fig. 6:2. For simplicity all the molecules are considered planar, the moment of inertia about the axis perpendicular to the plane of the ring is then equal to the sum of the other two. The results of these calculations are presented in Table 6:2, together with those of three rigid carbonyl compounds determined by Pitt and Smyth(120). Except for the latter and the meta substituted compounds the resultant dipole moment of the molecules lies parallel to the a-axis, as there is no orientating torque about this axis, only the remaining two moments of inertia were used in averaging for I. With Smyth's compounds and the meta substituted molecules no rotation would be observed about the b-axis and thus, the mean of Ia and Ib was taken. Verification of the calculation method may be had by comparing the values with those determined by other workers, only a ± 2% variation is observed. This good agreement may be fortuitous, the error will be greater with the non-planar ortho compounds, although the overall error is

TABLE 6:3

COMPARISON OF CALCULATED I VALUES (X 10^{40}) WITH THOSE OF OTHER WORKERS

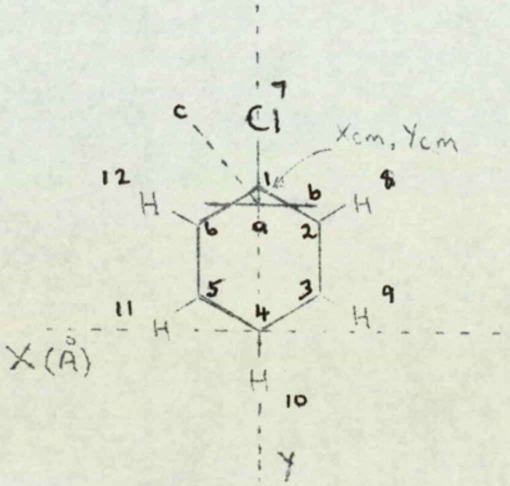
Reference	g cm²			
	This study	121	111	122
Compound				
Fluorobenzene	404	402		
Chlorobenzene	616	615		
Bromobenzene	931	940	912	
Iodobenzene	1156	1210		
Nitrobenzene	785	766	793	
Benzonitrile	619	618		617†

†determined by microwave spectroscopy

not considered to be any larger than 10%. The discrepancy will of course be diminished in the $\sqrt{I}$ term. Using the relaxation times observed by Farmer(1), Hassell(17) and Smyth(120) together with those obtained here, plots of $\sqrt{I}$ vs τ were made for p-xylene solutions at 15^{0} and 60^{0}C and for cyclohexane solutions at 25^{0}C cf. Figs. 6:3→5. No physical significance has been attached to compounds which exhibited distribution coefficients of 0.04 or less, and the normal error limits have been placed on the relaxation term; with compounds such as the 2-halonaphthalenes which produced large αs, the error limits on τ have been increased accordingly.

Fig. 6:2

Moment of Inertia Calculation for chlorobenzene



The atoms are numbered as shown in diagram (not drawn to scale). Thus co-ordinates of $C_{(1)}$ are X_1Y_1 etc.

Centre of Mass Co-ordinates

$$X_{cm} = 0$$

$$Y_{cm} = \frac{M_C (Y_1 + 2Y_2 + 2Y_3) + M_H (2Y_8 + 2Y_9 - Y_{10}) + M_{Cl} Y_7}{6M_C + 5M_H + M_{Cl}}$$

Moments of Inertia

$1 \text{ Å} = 10^{-8}$ cm

$$I_a = \left[4M_C X_2^2 + 4M_H X_8^2\right] \frac{10^{-16}}{N} = 149.22 \times 10^{-40} \text{ g cm}^2$$

$$I_b = \left[M_C(\overline{Y_{cm} - Y_1}^2 + 2.\overline{Y_{cm} - Y_2}^2 + \cdots\cdots) + M_H(2.\overline{Y_{cm} - Y_8}^2 + \cdots\cdot) + M_{Cl}(Y_7 - Y_{cm})^2\right] \frac{10^{-16}}{N}$$

$$= 541.31 \times 10^{-40} \text{ g cm}^2$$

As chlorobenzene is a planar molecule

$$I_c = I_a + I_b$$

$$= 690.5 \times 10^{-40} \text{ g cm}^2$$

NB. The following order is always observed: $I_a < I_b < I_c$.

In this case the mean moment $I = \frac{1}{2}(541.3 + 690.5) = 616 \times 10^{-40}$ g cm^2

