DIELECTRIC RELAXATION STUDIES OF SOME DIARYL MOLECULES IN POLYSTYRENE MATRICES

A Thesis Submitted By

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ABSTRACT

Dielectric relaxation studies of a number of diaryl molecules dispersed in atactic polystyrene and in some cases as solid discs have been carried out. Preparation of the polystyrene matrices and the solid disks, and the dielectric measurements using a General Radio 1615-A capacitance bridge and a Hewlett-Packard Q-meter with appropriate temperature-controllable cells have been described. The experimental data as a function of frequency at different temperatures were subjected to analysis by a series of computer programmes written in the APL language. The activation energy barriers for the dielectric relaxation processes were obtained by the application of the Eyring rate equation.

A number of diaryl molecules with different central bridging atom or group, and different ring substituents have been studied. Attempts have been made to identify and study a unique type of rapid, intramolecular rotation process termed "double-internal rotation", in which the two aryl rings undergo simultaneous, coupled rotation.

Studies have been made to correlate molecular properties such as symmetry, and electronic and steric effects to the occurrence of double-internal rotation. Symmetric diaryl molecules such as sulfones, sulfoxides, and dibenzothiophenes were found to undergo predominantly over-all molecular rotation in polystyrene matrices. Asymmetric diaryl ethers and ketones displayed a major contribution to dielectric relaxation from over-all molecular rotation. Symmetric diaryl ethers, ketones, and sulfides (e.g., diphenyl ether, benzophenone, and diphenyl sulfide) were found to undergo primarily double-internal rotation, both in polystyrene and as compressed solids.

Some large molecules such as 1,2-diphenylcyclopropenone underwent co-operative motion with the polymer chains near the glass-transition temperature of polystyrene. A linear correlation was observed between the enthalpy of activation and the entropy of activation for molecules undergoing the same type of relaxation process. There was also found to be a linear correlation between the volume swept out during molecular reorientation and the energy of activation for the process in rigid symmetric diaryl molecules.

Energy barriers for the molecular rotation of non-planar symmetric diaryl molecules (e.g., diphenyl sulfone and diphenyl sulfoxide) were found to be ≥ 60 kJ mol^{-1} depending on the size of the substituents. Planar molecules the size of dibenzothiophene were found to have energy barriers for molecular rotation of about 40 kJ mol^{-1}. The energy barrier for symmetric diaryl molecules which undergo double-internal rotation were observed in most cases to be in the range 5 - 15 kJ mol^{-1} at temperatures below 100 K.

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CHAPTER I

INTRODUCTION

INTRODUCTION

With the development of dielectric studies many chemical systems have been studied, particularly in the microwave and radio-frequency regions of the electromagnetic spectrum. These types of studies were mostly performed on liquid solutions at microwave frequencies. In many studies of solutions the solvent viscosity was found to be an important factor affecting rotational motions. Consequently, a number of non-polar solvent systems of varying viscosity has been investigated, in which polar solute molecules have been dissolved and studied for dielectric relaxation.

With the advent of polymer science solutions of very high viscosity could be made with polymers as solvents.[1,2] One of the most commonly used polymer solvents is polystyrene. Polystyrene is used as the solvent for a matrix, which contains cavities within which solute molecules can be trapped. Since polystyrene is almost a non-polar polymer, studies in which polar molecules are molecularly dispersed in the matrix are simplified by the very low loss of polystyrene. Samples of polystyrene have losses which are less than $1x10^{-3}$ over the frequency range 100 Hz to 1 GHz.

The research work which is presented in this thesis concerns itself primarily with dielectric relaxation studies of diaryl molecules of different sizes and shapes in matrices in which polystyrene is utilized as the solvent.

In a polystyrene matrix molecular and intramolecular processes can be separated and studied by observing dielectric parameters such as enthalpy of activation (ΔH_E), entropy of activation (ΔS_E), and relaxation time (τ).

The polystyrene matrices are placed in an oscillating electric field and their behaviour is studied. From these studies various dielectric parameters such as permittivity, dielectric loss, distribution parameter, dipole moment, and free energy can be determined. The theory behind these parameters is presented in Chapter II.