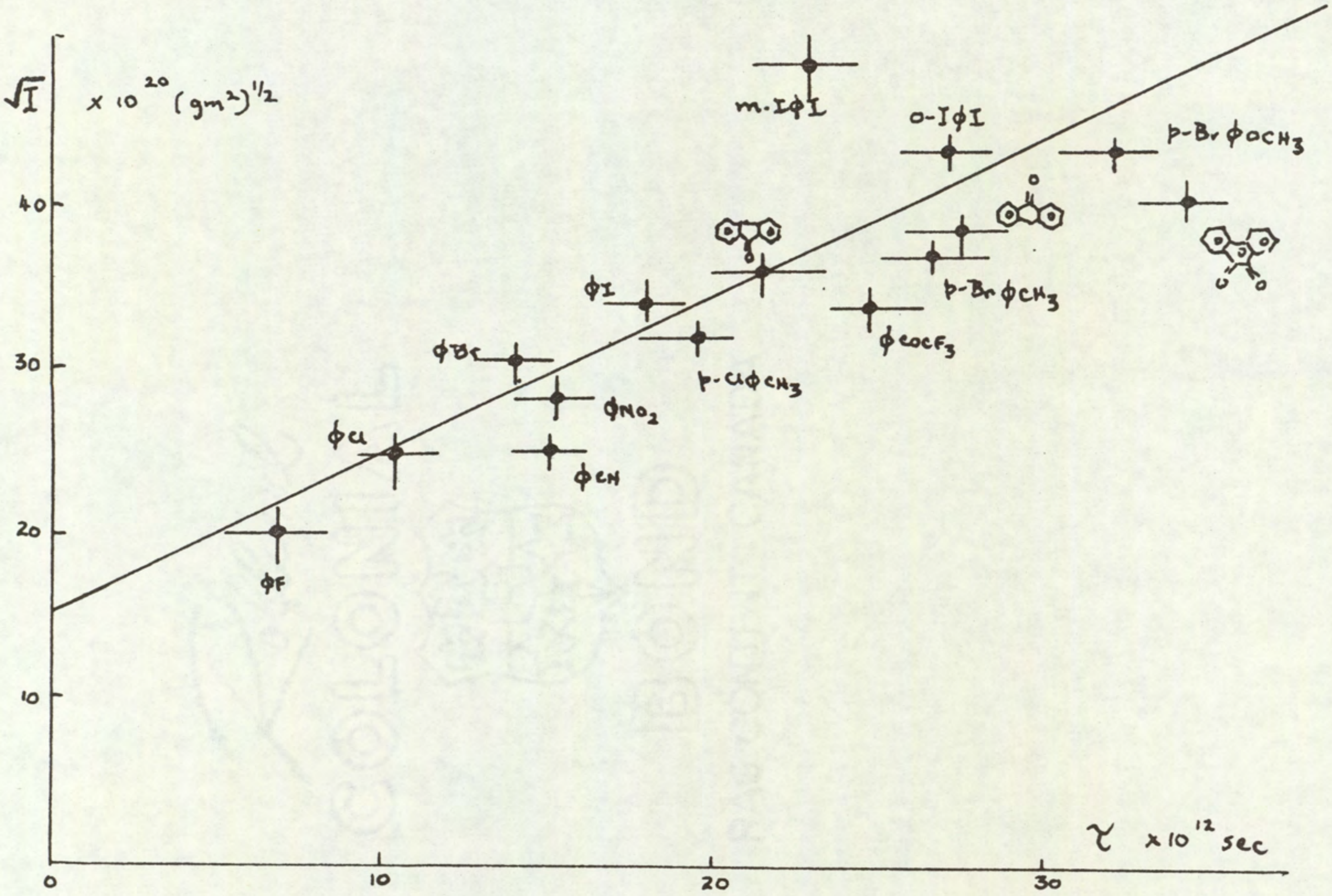


FIG. 6:3 PLOT $\sqrt{I}$ AGAINST τ FOR MOLECULES MEASURED IN p-XYLENE AT 15°C

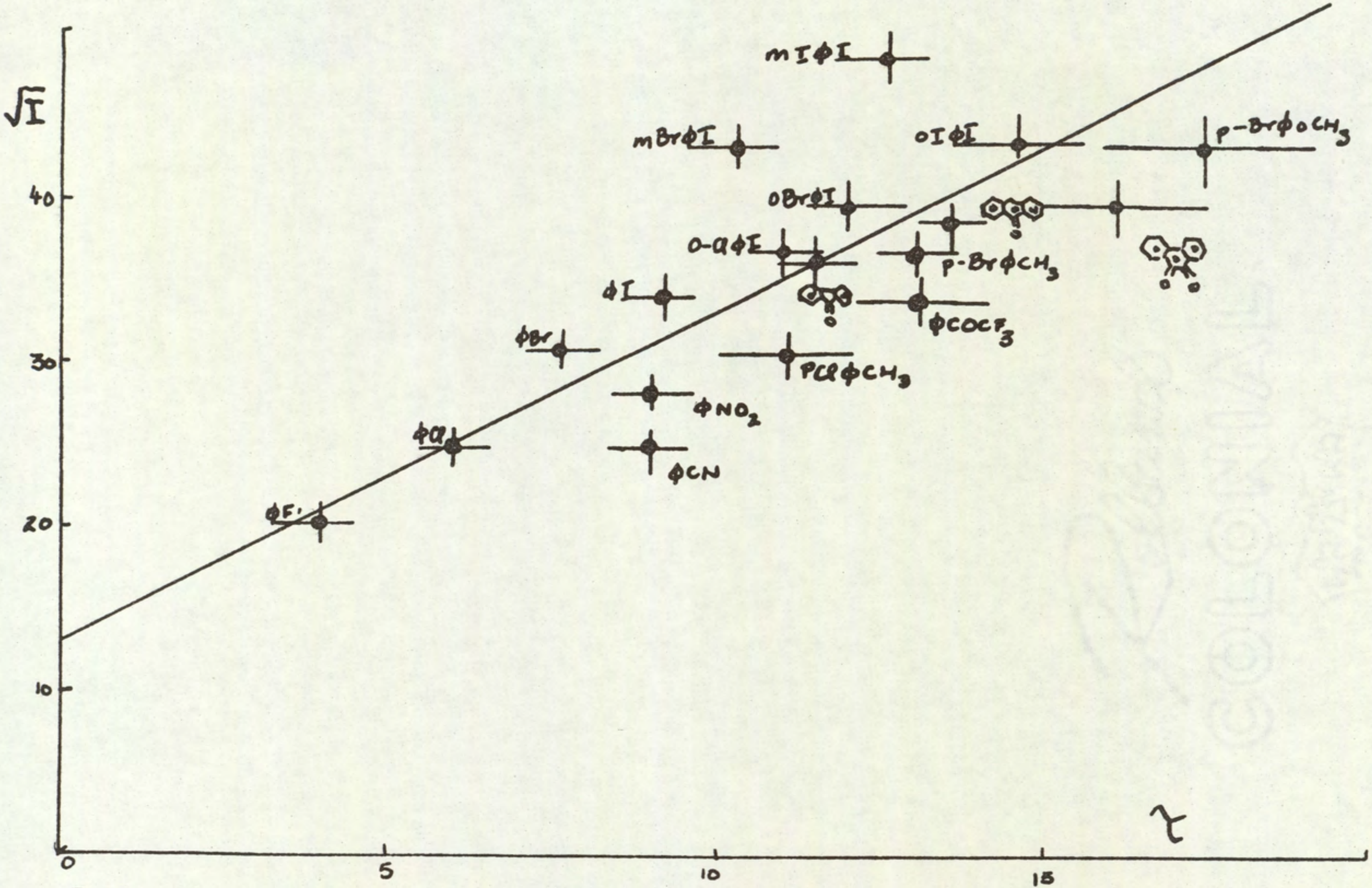


FIG 6:4 PLOT OF $\sqrt{I}$ AGAINST τ FOR MOLECULES MEASURED IN p-XYLENE AT 60°C

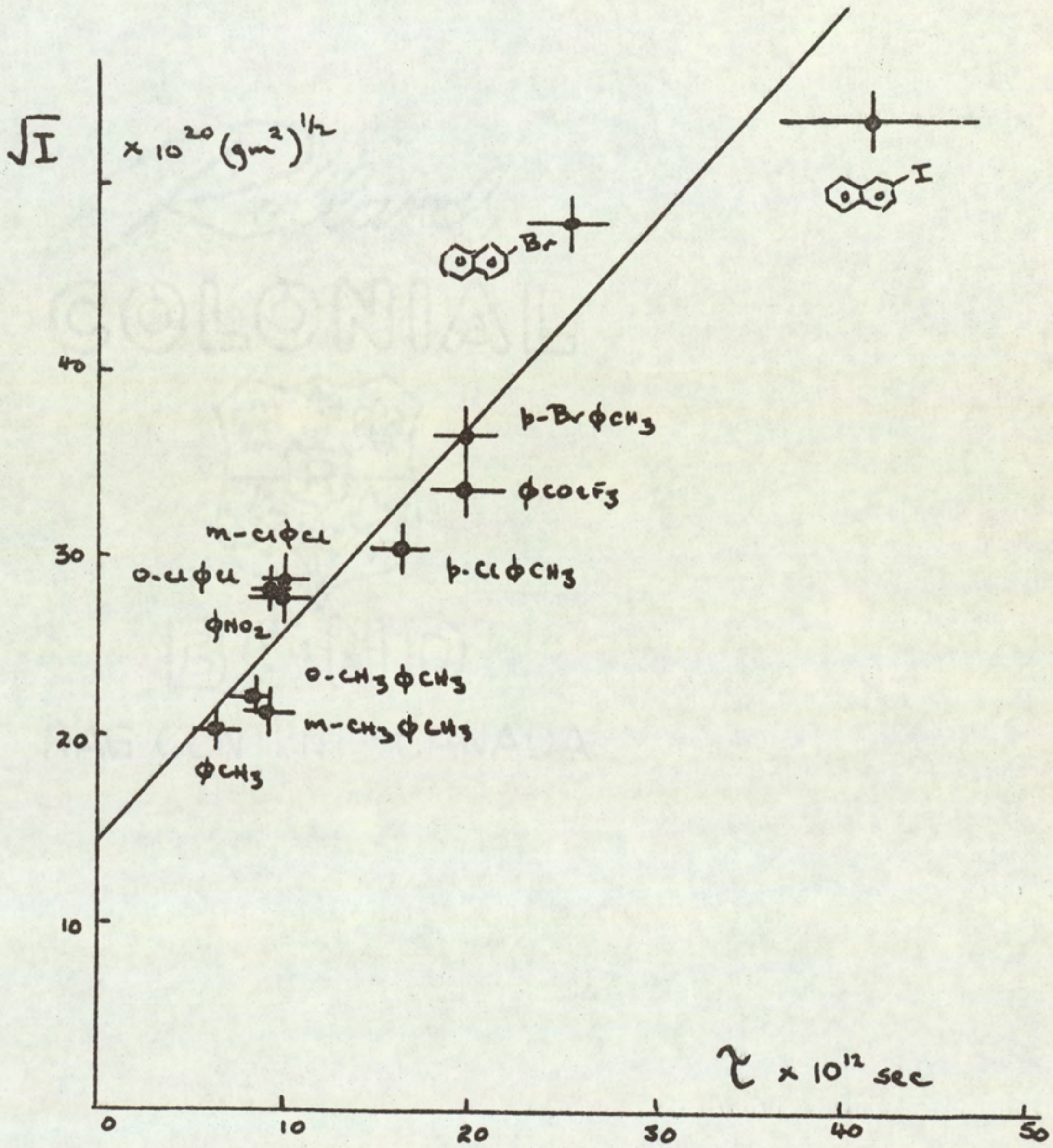


FIG 6:5 PLOT OF $\sqrt{I}$ AGAINST τ FOR MOLECULES MEASURED IN CYCLOHEXANE AT 25 °C

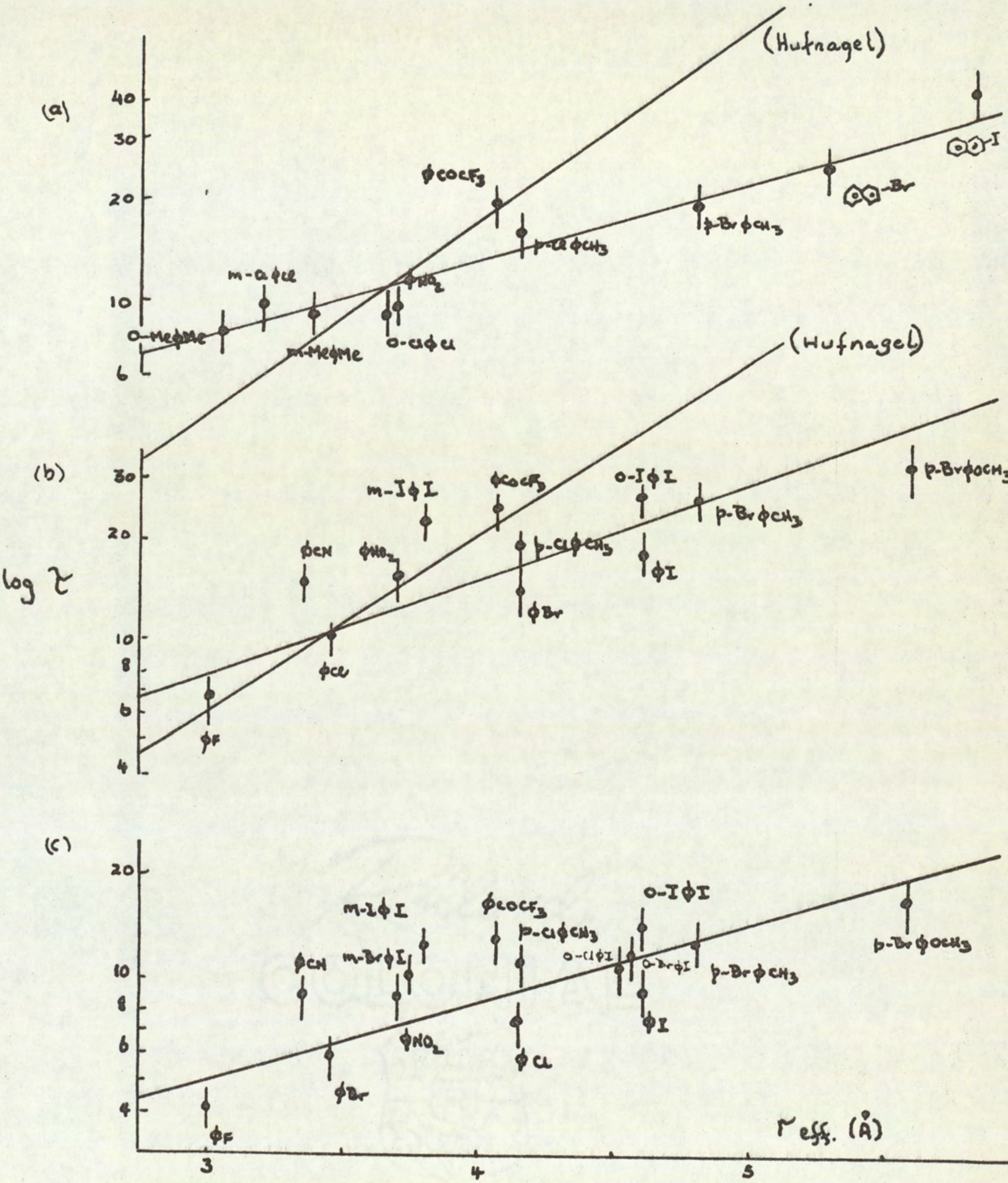


FIG 6:6 PLOTS OF LOG τ VS EFFECTIVE RADIUS FOR :

(a) CYCLOHEXANE SOLN.S AT 25°C
(b) P-XYLENE .. .. 15°C
(c) .. .. .. 60°C

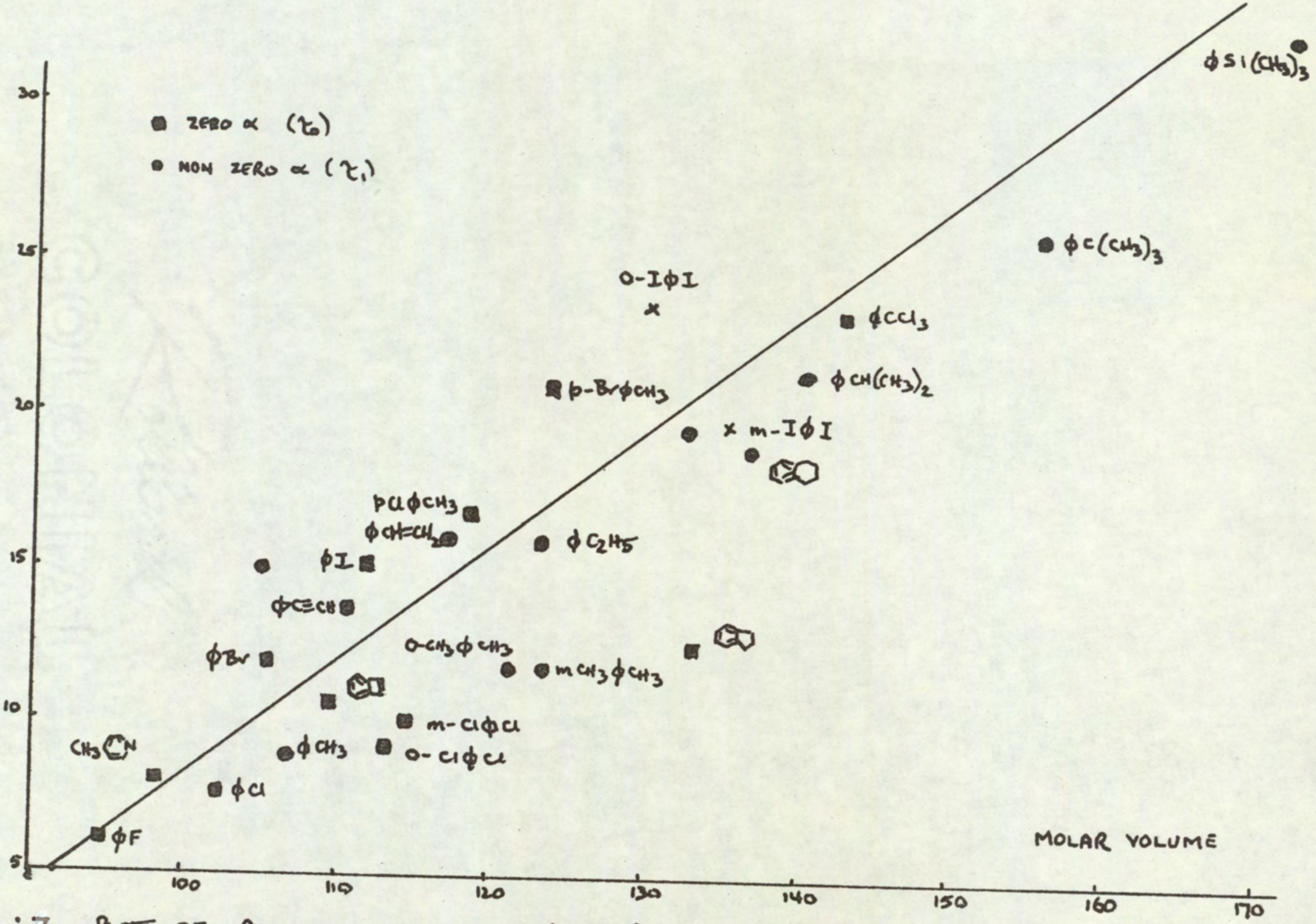


FIG 6:7 PLOT OF τ VS MOLAR VOLUME AT 25°C AS REPORTED BY CROSSLEY[16]

Within the accuracy of the two parameters a good correlation was observed for the majority of compounds examined. The slopes of the lines are approximately of the same magnitude as those obtained by Powles. although x (cf. equation 6:9) was not found to vary to any great extent with solvent viscosity as this author suggested. The slopes were similar for p-xylene at 15^oC (η = 0.68 c.p.s.) and cyclohexane at 25^oC (η = 0.9 c.p.s.), $x \approx 0.001$, while only a small increase was seen with a reduced p-xylene viscosity at 60^oC (η = 0.42 c.p.s.) $x = 0.004$. The plots are also at variance with Powles' theory in that the slopes do not pass through the origin. It is interesting to note that this also occurs with other correlations of τ against some molecular parameter, for example, volume(98). Eichhoff and Hufnagel(123) also observed this in plotting $\log_e \tau$ of nine compounds in several solvents against the effective radius (r_{eff}), calculated from the molecule's centre of mass to the periphery. The intercept on the $\log_e \tau$ axis at $r_{eff} = 0$ was attributed to the time interval between molecular collisons (τ_c), and they produced the following empirical equation

$$\tau = \tau_c \exp. ^{\sigma r_{eff}} \tag{6:15}$$

i.e. $$\log_e \tau = \sigma r_{eff} + \log_e \tau_c \tag{6:16}$$

where σ = a constant which was related to the Eyring rate expression, since $\tau_c \approx {}^h/kT$ (1.64×10^{-13} sec at 20^oC). The effective radius of the compounds examined here were determined (Table 6:2) and the results of similar plots are shown pictorially in Fig. 6:6. The slopes (σ)

and intercepts (τ_c) of these graphs are smaller and larger respectively than those obtained by Eichhoff and Hufnagel:

Solvent	Temperature	$\tau_c \times 10^{12}$ sec	$\sigma(\text{Å})^{-1}$	Source
p-xylene	15°C	1.28	0.62	This work
p-xylene	20°C	0.166	1.20	Hufnagel
p-xylene	60°C	0.70	0.58	This work
cyclohexane	20°C	0.087	1.32	Hufnagel
cyclohexane	25°C	1.22	0.59	This work

their slopes are also superimposed on the graphs in Fig.6:6 for comparison. The poor compatibility of the two results would appear to limit a quantitative approach to this relationship, yet for qualitative correlations, it may be useful.

In view of the various types of molecules examined the agreement between them in the τ vs $\sqrt{I}$ plots appears to be remarkably good, the exceptions being benzonitrile and the m-disubstituted iodobenzenes. Benzonitrile at 15°C exhibits an α of 0.06 in both cyclohexane and p-xylene solutions, unlike the m-substituted benzenes the moment of inertia about the two possible axes of rotation does not vary to any great extent and, therefore the increase in α cannot be accounted for by a distribution of varying molecular relaxation times. It has been suggested that the large τ and α, observed for this compound, are due to the formation of polar aggregates(29) and if this was the case a poor correlation between τ and I would be expected. In contrast to the o-substituted derivatives the m-substituted iodobenzenes fall consistently off the plots of both moment of inertia and effective radius. The behaviour of these compounds may, however, be explained by the qualitative use of the last parameter. Examination of Table 6:2 shows that m-bromo and m-diiodobenzene have a much shorter radius about their centre of masses than their ortho counterparts and, therefore, a shorter relaxation would be expected for these compounds, in comparison with the latter. Crossley's graph of molecular relaxation at 25^{0}C vs molar volume is presented in Fig. 6:7 and extrapolated τ values for the diiodobenzenes have been included. Here the meta compound is seen to fall closer to the plot than the ortho derivative, the actual significance of this is doubtful since both compounds are solids at 25^{0}C, the density and, therefore, the molar volume may contain appreciable errors. As the behaviour of the other meta and ortho compounds has not been adequately accounted for by a τ /volume relationship, it would seem unlikely that this would be the case for m-diiodobenzene, and rotation about the centre of mass is preferred.

The relaxation times of toluene and the two xylenes in cyclohexane are also seen to fall on the plots of $\sqrt{I}$ and r_{eff}, in contrast to that of the molar volume. This would seem to suggest that the lower τ_0s observed for these compounds in comparison with the equivalent chloro derivatives may be explained to some extent by relaxation about their centre of masses. The large difference in relaxation times of 2-bromonaphthalene and 2-iodonaphthalene may be explained by this relationship, too, as within the experimental limits they fall on the plots; although the τ of the 2-bromonaphthalene appears slightly short and the τ of the iodo derivative slightly long.

The advantage of plotting $\sqrt{I}$ against relaxation time in comparison to some other molecular factor is that the moment of inertia is calculated solely for the axes about which molecular rotation occurs. Although this factor may not be too important when considering small molecules, Cooke(97) in this laboratory has shown that for large compounds, such as rigid steroids, the relaxation time is very much dependent upon the direction of the resultant dipole moment, and, therefore, this method may be of some value in correlating the behaviour of this type of compound.

In order to see whether the relationship between I and τ could be used for predicting the molecular relaxation times of non-rigid compounds, the moments of inertia of $\omega\omega\omega$trifluoroacetophenone and p-bromoanisole were initially calculated. These compounds have high molecular weighting factors, $C_1 = 0.8 - 0.9$(1), and so the τ_0 could be used to describe the molecular process, thus avoiding any further errors which may be involved in a τ_1, τ_2 Budo analysis. Large assumptions, however, had to be made in the inertia calculations, the compounds were considered rigid, insofar that only three principle moments of inertia were determined, (thus, the inertia term of the rotating group was not considered) and the molecules were regarded as planar. In spite of these assumptions the acetyl and methoxy τ values were found to fall close to the plots well within the normal error limits. The centre of masses and the moments of inertia of acetophenone and anisole were then determined making the same assumptions, the relaxation times predicted for these values, taking into account the errors associated with each parameter, together with those obtained from the molar volume plot (Fig.6:7) are presented in Table 6:4. These τ values may then be

Solvent	P-xylene					Cyclohexane	
Temperature ^{o}C	15		25	60		25	
Method	$\sqrt{I}$	r_{eff}	V_m	$\sqrt{I}$	r_{eff}	$\sqrt{I}$	r_{eff}
Acetophenone	12.5-15.5	13.5-16	14.7	7-8.3	$\sim$6.8	12-15	12-13.5
Assigned τ_1 $C_1 = 0.55$	19.5		18.5	9.3		14.8	
Anisole	8.5-10.5	14-17	11.8	5-6	$\sim$7.0	7.5-9.5	12.5-14.0
Assigned τ_1 $C_1=0.25\pm0.1$	-		18.4	8.6		14.6	

ESTIMATIONS OFMOLECULAR RELAXATION TIMES (x 10^{12} sec) FOR ACETOPHENONE AND ANISOLE FROM PLOTS OF τ VS MOMENT OF INERTIA $\sqrt{I}$, EFFECTIVE RADIUS (r_{eff}) AND MOLAR VOLUMES (V_m)

TABLE 6:4.

compared with the assigned molecular relaxation times, although it should be pointed out that this comparison in anisole's case may not be very meaningful as a large error will exist in τ_1 with such a low weighting. The predicted relaxation times are slightly shorter than the assigned values. Fröhlich(114) has pointed out that theoretically the Debye viscosity relationship (equation 6:6) cannot be expected to hold quantitatively for axially unsymmetric molecules and this is most probably the reason for the low values obtained from the molar volume plot. The relaxation times obtained from the molecules maximum radius correlation are longer for anisole than acetophenone, owing to the centre of mass in the former being further away from its mobile group, having one carbon less than the latter. The discrepancy between the predicted and assigned relaxation times in the moment of inertia method could be due to the assumptions taken in the calculation. If a line is drawn between the ωωωtrifluoro acetophenone and p-bromoanisole points (as the calculation errors are the same for these compounds), τ values of 20 x 10^{-12} and 10.0 x 10^{-12} sec are obtained for acetophenone in p-xylene at 15^{0} and 60^{0}C, which are very close to the assigned relaxation times at these temperatures.

In conclusion, it has been seen that there is a correlation between τ and $\sqrt{I}$, and τ and r_{eff}, similar to that observed with molecular volume. Since none of these relationships strictly follow the accepted dielectric theory, it would be unwise to attempt to correlate the relaxation times of vastly different molecules by any of these methods. A comparison within a group type, bearing in mind the limitations, however, should be useful. Thus the principle of a molecule rotating around its centre of mass would seem to explain certain dielectric phenomena. The measurement of more accurate moments of inertia by microwave spectroscopy and an expanded examination of the dielectric data is required before any adjustments can be made to the existing dielectric theory. At this time, therefore, it would appear necessary to consider both the volume and the centre of mass of a molecule when qualitative comparisons of molecular relaxation times are made.

SUGGESTIONS FOR FUTURE WORK

From this work on dilute solutions, several basic points have emerged of which further investigations would be useful.

Increasing the temperature range to sub-zero temperatures, for example, may well decrease the errors involved in the energy barrier parameters and enable a greater distinction to be made by this technique between various molecular behaviour. Lowering the temperature should offer no difficulties with "Grant Cell" measurements, as the sample is completely enclosed, but the bridge determinations would require some form of dry atmosphere tent to prevent condensation polluting the sample. The only restriction in this type of measurement would lie in the individual compound's solubility at these low temperatures.

As has been seen, deductions of an intramolecular process are somewhat limited by the amount of dielectric information available on similar sized rigid molecules. Much scope is open for further research on rigid mono and multi substituted benzenes, naphthalenes, phenanthrenes and diphenyl compounds, not only to clarify intramolecular mechanisms, but also to assist in the understanding of the molecular processes as suggested in Chapter 6.

The viscous solution measurements of acetyl compounds with low molecular weighting factors, reported in Chapter 2, did not show the same behaviour as the analogous alkoxy compounds, yet employment of a sufficiently wide range of microwave frequencies was found to be a useful method for measuring the maximum relaxation time possible for the mobile group. In fact, practically this technique of increasing the τ_1/τ_2 ratio appears preferable to the measurement of very large molecules, since the latter are frequently difficult to synthesise and having a large molecular weight requires the compound to be in the liquid state or possess a very good solubility. Extension of the work described in this thesis for both these fields would be of value for defining limits for the acetyl and alkoxy relaxation processes as well as providing further knowledge of the effects of viscosity, mesomerism, etc. on dielectric behaviour.