Since the advent of polystyrene matrix studies in the late 1960's[1,2] many types of molecules have been studied by this technique, particularly for group rotation, such as that of the acetyl group.[3] Another category of compounds which has been examined for both molecular and intramolecular relaxation processes is that of symmetric and asymmetric diaryl molecules. It is the study of the dielectric relaxation of these symmetric and asymmetric diaryl molecules which this thesis concerns itself. These include some diaryl sulfones, sulfoxides, sulfides, ethers, ketones, and related compounds.

In the above list of compounds those which have been studied the most extensively by other workers are the ethers. The anomalous behaviour of some diaryl ethers was first noticed in the study of diphenyl ether by Fisher[4] in 1949. Most of this research was in the microwave region on liquid solutions.

The time required for a system of simple rigid polar molecules to achieve orientation in an applied electric field is 5 to 100 ps in most non-polar, low viscosity solvents. Chlorobenzene which was found to have a relaxation time of 8.3 ps in benzene at 293 K, has a smaller molecular volume than diphenyl ether.[5] This behaviour indicates that diphenyl ether with a relaxation time of 4.0 ps in benzene[16] at 293 K has a rapid intramolecular relaxation process in addition to over-all molecular rotation. In comparison with benzophenone which is similar in size and shape to diphenyl ether the relaxation times are 20.4 and 4.0 ps respectively in benzene at 293 K. Benzophenone has a molar molecular volume of 170 c.c. while diphenyl ether has one of 164 c.c.[6] Both molecules also have a dipole moment which lies on the Y axis which bisects the CXC angle, (X = O, CO).

Several mechanisms have been suggested for the rapid intramolecular relaxation process of diphenyl ether and related molecules.[5] One of the most popular and accepted ones is in that of a mechanical double-internal rotation. In this mechanism the aromatic rings undergo a coupled ring rotation which enables the molecule to almost rotate within its own volume,leading to a rapid change of molecular dipole moment direction. Throughout this thesis both the terms,"double-internal rotation" and "coupled ring rotations" are used to describe the same anomalously rapid intramolecular rotation process which occurs in diphenyl ether type molecules.

Besides ethers some symmetric diaryl sulfides and ketones have also been found to undergo double-internal rotation. There are two mechanisms which have been the most popular in explaining double-internal rotation. One mechanism was developed by Smyth and Higasi. In their mechanism involving the mesomeric effect[7] the anomalously short relaxation time of diphenyl ether is brought about by a shift of electronic charge into the rings from the lone electron pairs of the oxygen atom as the rings rotate,which is equivalent to a dipole altering its direction by 180°. The other mechanism is by Fong[8] in which double-internal rotation results from the mechanical rotation of the two rings in such a manner that there is conservation of angular momentum so that the centre of mass is not displaced. In this mechanism there is a simultaneous coupled rotation of the two rings,which leads to a situation which is equivalent to the dipole altering its direction by 180°. The average position of the two rings is one in which they are orthogonal. A more detailed discussion of the two mechanisms for rapid coupled ring rotations is given in Chapter VII. It may also be that there can be a contribution from both mechanisms, particularly if the magnitude of the mesomeric moment is near that of the net dipole moment of the molecule.

Since diphenyl ether shows an anomalously short relaxation time other diaryl molecules have been studied, particularly in solution at microwave frequencies. These include other ethers,[5,9] sulfides,[9,10,11] ketones,[12,13] and methanes[10,12]. The question of how important such criteria as symmetry and net dipole direction are for double-internal rotation was investigated by studying asymmetric ethers and ketones.[11,12,13] Further study of double-internal rotation as presented in this thesis was performed with polystyrene matrices in which the solute molecules have different groups or atoms at the 4,4' or 2,2' positions of the two aromatic rings. These include halogen atoms, methyl groups, nitrogen atoms, and methoxy groups.

Matrix studies also included the effect of various bridge groups joining the two aromatic rings on double-internal rotation. Some groups studied include sulfonyl, sulfinyl, thioketone, methylene, ethylene, cyclopropenone, and oxazole groups. Such groups give information about the effect of conjugation on stereochemistry and therefore on double-internal rotation. It will be seen that di-2-pyridyl ketone has a larger enthalpy of activation (27.5 kJ mol^{-1}) than benzophenone (21.4 kJ mol^{-1}), which in turn has a larger enthalpy of activation than diphenyl sulfide (13.6 kJ mol^{-1}). Consequently, it appears that as conjugation between the two aromatic rings increases so does the energy barrier for double-internal rotation.