The study of sterically hindered compounds gave some interesting results, further work in this area is obviously required and may be coupled with the examination of mobile groups which possess varying degrees of conjugation with the parent molecule. A particular example of this would be in the 2 and 2,6 substituted acetylcyclohex-1-ene systems although here again a dielectric study of rigid cyclic molecules is required. This area of research would be of further value as a direct correlation with other physico-chemical methods is possible.

The above are thought to be the most profitable regions for future research arising directly from this investigation, more specific suggestions may be found in the relevant chapters.

APPENDIX

TABLE A:1 τ_o AND α DATA FOR THE THEORETICAL COLE-COLE PLOTS OF THE DIELECTRIC ABSORPTION OF TWO RELAXATION PROCESSES τ_1 AND τ_2 WITH THE RESPECTIVE WEIGHT FACTORS C_1 AND C_2. (ALL RELAXATION TIMES IN THIS TABLE ARE GIVEN x 10^{12} SEC).

(A) τ_1 = 2.0: τ_2 = 10.0

C_1	C_2	τ_o	α
1.0	0.0	2.0	0.00
0.9	0.1	2.2	0.04
0.8	0.2	2.5	0.10
0.7	0.3	3.0	0.12
0.6	0.4	3.7	0.15
0.5	0.5	4.5	0.16
0.4	0.6	5.5	0.14
0.3	0.7	6.7	0.12
0.2	0.8	7.9	0.08

(B) τ_1 = 3.0: τ_2 = 10.0

C_1	C_2	τ_o	α
1.0	0.0	3.0	0.00
0.9	0.1	3.3	0.04
0.8	0.2	3.7	0.06
0.7	0.3	4.1	0.08
0.6	0.4	4.8	0.10
0.5	0.5	5.5	0.11
0.4	0.6	6.3	0.10
0.3	0.7	7.3	0.08
0.2	0.8	8.2	0.06

(C) τ_1 = 4.0: τ_2 = 10.0

C_1	C_2	τ_o	α
1.0	0.0	4.0	0.00
0.9	0.1	4.3	0.02
0.8	0.2	4.7	0.05
0.7	0.3	5.2	0.06
0.6	0.4	5.7	0.06
0.5	0.5	6.3	0.07
0.4	0.6	6.9	0.06
0.3	0.7	7.6	0.06
0.2	0.8	8.4	0.04

TABLE A:1 (continued)

C_1	C_2	τ_o	α	C_1	C_2	τ	α	C_1	C_2	τ_o	α
0.1	0.9	9.1	0.04	0.1	0.9	9.1	0.03	0.1	0.9	9.2	0.02
0.0	1.0	10.0	0.00	0.0	1.0	10.0	0.00	0.0	1.0	10.0	0.00

(D) $\tau_1 = 6.0$: $\tau_2 = 10.0$

C_1	C_2	τ_o	α
1.0	0.0	6.0	0.00
0.9	0.1	6.3	0.01
0.8	0.2	6.6	0.01
0.7	0.3	7.0	0.02
0.6	0.4	7.4	0.02
0.5	0.5	7.8	0.02
0.4	0.6	3.2	0.02
0.3	0.7	8.6	0.02
0.2	0.8	9.0	0.01
0.1	0.9	9.5	0.01
0.0	1.0	10.0	0.00

(E) $\tau_1 = 8.0$: $\tau_2 = 10.0$

C_1	C_2	τ_0	α
1.0	0.0	8.0	0.00
0.9	0.1	8.1	0.00
0.8	0.2	8.3	0.00
0.7	0.3	8.5	0.01
0.6	0.4	8.7	0.01
0.5	0.5	8.9	0.01
0.4	0.6	9.1	0.01
0.3	0.7	9.4	0.01
0.2	0.8	9.7	0.00
0.1	0.9	9.9	0.00
0.0	1.0	10.0	0.00

TABLE A:2 EXPERIMENTAL RESULTS.

The following tables contain the ε'(measured) and ε''(measured) values for each of the systems studied in the order in which they appear in the Results Tables given in Chapters 2-6.For systems which can be represented by a single relaxation time or where an analysis into two relaxation times is questionable the ε'(calculated) and ε''(calculated) values have been determined by using the Cole-Cole computer programme and are represented by †.The remaining unmarked calculated values have been determined by the Budo computer programme for the $\tau_1 \tau_2 c_1$ values reported.In viscous solutions and where separation of two relaxation times occur,the computer has not been used,<u>cf</u> relevant chapters for further discussion.

The Miscellaneous column contains the following parameters,identified by the bracketed number:

(1)Weight fraction (w_2) of solute (in the solvent mixtures values for both the solute and minor solvent are given),where no value occurs,w_2 is the same as for the preceding result.

(2) Static dielectric constant ε_0

(3) Dielectric constant at infinite frequency ε_∞

(4) Square of the refractive index at the sodium D line frequency (n_D^2)

(5) Density of the solution d_{12}

(6) Density of the solvent d_1

(7) Solvent dielectric constant ε_1

Solution	$T^{o}C$	Misc.	Freq. G.C/sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
p-fluoroacetophenone	15	(1) 0.04	35.11	2.068	0.0425	2.070	0.0421
		(2) 2.190	23.98	2.076	0.0516	2.084	0.0532
in cyclohexane		(3) 2.053	16.2	2.112	0.0616	2.104	0.0609
			9.313	2.139	0.600	2.135	0.0602
	25		35.11	2.054	0.0448	2.060	0.0448
		(2) 2.165	23.98	2.071	0.0536	2.076	0.0544
		(3) 2.039	16.20	2.104	0.0587	2.097	0.0591
			9.313	2.128	0.0547	2.126	0.0541
			6.7	2.141	0.0458	2.140	0.0465
	40	(1) 0.038	35.11	2.036	0.0445	2.037	0.0441
		(2) 2.121	23.98	2.045	0.0507	2.053	0.0515
		(3) 2.013	16.20	2.081	0.0529	2.073	0.0528
			9.313	2.098	0.0433	2.098	0.0433
			6.7	2.109	0.0347	2.108	0.0348

Solution	T°C	Misc.	Freq. G.C/sec.	ε' Measured	ε" Measured	ε' Calculated	ε " Calculated
	50		35.11	2.027	0.0439	2.021	0.0450
		(2) 2.098	23.98	2.032	0.0510	2.038	0.0507
		(3) 1.994	16.2	2.069	0.0499	2.058	0.0500
			9.313	2.083	0.0389	2.080	0.0393
			6.7	2.090	0.0323	2.088	0.0311
p-fluoroacetophenone	15	(1) 0.04	35.11	2.312	0.0436	2.315	0.0435
		(2) 2.472	23.98	2.323	0.0559	2.327	0.0581
in p-xylene		(3) 2.302	16.20	2.348	0.0749	2.348	0.0721
			9.313	2.390	0.0788	2.388	0.0802
			6.7	2.414	0.0760	2.412	0.0759
	25		35.11	2.294	0.0462	2.2981	0.0464
		(2) 2.442	23.98	2.315	0.0583	2.312	0.0604
		(3) 2.282	16.20	2.338	0.0754	2.335	0.0722
			9.313	2.379	0.0737	2.375	0.0751
			6.7	2.389	0.0686	2.396	0.0684

Solution	T^{o}C	Misc.	Freq. G.C/sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	40	(1) 0.038	35.11	2.270	0.0478	2.273	0.0474
		(2) 2.391	23.98	2.286	0.0564	2.289	0.0592
		(3) 2.253	16.20	2.319	0.0672	2.312	0.0665
			9.313	2.350	0.0635	2.347	0.0623
			6.7	2.362	0.0514	2.363	0.0534
	50		35.11	2.264	0.0477	2.258	0.0497
		(2) 2.367	23.98	2.279	0.0587	2.276	0.0602
		(3) 2.235	16.20	2.305	0.0673	2.300	0.0648
			9.313	2.333	0.0554	2.333	0.0566
			6.7	2.3400	0.0455	2.346	0.0467
	60	(1) 0.03804	35.11	2.242	0.0488	2.244	0.0497
		(2) 2.341	23.98	2.262	0.0603	2.263	0.0584
		(3) 2.218	16.2	2.290	0.0589	2.286	0.0602
			9.313	2.316	0.0498	2.314	0.0498
			6.7	2.324	0.0397	2.325	0.0402

Solution	T^oC	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
p-chloroacetophenone	15	(1) 0.04398	35.11	2.071	0.0358	2.071	0.0366
		(2) 2.188	23.98	2.084	0.0483	2.082	0.0473
in cyclohexane		(3) 2.058	16.20	2.103	0.0556	2.099	0.0565
			9.313	2.129	0.0595	2.130	0.0592
			6.7	2.146	0.0550	2.147	0.0547
	25	(1) 0.04395	70.0	2.056	0.0243	2.047	0.0217
		(2) 2.166	35.11	2.066	0.0383	2.058	0.0390
		(3) 2.043	23.98	2.074	0.0485	2.071	0.0493
			16.20	2.095	0.0563	2.090	0.0567
			9.313	2.118	0.0564	2.120	0.0558
			6.7	2.134	0.0511	2.135	0.0496
	40	(1) 0.044	70.00	2.024	0.0258	2.021	0.0245
		(2) 2.125	35.11	2.033	0.0403	2.035	0.0419
		(3) 2.015	23.98	2.050	0.0502	2.050	0.0503
			16.20	2.078	0.0541	2.070	0.0541
			9.313	2.096	0.0488	2.096	0.0483

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
p-chloroacetophenone	40	(1) 0.044	70	2.266	0.0253	2.262	0.0249
		(2) 2.399	35.11	2.270	0.0452	2.288	0.0584
in p-xylene		(3) 2.257	23.98	2.291	0.0576	2.311	0.0686
			16.20	2.317	0.070	2.349	0.0676
			9.313	2.350	0.0659	2.368	0.0587
p-bromoacetophenone	15	(1) 0.0431	70	2.051	0.0164	2.049	0.0145
		(2) 2.151	35.11	2.065	0.0267	2.056	0.0268
in cyclohexane		(3) 2.047	23.98	2.069	0.0330	2.063	0.0351
			16.20	2.082	0.0414	2.076	0.0429
			9.313	2.104	0.0470	2.099	0.0467
			6.7	2.118	0.0455	2.113	0.0445
	25		70	2.026	0.0182	2.036	0.0170
		(2) 2.135	35.11	2.046	0.0292	2.045	0.0306
		(3) 2.033	23.98	2.051	0.0386	2.055	0.0306
			9.313	2.096	0.0447	2.092	0.0443
			6.7	2.106	0.0415	2.104	0.0405

Solution	T°C	Misc.	Freq. G.C./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	40	(1) 0.04308	70	1.995	0.0184	2.01	0.0177
		(2) 2.097	35.11	2.012	0.0293	2.02	0.0308
		(3) 2.006	23.98	2.025	0.0379	2.031	0.0376
			16.2	2.058	0.0414	2.05	0.0414
			9.313	2.069	0.0384	2.065	0.0388
p-bromoacetophenone	15	(1) 0.04283	70	2.299	0.0167	2.3011	0.0158
		(2) 2.426	35.11	2.303	0.0289	2.307	0.0301
in p-xylene		(3) 2.299	23.98	2.314	0.0394	2.315	0.0406
			16.20	2.332	0.0539	2.329	0.0520
			9.313	2.357	0.0603	2.358	0.0610
	40	(1) 0.04231	70	2.256	0.018	2.255	0.0187
		(2) 2.358	35.11	2.270	0.0343	2.264	0.0341
		(3) 2.251	23.98	2.275	0.0417	2.274	0.0436
			16.20	2.293	0.0522	2.291	0.0511
			9.313	2.319	0.0503	2.319	0.0506
			6.7	2.337	0.0438	2.333	0.0443

Solution	T^{o}C	Misc.	Freq. G.C./sec.	ε' Measured	ε'' Measured	ε' Calculated	ε'' Calculated
p-iodoacetophenone	25	(1) 0.03482	70	2.032	0.0109	2.031	0.0100
		(2) 2.0940	35.11	2.036	0.0179	2.03	0.0181
in cyclohexane		(3) 2.0290	23.98	2.040	0.0222	2.041	0.0232
			16.20	2.058	0.0271	2.050	0.0272
			9.313	2.064	0.0282	2.064	0.0278
	40		35.11	2.018	0.0193	2.016	0.0194
		(2) 2.065	23.98	2.024	0.0236	2.023	0.0236
		(3) 2.007	16.20	2.038	0.0272	2.031	0.0256
			9.313	2.043	0.0238	2.044	0.0239
			1.9	2.060	0.0112	2.062	0.0098
p-iodoacetophenone	15	(1) 0.03490	70	2.305	0.0139	2.301	0.0118
		(2) 2.390	35.11	2.304	0.022	2.306	0.022
in p-xylene		(3) 2.299	23.98	2.312	0.0267	2.312	0.0294
		(4) 2.255	16.2	2.326	0.0381	2.322	0.0366
			9.313	2.341	0.0409	2.342	0.0410

Solution	T°C	Misc.	Freq. G.c./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	25		70	2.297	0.0146	2.286	0.0124
		(2) 2.369	35.11	2.289	0.0213	2.292	0.0229
		(3) 2.284	23.98	2.297	0.0283	2.298	0.0301
		(4) 2.240	16.2	2.310	0.0378	2.309	0.0364
			9.313	2.326	0.0388	2.329	0.0390
	40		70	2.267	0.0147	2.259	0.0137
		(2) 2.332	35.11	2.267	0.0247	2.266	0.0244
		(3) 2.256	23.98	2.277	0.0299	2.274	0.0308
		(4) 2.214	9.313	2.302	0.0351	2.304	0.0343
	50		35.11	2.248	0.0235	2.243	0.0244
		(2) 2.302	23.98	2.251	0.0287	2.251	0.0295
		(3) 2.234	16.2	2.267	0.0339	2.263	0.0337
			9.313	2.285	0.0323	2.281	0.0318

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
p-methylacetophenone	25	(1) 0.01993	35.11	2.0451	0.0326	2.043	0.0337
		(2) 2.153	23.98	2.054	0.0425	2.053	0.0423
in cyclohexane		(3) 2.029	16.2	2.071	0.0491	2.068	0.0493
			9.313	2.090	0.0539	2.092	0.0534
			6.7	2.110	0.0515	2.107	0.0520
	50		35.11	2.0106	0.0365	2.008	0.0374
		(2) 2.097	23.98	2.0251	0.0442	2.021	0.0437
		(3) 1.987	16.2	2.0407	0.0479	2.036	0.0475
			9.313	2.0521	0.0466	2.059	0.0465
p-methylacetophenone	25	(1) 0.02021	70	2.269	0.0195	2.277	0.0210
		(2) 2.429	35.11	2.291	0.0378	2.286	0.0380
in p-xylene		(3) 2.273	23.98	2.293	0.0491	2.297	0.0494
		(4) 2.231	16.2	2.321	0.0607	2.314	0.0600
			9.313	2.345	0.0680	2.344	0.0684
			6.7	2.366	0.0678	2.364	0.0682

Solution	$T^{o}C$	Misc.	Freq. G.C./sec.	ε' Measured	ε'' Measured	ε' Calculated	ε'' Calculated
	50		70	2.237	0.0242	2.239	0.0239
		(2) 2.367	35.11	2.255	0.0412	2.252	0.0416
		(3) 2.234	23.98	2.272	0.0514	2.265	0.0518
			16.2	2.287	0.0594	2.284	0.0593
			9.313	2.312	0.0611	2.315	0.0602
p-ethylacetophenone	25	(1) 0.02034	70	2.031	0.0170	2.030	0.0159
		(2) 2.1465	35.11	2.041	0.0257	2.038	0.0277
in cyclohexane		(3) 2.027	23.98	2.046	0.0346	2.046	0.0349
			16.2	2.062	0.0422	2.057	0.0415
			9.313	2.075	0.0485	2.076	0.0486
			6.7	2.094	0.0503	2.090	0.0507
	50	(2) 2.091	70	1.993	0.0187	1.992	0.0187
		(3) 1.987	35.11	2.005	0.0295	2.003	0.0307
			23.98	2.016	0.0370	2.012	0.0367
			16.2	2.029	0.0419	2.024	0.0412
			9.313	2.039	0.0438	2.044	0.0439

Solution	T°C	Misc.	Freq. G.C./sec.	Measured	Measured	Calculated	Calculated
p-ethylacetophenone	25	(1) 0.01999	70	2.285	0.0172	2.277	0.0162
		(2) 2.417	35.11	2.280	0.0288	2.284	0.0297
in p-xylene		(3) 2.275	23.98	2.291	0.0388	2.292	0.0392
		(4) 2.232	16.2	2.309	0.0490	2.304	0.0489
			9.313	2.326	0.0601	2.328	0.0597
			6.7	2.349	0.0625	2.346	0.0628
	50		70	2.239	0.0189	2.237	0.0190
		(2) 2.355	35.11	2.249	0.0328	2.246	0.0337
		(3) 2.33	23.98	2.263	0.0438	2.256	0.0428
			16.2	2.270	0.0511	2.271	0.0508
			9.313	2.296	0.0551	2.298	0.0556
			6.7	2.313	0.0538	2.314	0.0530
2-acetonaphthone	25	(1) 0.02093	70	2.032	0.0105	2.033	0.0086
		(2) 2.127	35.11	2.041	0.0162	2.036	0.0163
in cyclohexane		(3) 2.032	23.98	2.041	0.0210	2.04	0.0222
			16.2	2.051	0.0289	2.046	0.0291
			6.7	2.068	0.0427	2.071	0.0419

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	40		35.11	2.014	0.0180	2.014	0.0180
		(2) 2.095	23.98	2.021	0.024	2.018	0.0243
		(3) 2.009	16.2	2.031	0.0325	2.026	0.0316
			9.313	2.038	0.0398	2.043	0.0399
			6.7	2.050	0.0414	2.055	0.0412
2-acetonapthone	15	(1) 0.02496	70	2.302	0.0142	2.299	0.0113
		(2) 2.450	35.11	2.303	0.0212	2.303	0.0217
in p-xylene		(3) 2.298	23.98	2.308	0.0277	2.307	0.0300
			16.2	2.319	0.0409	2.315	0.0403
			9.313	2.334	0.0562	2.333	0.0554
			6.7	2.347	0.0630	2.349	0.0634
	25		70	2.278	0.0121	2.285	0.0113
		(2) 2.424	35.11	2.294	0.0226	2.289	0.0218
		(3) 2.284	23.98	2.295	0.0300	2.293	0.0305
			16.2	2.303	0.0399	2.301	0.0413
			9.313	2.322	0.0581	2.321	0.0568
			6.7	2.337	0.0634	2.338	0.0635

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	50		35.11	2.245	0.0255	2.246	0.0261
		(2) 2.360	23.98	2.253	0.0357	2.253	0.0354
		(3) 2.239	16.2	2.268	0.0456	2.264	0.0455
			9.313	2.286	0.0561	2.288	0.0561
1-Acetylcyclohexene	15	(1) 0.0175	35.11	2.302	0.0409	2.303	0.0406
		(2) 2.4462	23.98	2.316	0.0516	2.315	0.0537
in p-xylene		(3) 2.290	16.2	2.344	0.0678	2.335	0.0657
		(4) 2.245	9.313	2.367	0.0706	2.371	0.0705
			6.7	2.390	0.0657	2.391	0.0655
	32.5		70	2.274	0.0261	2.265	0.0248
		(2) 2.404	35.11	2.268	0.0441	2.276	0.0443
		(3) 2.260	23.98	2.291	0.0551	2.292	0.056
		(4) 2.219	16.2	2.320	0.0636	2.314	0.064
			9.313	2.348	0.0619	2.347	0.0618
			6.7	2.367	0.0554	2.363	0.0549

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	50		35.11	2.245	0.0463	2.2510	0.0465
		(2) 2.355	23.98	2.266	0.0549	2.268	0.0562
		(3) 2.229	16.2	2.300	0.0621	2.290	0.0603
		(4) 2.192	9.313	2.316	0.0520	2.320	0.0534
			6.7	2.333	0.0454	2.332	0.0451
Trans 4-Phenyl-3-Buten-2-one	15	(1) 0.02063	35.11	2.306	0.0265	2.303	0.0268
		(2) 2.458	23.98	2.309	0.0355	2.309	0.0370
		(3) 2.297	16.2	2.324	0.0510	2.320	0.0489
in p-xylene		(4) 2.256	9.313	2.343	0.0614	2.346	0.0624
			6.7	2.366	0.0661	2.364	0.0658
	60		35.11	2.231	0.0336	2.230	0.0346
		(2) 2.342	23.98	2.244	0.0444	2.2410	0.0440
		(3) 2.217	16.2	2.262	0.0515	2.257	0.0515
		(4) 2.182	9.313	2.282	0.0546	2.283	0.0545

Solution	T^{o}C	Misc.	Freq. G.C./sec.	ε' Measured	ε'' Measured	ε' Calculated	ε'' Calculated
2-acetylphenthrene	60	(1) 0.03001	35.11	2.226	0.0170	2.227	0.0191
		(2) 2.337	23.98	2.236	0.0283	2.232	0.0256
in p-xylene		(3) 2.222	16.2	2.240	0.0317	2.239	0.033
		(4) 2.192	9.313	2.250	0.0436	2.254	0.0433
			6.7	2.269	0.0485	2.266	0.0486
3-acetylphenanthrene	25	(1) 0.03724	35.11	2.298	0.0167	2.295	0.0182
		(2) 2.454	23.98	2.300	0.0241	2.299	0.0254
in p-xylene		(3) 2.292	16.2	2.306	0.0334	2.304	0.0346
		(4) 2.249	9.313	2.313	0.0486	2.318	0.0497
			6.7	2.327	0.0600	2.331	0.0593
			1.9	2.407	0.0592	2.410	0.0679
			0.95	2.435	0.0472	2.440	0.0440
9-acetylphenanthrene	15	(1) 0.03682	70	2.317	0.0188		
		(2) 2.469	35.11	2.331	0.0265		
in p-xylene		(3) 2.323	23.98	2.335	0.0313		
		(4) 2.262	16.2	2.345	0.0362		
			9.313	2.351	0.0415		

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
			2.455	2.408	0.0649		
			2.1	2.418	0.0621		
			1.9	2.418	0.0620		
			1.8	2.426	0.0608		
			1.4	2.434	0.0539		
			1.3	2.441	0.0526		
			1.0	2.446	0.0460		
	25		70	2.305	0.0188		
		(2) 2.441	35.11	2.311	0.0262		
		(3) 2.306	23.98	2.322	0.0309		
		(4) 2.247	16.20	2.328	0.0362		
			9.813	2.335	0.0418		
			6.7	2.346	0.0474		
			1.9	2.403	0.0474		
			1.4	2.415	0.0424		
			1.0	2.426	0.0247		