The importance of the mesomeric effect on double-internal rotation has been studied in this work by examining alkyl ethers and sulfides. Some non-aromatic ethers such as n-butyl ether also show anomalously short relaxation times which are indicative of some form of intramolecular rotation.[9,14]

Most compounds which were studied were commercially available, those which were not were synthesized. Two compounds which were synthesized were di-p-tolyl sulfide and di-4-pyridyl sulfide. The synthesis of di-p-tolyl sulfide involved a new technique in which di-p-tolyl sulfone was chemically reduced to di-p-tolyl sulfide. In this case diisobutyl aluminum hydride was used as the reducing agent. Before this reducing agent was utilized a study of a relatively large number of reducing agents was performed, including a new organometallic compound.

The synthesis of di-4-pyridyl sulfide involved a re-examination of an old synthetic technique utilizing the reaction of N-(4-pyridyl)-pyridinium dichloride with 4-mercaptopyridine.[15] In this synthesis the experimental conditions were studied and revised in order to obtain larger yields of product.

The compounds were chosen to gain insight to the phenomenon of double-internal rotation. It was found that the molecules could be classified as rigid-symmetric, rigid-asymmetric, and non-rigid symmetric. Most of the compounds were studied in a polystyrene matrix form, but whenever necessary solid compounds were also studied as compressed crystalline solids. In most compressed crystalline solids the molecular mode of relaxation for many solids is not observable. As a result intramolecular relaxation processes can be isolated and studied.

Once experimental data,such as the real and imaginary components of the complex dielectric permittivity as a function of frequency and temperature were obtained they were submitted for computer analysis. The computer analysis gave information about energy barriers and related parameters for molecular and intramolecular relaxation processes.

The following chapter gives more information concerning the theory behind the dielectric parameters relevant to molecular behaviour in oscillating electric fields.

REFERENCES

1. M. Davies and A. Edwards, Trans. Faraday Soc., 63, 2163 (1967).
2. M. Davies and J. Swain, Trans. Faraday Soc., 67, 1637 (1971).
3. C. K. McLelland and S. Walker, Can. J. Chem., 55, 583 (1977).
4. E. Fischer, Z. Electrochem., 53, 16 (1949).
5. R. D. Nelson and C. P. Smyth, J. Phys. Chem., 69, 1006 (1965).
6. K. Higasi and C. P. Smyth, J. Am. Chem. Soc., 82, 4759 (1960).
7. K. Higasi, "Dielectric Relaxation and Molecular Structure", Research Institute of Applied Electricity, Hokkaido University, Japan, 1961.
8. F. Fong, J. Chem. Phys., 40, 132 (1964).
9. S. Dasgupta, K. N. Abd El Nour, and C. P. Smyth, J. Chem. Phys., 50, 4810 (1969).
10. E. N. DiCarlo and C. P. Smyth, J. Am. Chem. Soc., 84, 3638 (1962).
11. D. B. Farmer and S. Walker, Trans. Faraday Soc., 63, 966 (1967).
12. G. P. Johari, J. Crossley, and C. P. Smyth, J. Am. Chem. Soc., 91, 5197 (1969).
13. W. E. Vaughan and C. P. Smyth, J. Phys. Chem., 65, 98 (1961).
14. J. T. Vig and K. K. Srivastava, Bull. Chem., Soc. Japan, 43, 2313 (1970).
15. D. Jerchel, H. Fischer and K. Thomas, Chem. Ber., 89, 2921, (1956).
16. F. Hufnagel, G. Klages, and P. Knoblock, Z. Naturforsh, 17a, 96 (1962).

CHAPTER II

BASIC THEORY

Throughout the course of scientific research many experiments have been performed which illustrate that matter interacts with electromagnetic radiation. It has also been shown that the modes of interaction with matter vary widely as the frequency changes by orders of magnitude. Fig. II-1 illustrates the spectrum of electromagnetic waves.

The electromagnetic spectrum which has been investigated experimentally extends continuously from the audiofrequency region to the very high energy gamma rays observed in cosmic radiation. In the former case the frequencies range from 20 - 20,000 Hz and the wavelengths range from 1.5×10^{4} - 1.5×10^{7} m, in the latter case the frequencies are of the order of 10^{24} Hz and higher, and the wavelengths of the order of 3×10^{-16} m and shorter.