Solution	T^{o}C	Misc.	Freq. G.C/sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	50		70	2.256	0.0201		
		(2) 2.380	35.11	2.276	0.0290		
		(3) 2.259	23.98	2.284	0.0335		
		(4) 2.209	16.2	2.288	0.0375		
			9.313	2.303	0.0424		
			2.455	2.360	0.0451		
			2.1	2.363	0.0428		
			1.9	2.366	0.0411		
			1.3	2.371	0.0298		
Acetophenone		(1) 0.02864	16.2	2.231	0.0387		
in		(2) 2.404	9.313	2.245	0.0473		
nujol		(3) 2.2	6.7	2.245	0.0531		
		(4) 2.193	2.455	2.310	0.0690		
		(6) 0.8787	2.1	2.316	0.0701		
		(7) 2.186	1.9	2.323	0.0705		
			1.5	2.336	0.0694		
			1.0	2.357	0.0604		
			0.85	2.362	0.0577		

Solution	T^oC	misc.	Freq. G.C/sec.	ε' Measured	ε'' Measured	ε' Calculated	ε'' Calculated
4-acetylpyridine	25	(1)$W_2$0.02612	16.20	2.221	0.0291		
in		$W_3$0.08073	9.313	2.234	0.0358		
nujol		(2) 2.326	6.7	2.293	0.0414		
and p-xylene (W_3)		(3) 2.209	2.455	2.285	0.0453		
		(4) 2.195	2.1	2.291	0.0437		
		(5) 0.8810	1.8	2.294	0.0409		
		(6) 0.8769	1.4	2.299	0.0365		
		(7) 2.191	1.0	2.307	0.0304		
			0.85	2.309	0.0279		
p-bromoacetophenone	25	(1) 0.04175	16.2	2.198	0.0136		
		W_3=0.09803	2.455	2.227	0.0392		
in nujol		(2) 2.293	1.9	2.236	0.0424		
and cyclohexane (W_3)		(3) 2.189	1.3	2.247	0.0426		
		(4) 2.180	0.95	2.258	0.0413		
		(5) 0.8816					
		(6) 0.8673					
		(7) 2.165					

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
p-bromoacetophenone		(1) 0.04182	16.2	2.210	0.0128		
		(2) 2.317	9.313	2.212	0.0174		
in nujol		(3) 2.204	2.455	2.235	0.0345		
		(4) 2.197	1.9	2.240	0.0365		
		(5) 0.8937	1.3	2.245	0.0397		
		(6) 0.8787					
		(7) 2.186					
3-acetylphenanthrene		(1) 0.03168	16.2	2.232	0.0094		
		W_3=0.2750	9.313	2.232	0.0163		
in nujol		(2) 2.363	6.7	2.234	0.0200		
		(3) 2.227	2.455	2.248	0.0414		
and p-xylene (W_3)		(4) 2.214	1.9	2.257	0.0481		
		(6) 0.8727	1.4	2.266	0.0532		
		(7) 2.200	1.0	2.283	0.0580		

Solution	T°C	Misc.	Freq. G.C./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
2-chloroacetophenone	15	(1) 0.01652	70	2.306	0.0217	2.301 †	0.0212
		(2) 2.398	35.11	2.318	0.0354	2.312	0.0344
in p-xylene		(3) 2.293	23.98	2.328	0.0407	2.324	0.0415
			16.2	2.344	0.0457	2.339	0.0459
			9.313	2.359	0.0437	2.362	0.0438
			6.7	2.371	0.0415	2.374	0.0385
	25		70	2.285	0.0208	2.285 †	0.0210
		(2)2.376	35.11	2.310	0.0362	2.297	0.0342
		(3)2.278	23.98	2.314	0.0403	2.309	0.0410
		(4)2.244	16.2	2.331	0.0432	2.324	0.0445
			9.313	2.342	0.0409	2.346	0.0407
			6.7	2.353	0.0385	2.356	0.0348
	40		35.11	2.284	0.0356	2.274 †	0.0339
		(2)2.344	23.98	2.292	0.0384	2.287	0.0398
		(3)2.256	16.2	2.308	0.0409	2.302	0.0417
			9.313	2.322	0.0372	2.322	0.0355
			6.7	2.330	0.0310	2.330	0.0292

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
2,5 dichloroacetophenone		(1) 0.02424	70	2.303	0.0212	2.301 †	0.0193
	15	(2) 2.387	35.11	2.316	0.0297	2.312	0.0306
in p-xylene		(3) 2.295	23.98	2.325	0.0365	2.322	0.0366
			16.2	2.338	0.0403	2.335	0.0401
			9.313	2.349	0.0392	2.355	0.0381
			6.7	2.359	0.0342	2.364	0.0336
	25						
		(2) 2.366	70	2.289	0.0197	2.287 †	0.0198
		(3) 2.280	35.11	2.301	0.0313	2.301	0.0315
		(4) 2.245	23.98	2.313	0.0370	2.310	0.0366
			16.2	2.324	0.0386	2.324	0.0386
			9.313	2.335	0.0341	2.340	0.0346
			6.7	2.343	0.0311	2.349	0.0295

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	40		70	2.264	0.0231	2.261 †	0.0215
		(2) 2.333	35.11	2.284	0.0322	2.274	0.0328
		(3) 2.252	23.98	2.292	0.0356	2.286	0.0367
			16.2	2.304	0.0351	2.300	0.0365
			9.313	2.314	0.0312	2.316	0.0296
			6.7	2.325	0.0267	2.322	0.0240
	50		70	2.273	0.0236	2.243 †	0.0222
		(2) 2.310	35.11	2.273	0.0323	2.259	0.0334
		(3) 2.235	23.98	2.280	0.0347	2.271	0.0361
			16.2	2.287	0.0337	2.285	0.0341
			9.313	2.297	0.0284	2.298	0.0256
2,4,6 trimethyl	25	(1) 0.01952	70	2.282	0.0072	2.277 †	0.0068
		(2) 2.365	35.11	2.281	0.0145	2.278	0.0133
acetophenone in		(3) 2.276	23.98	2.285	0.0192	2.281	0.0189
		(4) 2.230	16.2	2.284	0.0258	2.285	0.0266
p-xylene			9.313	2.293	0.0390	2.298	0.0385
			6.7	2.307	0.0437	2.311	0.0435

Solution	T^{o}C	Misc.	Freq. G.C./sec.	ε' Measured	ε" Measured	ε- Calculated	ε" Calculated
	50		70	2.230	0.0089	2.229 †	0.0088
		(2) 2.314	35.11	2.238	0.0163	2.232	0.0160
		(3) 2.227	23.98	2.238	0.0222	2.235	0.0223
		(4) 2.194	16.2	2.248	0.0313	2.243	0.0305
			9.313	2.258	0.0388	2.257	0.0384
			6.7	2.270	0.0396	2.270	0.0395
9-acetylanthracene in p-xylene	25	(1) 0.02924	35.11	2.288	0.0099	2.280 †	0.0103
		(2) 2.386	23.98	2.286	0.0140	2.282	0.0144
		(3) 2.278	16.2	2.295	0.0228	2.284	0.0201
		(4) 2.245	9.313	2.295	0.0316	2.292	0.0307
			6.7	2.303	0.0380	2.300	0.0378
			0.95	2.374	0.0357	2.372	0.0315
	50		35.11	2.245	0.0123	2.246 †	0.0121
		(2) 2.334	23.98	2.249	0.0158	2.248	0.0171
		(3) 2.244	16.2	2.257	0.0261	2.2520	0.024
		(4) 2.207	9.313	2.261	0.0343	2.263	0.0354
			6.7	2.271	0.0412	2.274	0.0411

Solution	T°C	Misc.	Freq. G.C./sec.	ε' Measured	ε'' Measured	ε' Calculated	ε'' Calculated
2-fluoroanisole	25	(1) 0.024	35.11	2.297	0.0361	2.294 †	0.0358
		(2) 2.381	23.98	2.310	0.0435	2.306	0.0440
in p-xylene		(3) 2.277	16.2	2.328	0.0498	2.323	0.0489
		(4) 2.229	9.313	2.337	0.0452	2.348	0.0453
			6.7	2.357	0.0389	2.360	0.0387
	50		70	2.231	0.0271	2.237 †	0.0248
		(2) 2.318	35.11	2.257	0.0359	2.253	0.0381
		(3) 2.228	23.98	2.272	0.0415	2.267	0.0424
		(4) 2.196	16.2	2.289	0.0433	2.283	0.0415
			9.313	2.303	0.0326	2.301	0.0327
			6.7	2.308	0.0271	2.308	0.0261
2-bromoanisole	15	(1) 0.03184	70	2.279	0.0122	2.293	0.0123
		(2) 2.408	35.11	2.301	0.0231	2.297	0.0234
in p-xylene		(3) 2.291	23.98	2.306	0.0318	2.303	0.0322
		(4) 2.251	16.2	2.317	0.0432	2.313	0.0427
			9.313	2.335	0.0541	2.336	0.0545
			6.7	2.355	0.0557	2.354	0.0559

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	50		70.00	2.224	0.0157	2.232	† 0.0150
		(2)2.325	35.11	2.241	0.0285	2.239	0.0279
		(3)2.229	23.98	2.254	0.0367	2.247	0.0368
		(4)2.196	16.20	2.269	0.0459	2.261	0.0447
			9.313	2.291	0.0460	2.287	0.0466
			6.70	2.304	0.415	2.301	0.0415
2-iodoanisole	15	(1)0.03867	35.11	2.294	0.0163	2.297	0.0176
		(2)2.395	23.98	2.298	0.0240	2.300	0.0245
in p-xylene		(3)2.292	16.20	2.3130	0.0359	2.307	0.0332
		(4)2.251	9.313	2.322	0.0439	2.324	0.0451
			6.700	2.338	0.0486	2.339	0.0487
	50		70.00	2.238	0.0105	2.235	0.0112
		(2)2.318	35.11	2.238	0.0209	2.239	0.0212
		(3)2.233	23.98	2.247	0.0300	2.245	0.0288

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
		(4) 2.199	16.20	2.260	0.0382	2.255	† 0.0368
			9.313	2.273	0.0413	2.277	0.0422
			6.700	2.290	0.0398	2.290	0.0398
2,4,6-tri- bromoanisole in p-xylene	25	(1) 0.10482	35.11	2.299	0.0096	2.292	0.0086
		(2) 2.356	23.98	2.293	0.0130	2.293	0.0122
		(3) 2.290	16.20	2.299	0.0165	2.296	0.0172
		(4) 2.249	9.313	2.300	0.0259	2.304	0.0256
			6.700	2.306	0.0299	2.312	0.0300
	50		70.00	2.243	0.0065	2.248	† 0.0059
		(2) 2.305	35.22	2.253	0.0114	2.250	0.0113
		(3) 2.247	23.98	2.253	0.0155	2.253	0.0156
		(4) 2.210	16.20	2.264	0.0205	2.257	0.0209
			9.313	2.265	0.0276	2.269	0.0271

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
2,6-dimethyl-	25	(1) 0.05144	35.11	2.285	0.0125	2.275	† 0.0120
anisole		(2) 2.329	23.98	2.284	0.0170	2.278	0.0166
in p-xylene		(3) 2.273	16.20	2.284	0.0214	2.283	0.0221
		(4) 2.231	9.313	2.295	0.0283	2.296	0.0278
			6.70	2.303	0.0294	2.305	0.0280
	50		70.00	2.225	0.0066	2.229	† 0.0076
		(2) 2.277	35.11	2.237	0.0137	2.232	0.0142
		(3) 2.227	23.98	2.243	0.0191	2.236	0.0188
		(4) 2.193	16.20	2.251	0.0237	2.243	0.0230
			9.313	2.251	0.0253	2.256	0.0242
phenetole	25	(1) 0.10025	70.00	2.305	0.0270	2.299	0.0273
		(2) 2.429	35.11	2.310	0.0447	2.313	0.049
in p-xylene		(3) 2.290	23.98	2.323	0.0557	2.328	0.0547
		(4) 2.234	16.20	2.349	0.0617	2.349	0.0612

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calcualated
			9.313	2.373	0.0575	2.380	0.0590
			6.700	2.393	0.0518	2.395	0.0521
2-ethoxy-naphthalene in p-xylene	25	(1) 0.100	35.11	2.305	0.0188	2.308	0.0193
		(2) 2.397	23.98	2.311	0.0250	2.313	0.0248
		(3) 2.298	16.20	2.324	0.0315	2.320	0.0309
		(4) 2.259	9.313	2.335	0.0374	2.336	0.0377
			6.700	2.347	0.0390	2.347	0.0392
2-bromophenetole	15	(1) 0.04695	70.00	2.314	0.0165	2.301	+ 0.0146
		(2) 2.466	35.11	2.305	0.0288	2.305	0.0276
		(3) 2.298	23.98	2.309	0.0395	2.310	0.0384
		(4) 2.252	16.20	2.328	0.0525	2.321	0.0522
			9.313	2.348	0.0713	2.348	0.0718
			6.70	2.367	0.0799	2.370	0.0785

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	25		35.11	2.287	0.0288	2.286	† 0.0305
		(2) 2.433	23.98	2.295	0.0423	2.293	0.0418
		(3) 2.280	16.20	2.309	0.0573	2.306	0.0552
		(4) 2.236	9.313	2.333	0.0706	2.336	0.0708
			6.70	2.352	0.0726	2.359	0.0734
	37.5		23.98	2.278	0.0437	2.277	† 0.0430
		(2) 2.400	16.20	2.295	0.0561	2.291	0.0564
		(3) 2.262	9.313	2.315	0.0680	2.324	0.0687
			6.70	2.339	0.0685	2.346	0.0674
			1.90	2.393	0.0286	2.393	0.0298
			1.30	2.390	0.0204	2.397	0.0209
			0.95	2.389	0.0150	2.398	0.0154
	50		70.00	2.243	0.0196	2.238	† 0.0185
		(2) 2.365	23.98	2.266	0.0474	2.255	0.0466

			Freq.	ε'	ε''	ε'	ε''
Solution	T°C	Misc.	G.c./sec	Measured	Measured	Calculated	Calculated
		(3) 2.235	16.20	2.280	0.0589	2.272	0.0584
		(4) 2.212	9.313	2.304	0.0639	2.306	0.0645
			6.70	2.325	0.0613	2.326	0.0594
Cholesteryl-	25	(1) 0.21563	35.11	2.080	0.0142		
methylether		(2)(i) 2.159	23.98	2.085	0.0151		
in cyclohexane		(ii) 2.105	16.20	2.096	0.0151		
		(3)(i) 2.105	9.313	2.094	0.0143		
		(ii) 2.072	6.70	2.102	0.0137		
		(4) 2.068	2.455	2.111	0.0191		
		(5) 0.7842	1.90	2.115	0.0207		
			1.50	2.116	0.0210		
			1.10	2.119	0.0217		
			0.87	2.120	0.0226		

			Freq.	ε'	ε"	ε'	ε"
Solution	T°C	Misc.	G.c./sec	Measured	Measured	Calculated	Calculated
Cholesteryl-	25	(1) 0.24807	35.11	2.292	0.0198		
methyl ether		(2)(i)2.403	23.98	2.307	0.0239		
in p-xylene		(ii)2.327	16.20	2.311	0.0255		
		(3)(i)2.327	9.313	2.316	0.0239		
		(ii)2.276	2.455	2.335	0.0292		
		(4) 2.241	1.90	2.339	0.0308		
		(5) 0.8845	1.30	2.348	0.0334		
			0.87	2.354	0.0348		
Benzaldehyde	15	(1) 0.01999	70.00	2.056	0.0373	2.058	0.0372
		(2) 2.192	34.86	2.077	0.0566	2.081	0.0571
in cyclohexane		(3) 2.048	23.98	2.094	0.0651	2.101	0.0648
			16.20	2.130	0.0662	2.124	0.0673
			9.313	2.159	0.0590	2.157	0.0587
			6.70	2.177	0.0485	2.171	0.0487

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	25		34.86	2.061	0.0568	2.065	0.0576
		(2) 2.167	23.98	2.073	0.0645	2.085	0.0644
		(3) 2.028	16.20	2.121	0.0646	2.109	0.0648
			93.31	2.141	0.0524	2.139	0.0535
			6.70	2.150	0.0436	2.150	0.0433
	40		70.00	2.013	0.0396	2.019	0.0404
		(2) 2.132	34.86	2.046	0.0580	2.047	0.0589
		(3) 2.003	23.98	2.071	0.0630	2.069	0.0623
			16.20	2.098	0.0575	2.091	0.0580
			9.313	2.117	0.0406	2.114	0.0430
			6.70	2.122	0.0358	2.122	0.0333
Benzaldehyde in	15	(1) 0.018	70.00	2.304	0.0296	2.297	† 0.0276
		(2) 2.449	23.98	2.323	0.0598	2.326	0.0609
p-xylene		(3) 2.290	16.20	2.354	0.0712	2.349	0.0712
			9.313	2.391	0.0715	2.387	0.0720

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
		(3) 2.235	16.20	2.280	0.0589	2.272	0.0584
		(4) 2.212	9.313	2.304	0.0639	2.306	0.0645
			6.70	2.325	0.0613	2.326	0.0594
Cholesteryl-	25	(1) 0.21563	35.11	2.080	0.0142		
methylether		(2)(i) 2.159	23.98	2.085	0.0151		
in cyclohexane		(ii) 2.105	16.20	2.096	0.0151		
		(3)(i) 2.105	9.313	2.094	0.0143		
		(ii) 2.072	6.70	2.102	0.0137		
		(4) 2.068	2.455	2.111	0.0191		
		(5) 0.7842	1.90	2.115	0.0207		
			1.50	2.116	0.0210		
			1.10	2.119	0.0217		
			0.87	2.120	0.0226		

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
Cholesteryl-	25	(1) 0.24807	35.11	2.292	0.0198		
methyl ether		(2)(i)2.403	23.98	2.307	0.0239		
in p-xylene		(ii)2.327	16.20	2.311	0.0255		
		(3)(i)2.327	9.313	2.316	0.0239		
		(ii)2.276	2.455	2.335	0.0292		
		(4) 2.241	1.90	2.339	0.0308		
		(5) 0.8845	1.30	2.348	0.0334		
			0.87	2.354	0.0348		
Benzaldehyde	15	(1) 0.01999	70.00	2.056	0.0373	2.058	0.0372
		(2) 2.192	34.86	2.077	0.0566	2.081	0.0571
in cyclohexane		(3) 2.048	23.98	2.094	0.0651	2.101	0.0648
			16.20	2.130	0.0662	2.124	0.0673
			9.313	2.159	0.0590	2.157	0.0587
			6.70	2.177	0.0485	2.171	0.0487

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	25		34.86	2.061	0.0568	2.065	0.0576
		(2) 2.167	23.98	2.073	0.0645	2.085	0.0644
		(3) 2.028	16.20	2.121	0.0646	2.109	0.0648
			93.31	2.141	0.0524	2.139	0.0535
			6.70	2.150	0.0436	2.150	0.0433
	40		70.00	2.013	0.0396	2.019	0.0404
		(2) 2.132	34.86	2.046	0.0580	2.047	0.0589
		(3) 2.003	23.98	2.071	0.0630	2.069	0.0623
			16.20	2.098	0.0575	2.091	0.0580
			9.313	2.117	0.0406	2.114	0.0430
			6.70	2.122	0.0358	2.122	0.0333
Benzaldehyde in	15	(1) 0.018	70.00	2.304	0.0296	2.297	† 0.0276
		(2) 2.449	23.98	2.323	0.0598	2.326	0.0609
p-xylene		(3) 2.290	16.20	2.354	0.0712	2.349	0.0712
			9.313	2.391	0.0715	2.387	0.0720

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
			6.70	2.408	0.0667	2.407	0.0645
	25		70.00	2.294	0.0343	2.288	† 0.0324
		(2) 2.447	34.86	2.306	0.0554	2.306	0.0556
		(3) 2.279	23.98	2.316	0.0674	2.324	0.0686
			16.20	2.346	0.0773	2.350	0.0775
			9.313	2.399	0.0755	2.390	0.0740
			6.70	2.409	0.0632	2.410	0.0643
	40		70.00	2.259	0.0341	2.262	† 0.0344
		(2) 2.407	34.86	2.281	0.0580	2.282	0.0596
		(3) 2.253	23.98	2.306	0.0754	2.303	0.0718
			16.20	2.325	0.0743	2.332	0.0768
			9.313	2.369	0.0661	2.370	0.0657
			6.70	2.379	0.0527	2.386	0.0535

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	60		70.00	2.230	0.0391	2.227	†0.0385
		(2) 2.355	34.86	2.258	0.0606	2.252	0.0610
		(3) 2.214	23.98	2.272	0.0682	2.275	0.0684
			16.20	2.304	0.0681	2.301	0.0671
			9.313	2.331	0.0519	2.330	0.0523
			6.70	2.338	0.0420	2.341	0.0413
Crotonaldehyde	15	(1) 0.0070	70.00	2.048	0.0257	2.050	†0.0277
		(2) 2.138	35.11	2.064	0.0374	2.068	0.0384
in cyclohexane		(3) 2.038	23.98	2.078	0.0412	2.081	0.0414
		(4) 2.030	9.313	2.111	0.0372	2.113	0.0373
			6.70	2.123	0.0279	2.123	0.0317
	40		70.00	2.010	0.0263	2.014	† 0.0256
		(2) 2.083	35.11	2.030	0.0359	2.031	0.0361

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
		(3) 2.001	23.98	2.043	0.0377	2.045	0.0377
		(4) 2.000	9.313	2.067	0.0258	2.071	0.0259
			6.700	2.074	0.0185	2.076	0.0203
Crotonaldehyde in	15	(1) 0.00696	35.11	2.312	0.0371	2.310	† 0.0371
		(2) 2.417	23.98	2.316	0.0473	2.321	0.0483
p-xylene		(3) 2.296	16.20	2.345	0.0590	2.340	0.0575
		(4) 2.243	9.313	2.370	0.0576	2.373	0.0577
			6.70	2.388	0.0500	2.389	0.0504
	50		70.00	2.245	0.0270	2.239	† 0.0253
		(2) 2.331	35.11	2.257	0.0410	2.255	0.0404
		(3) 2.231	23.98	2.275	0.0471	2.270	0.0464
		(4) 2.192	16.20	2.296	0.0466	2.288	0.0471
			9.313	2.308	0.0380	2.310	0.0385
			6.70	2.317	0.0321	2.318	0.0311