In the ultraviolet and visible regions of the electromagnetic spectrum electronic transitions can occur, in the infrared region molecular vibrations can be studied, and in the far infrared region torsions about chemical bonds can be observed. At microwave frequencies (wavelength 1 mm to 30 cm) molecular and intramolecular rotational processes can be examined. At lower frequencies than those in the microwave region of the electromagnetic spectrum are the radio wave frequencies. It is in the last two regions that much study of dielectric relaxation has taken place.

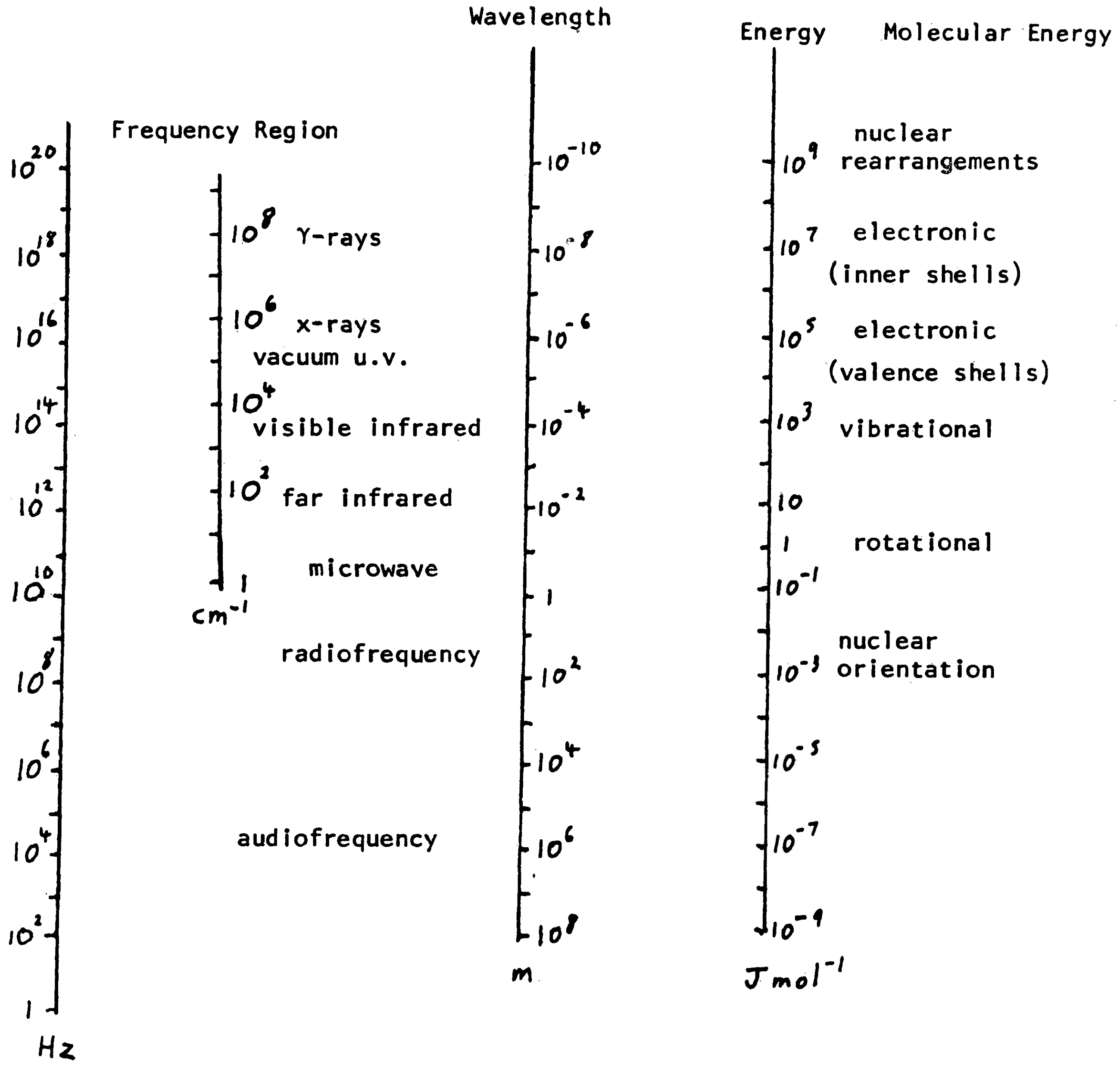


FIGURE II-1 REGIONS OF THE ELECTROMAGNETIC SPECTRUM AND ASSOCIATED MOLECULAR ENERGIES

Dielectric materials differ from conductors in that they have no free charges that can move through the material under the influence of an electric field. In non-polar dielectrics all the electrons are bound, and the only motion possible in the presence of an electric field is a very small displacement of positive and negative charges in opposite directions. A non-polar dielectric material in which charge displacement has taken place is said to be polarized, and its molecules possess induced dipole moments. These dipoles produce their own field which adds to those of the external charges.

The total polarization in a material is made up of different components, such as the electronic polarization (P_E), which is due to the relative displacement of the electrons and nuclei. There is also atomic polarization (P_A) which arises from the relative displacement of atoms in a molecule and orientational polarization (P_0) in which the molecules rotate in positions favourable to an electric field. The total polarization (P_T) of a dielectric material in an electric field can be expressed as:

$$P_T = P_E + P_A + P_0 \qquad \text{II-1}$$

In the case of polar dielectrics an applied electric field can also polarize a dielectric material by orientating molecules that possess a permanent dipole moment. Such molecules experience a torque which aligns them with the electric field. In polar molecules the total amount of positive and negative charges are equal so that there is no net charge, and the molecules are electrically neutral. The distribution of the charges are such that the positive and negative charges are separated by a distance of molecular dimensions. If the dipole is made up of charges +q and -q separated by distance d, then the dipole moment can be expressed as qd. Since the magnitude of the charges is 10^{-10} e.s.u. and the separation distance is 10^{-8} cm the dipole moment is of the order of magnitude of 10^{-18} e.s.u. Such a unit is known as a Debye unit.

The magnitude of a dipole moment depends in part on the size and symmetry of a molecule, consequently molecules such as chloroform, 1,1-dichloroethane, and p-nitrodiphenyl ether which have no centre of symmetry are polar. Molecules such as benzene and anthracene which have a centre of symmetry have no permanent dipole moment and are non-polar.

If compounds which are polar are placed in an electric field which alternates at low frequency the polarization will also alternate. As the frequency is increased the P_0 term will have difficulty in following the alternating field and will not have full time to attain its full polarization value before the field reverses. With increasing frequency the relative permittivity decreases and there is a loss, or