Solution	T°C	Misc.	Freq. G.c./sed	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
2-Naphthaldehyde	15	(1) 0.01831	70.00	2.297	0.0136	2.297	† 0.0110
		(2) 2.453	35.11	2.300	0.0203	2.300	0.0207
in p-xylene		(3) 2.295	23.98	2.302	0.0263	2.304	0.0288
			16.20	2.312	0.0411	2.3101	0.0397
			9.313	2.328	0.0584	2.328	0.0577
			6.70	2.344	0.0662	2.345	0.0670
	25		70.00	2.276	0.0142	2.277	† 0.0122
		(2) 2.426	35.11	2.279	0.0218	2.280	0.0229
		(3) 2.275	23.98	2.287	0.0292	2.285	0.0318
			16.20	2.299	0.0465	2.293	0.0432
			9.313	2.313	0.0601	2.314	0.0605
			6.700	2.325	0.0671	2.333	0.0677

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	40		70.00	2.248	0.0124	2.253	† 0.0128
		(2) 2.387	35.11	2.258	0.0245	2.257	0.0246
		(3) 2.252	23.98	2.263	0.0340	2.262	0.0345
			16.20	2.278	0.0472	2.272	0.0468
			9.313	2.299	0.0632	2.298	0.0627
			6.70	2.313	0.0660	2.318	0.0664
	50		70.00	2.232	0.0141	2.235	† 0.0134
		(2) 2.361	35.11	2.247	0.0260	2.240	0.0256
		(3) 2.234	23.98	2.245	0.0356	2.245	0.0355
			16.20	2.261	0.0473	2.256	0.0473
			9.313	2.281	0.0593	2.283	0.0607
			6.70	2.302	0.0640	2.303	0.0622
2-naphthaldehyde	25	(1) 0.01831	70.00	2.030	0.0111	2.031	0.0109
		(2) 2.132	35.11	2.036	0.0193	2.035	0.0194

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε'' Measured	ε' Calculated	ε'' Calculated
in cyclohexane		(3) 2.029	23.98	2.041	0.0253	2.040	0.0257
			16.20	2.051	0.0344	2.046	0.0336
			9.313	2.059	0.0453	2.063	0.0450
			6.70	2.075	0.0484	2.078	0.0488
Terephthalaldehyde		(1) 0.02895	70.00	2.287	0.0179	2.290	† 0.0178
	25	(2) 2.396	35.11	2.289	0.0322	2.298	0.0328
in p-xylene		(3) 2.287	23.98	2.310	0.0414	2.308	0.0430
			16.20	2.329	0.0543	2.324	0.0518
			9.313	2.353	0.0517	2.354	0.0531
			6.70	2.363	0.0468	2.369	0.0470
p-nitrobenzaldehyde		(1) 0.0250	70.00	2.250	0.0135	2.252	† 0.0137
		(2) 2.337	35.11	2.259	0.0237	2.258	0.0238
		(3) 2.248	23.98	2.266	0.0295	2.265	0.0303

Solution	T°C	Misc.		Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
				16.20	2.275	0.0384	2.275	0.0365
				9.313	2.292	0.0392	2.295	0.0397
				6.70	2.303	0.0363	2.307	0.0373
p-fluorobenzaldehyde	15	(1)	0.03904	70.00	2.297	0.0215	2.299	0.0200
in p-xylene		(2)	2.433	35.11	2.314	0.0359	2.308	0.0366
		(3)	2.296	23.98	2.322	0.0453	2.319	0.0477
				16.20	2.340	0.0590	2.337	0.0576
				9.313	2.369	0.0636	2.367	0.0624
				6.70	2.382	0.0580	2.385	0.0593
	25			70.00	2.291	0.0233	2.284	0.0222
		(2)	2.407	35.11	2.297	0.0383	2.295	0.0393
		(3)	2.279	23.98	2.311	0.0493	2.308	0.0494
				16.20	2.334	0.0571	2.326	0.0567
				9.313	2.355	0.0576	2.355	0.0572
				6.70	2.363	0.0530	2.371	0.0522

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε'' Measured	ε' Calculated	ε'' Calculated
	40		70.00	2.264	0.024	2.260	0.0237
		(2) 2.371	35.11	2.274	0.0399	2.273	0.0405
		(3) 2.254	23.98	2.287	0.0482	2.287	0.0492
			16.20	2.308	0.0542	2.306	0.0539
			9.313	2.336	0.0516	2.333	0.0507
			6.70	2.343	0.0432	2.346	0.0442
	50		35.11	2.263	0.0409	2.260	0.0417
		(2) 2.347	23.98	2.275	0.0480	2.274	0.0482
		(3) 2.236	16.20	2.296	0.0508	2.292	0.0503
			9.313	2.318	0.0452	2.316	0.0449
			6.70	2.323	0.0382	2.327	0.0385
p-chlorobenzaldehyde	15	(1) 0.0571	34.86	2.326	0.0407	2.321	0.0406
		(2) 2.480	23.98	2.336	0.0530	2.333	0.0537
in p-xylene		(3) 2.309	16.20	2.349	0.0661	2.351	0.0666

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calcualted
			9.313	2.388	0.0763	2.387	0.0757
			6.70	2.413	0.0741	2.409	0.0744
	25		34.86	2.313	0.0432	2.310	0.0433
		(2) 2.455	23.98	2.331	0.0549	2.323	0.0555
		(3) 2.294	16.20	2.343	0.0643	2.343	0.0657
			9.313	2.382	0.0709	2.371	0.0700
			6.70	2.397	0.0672	2.396	0.0670
	40		35.11	2.279	0.0322	2.272	0.0319
		(2) 2.355	23.98	2.278	0.0389	2.282	0.0397
		(3) 2.234	16.20	2.300	0.0455	2.297	0.0448
			9.313	2.322	0.0432	2.321	0.0434
			6.70	2.330	0.0385	2.332	0.0383
	50		35.11	2.257	0.0324	2.253	0.0328

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
		(2) 2.332	16.20	2.287	0.0439	2.280	0.0438
		(3) 2.238	9.313	2.303	0.0413	2.302	0.0409
			6.70	2.309	0.0358	2.313	0.0355
	60		35.11	2.238	0.0328	2.238	0.0332
		(2) 2.309	23.98	2.250	0.0406	2.250	0.0397
		(3) 2.222	16.20	2.273	0.0413	2.265	0.0413
			9.313	2.287	0.0380	2.286	0.0372
			6.70	2.294	0.0317	2.295	0.0311
p-chlorobenzaldehyde in cyclohexane	25	(1) 0.03811	34.86	2.046	0.0163	2.039	† 0.0158
		(2) 2.074	23.98	2.055	0.0190	2.045	0.0192
		(3) 2.032	9.313	2.061	0.0183	2.063	0.0181
			6.70	2.067	0.0163	2.068	0.0148

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
p-bromobenzaldehyde in p-xylene	15	(1) 0.04200	70	2.290	0.0122	2.298	0.0119
		(2) 2.392	35.11	2.304	0.0217	2.303	0.0221
		(3) 2.296	23.98	2.307	0.0275	2.309	0.0295
			16.20	2.322	0.0391	2.319	0.0369
			9.313	2.341	0.0416	2.338	0.0424
	25		70.00	2.285	0.0131	2.282	0.0127
		(2) 2.372	35.11	2.285	0.0230	2.288	0.0233
		(3) 2.280	23.98	2.296	0.0291	2.295	0.0305
			16.20	2.308	0.0386	2.305	0.0370
			9.313	2.324	0.0400	2.325	0.0406
	40		70.00	2.245	0.0139	2.256	0.0137
		(2) 2.335	35.11	2.266	0.0254	2.262	0.0248
		(3) 2.253	23.98	2.274	0.0295	2.270	0.0319

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
			16.20	2.288	0.0395	2.282	0.0376
			9.313	2.306	0.0376	2.302	0.0385
			6.70	2.308	0.0358	2.313	0.0347
	50		35.11	2.254	0.0251	2.251	0.0246
		(2) 2.314	23.98	2.260	0.0307	2.259	0.0311
		(3) 2.241	16.20	2.275	0.0352	2.271	0.0354
			9.313	2.288	0.0344	2.290	0.0335
o-diiodobenzene	15	(1) 0.13554	70.00	2.312	0.0127	2.318	† 0.0138
		(2) 2.467	35.22	2.320	0.0259	2.322	0.0259
in p-xylene		(3) 2.315	23.98	2.327	0.0354	2.327	0.0357
		(4) 2.278	16.20	2.342	0.0483	2.337	0.0480
		(5) 0.9518	9.313	2.364	0.0652	2.362	0.0648
			6.70	2.382	0.0698	2.382	0.0702

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
	60		35.22	2.250	0.0322	2.248	† 0.0339
		(2) 2.357	23.98	2.262	0.0464	2.257	0.0451
		(3) 2.237	16.20	2.280	0.0559	2.274	0.0555
		(4) 2.209	6.70	2.322	0.0545	2.324	0.0536
		(5) 0.9107					
o-bromoiodo-	60	(1) 0.1215	70.00	2.230	0.0276	2.233	† 0.0283
benzene		(2) 2.382	35.22	2.251	0.0484	2.247	0.0510
in p-xylene		(3) 2.228	23.98	2.275	0.0662	2.264	0.0653
		(4) 2.200	16.20	2.295	0.0779	2.290	0.0756
		(5) 0.8976	9.313	2.331	0.0728	2.331	0.0724
o-chloroiodo-	60	(1) 0.08992	70.00	2.215	0.0273	2.227	† 0.0285
benzene		(2) 2.365	35.22	2.249	0.0491	2.242	0.0507
in p-xylene		(3) 2.221	23.98	2.270	0.0648	2.260	0.0635
		(4) 2.193	16.20	2.292	0.0716	2.285	0.0713

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
		(5) 0.8749	9.313	2.323	0.0661	2.323	0.0653
m-diiodobenzene	15	(1) 0.14832	70.00	2.315	0.0102	2.318	† 0.0102
		(2) 2.405	35.22	2.321	0.0178	2.322	0.0182
in p-xylene		(3) 2.315	23.98	2.327	0.0240	2.326	0.0241
		(4) 2.281		2.350	0.0391	2.350	0.0382
		(5) 0.9594	6.70	2.362	0.0383	2.362	0.0393
			70.00	2.244	0.0131	2.240	† 0.0122
	60		35.22	2.247	0.0228	2.246	0.0223
		(2) 2.308	23.98	2.260	0.0296	2.253	0.0289
		(3) 2.237	16.20	2.275	0.0351	2.264	0.0340
		(4) 2.215	9.313	2.286	0.0331	2.283	0.0334
		(5) 0.9194	6.70	2.297	0.0295	2.293	0.0290

Solution	T°C	Misc.	Freq. G.c./sec	ε' Measured	ε" Measured	ε' Calculated	ε" Calculated
m-bromoiodo-	60	(1) 0.1196	70.00	2.323	0.0147	2.231	† 0.0153
benzene		(2) 2.301	35.22	2.242	0.0260	2.240	0.0269
in p-xylene		(3) 2.228	23.98	2.259	0.0350	2.249	0.0333
		(4) 2.200	16.20	2.265	0.0358	2.263	0.0366
		(5) 0.8963	9.313	2.282	0.0343	2.282	0.0326
2-iodonaphthalene	25	(1) 0.1289	35.22	2.072	0.0140	2.069	† 0.0134
		(2) 2.176	23.98	2.074	0.0183	2.072	0.0183
in cyclohexane		(3) 2.066	16.20	2.079	0.0254	2.076	0.0250
		(4) 2.048	1.90	2.145	0.0423	2.148	0.0412

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