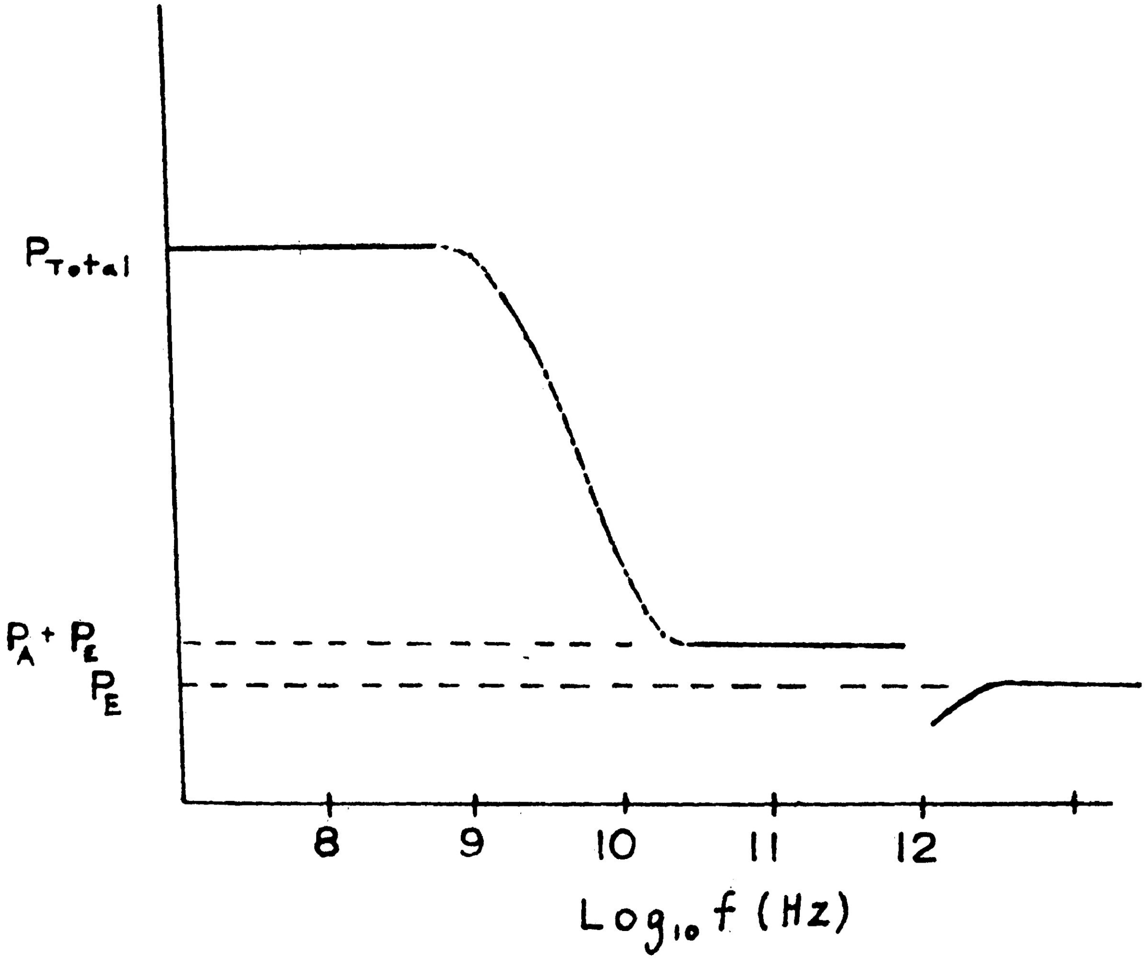


FIGURE II-2: TOTAL POLARIZATION VERSUS Log FREQUENCY absorption of electrical energy which causes heating in the dielectric material. The (static) relative permittivity (ε_o) of a dielectric is the ratio of the capacitance (C) of a condenser to the capacitance (C_o) of the condenser with a vacuum between the plates, therefore:

$$\varepsilon_o = C/C_o \qquad \text{II-2}$$

The absorption region associated with the different mechanisms of polarization occurs in different parts of the electromagnetic spectrum, as shown in Fig. II-2. For example, electronic polarization is a process which arises from the displacement of a molecule's electrons in an applied field. When the applied-field frequency is beyond that of molecular reorientation and atomic polarization, the polarizability is defined by the electric moment. The electronic polarization process occurs with a frequency of about 10^{15} Hz which corresponds to frequencies in the ultraviolet region. Atomic polarization arises from the displacement of atoms relative to one another in the molecule, and occurs at frequencies of 10^{12} to 10^{14} Hz, corresponding to the infrared region of the electromagnetic spectrum. The time required for the orientation polarization response depends in part on the frictional resistance of the medium to the change in molecular orientation. In a highly viscous medium a molecule will encounter more frictional drag as it rotates than in a low viscosity medium. This will result in a longer period of time for molecular reorientation in a more viscous medium. Small molecules in liquids of low viscosity reorientate themselves in a period of 10^{-11} s to 10^{-12} s with frequencies of 10^{11} to 10^{12} Hz. These frequencies correspond to the microwave region.

Dielectric relaxation is the exponential decay with time of the polarization in a dielectric when an external field is removed. The relaxation time, τ, is defined as the time (t) during which the polarization is reduced to 1/e times its original value (P_0), therefore:

$$P(t) = P_0 \exp(-t/\tau) \qquad \text{II-3}$$

where P(t) is the specific polarization at time t in an electromagnetic field.

The frequency dependence of the permittivity (ε') and the dielectric loss (ε'') in the region of dielectric absorption for a system is characterized by the Debye equation II-4:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \qquad \text{II-4}$$

where $\varepsilon^* = \varepsilon' - j\,\varepsilon''$ and $j = \sqrt{-1}$

ε_∞ is the infinite frequency permittivity

ε_0 is the static permittivity

τ is the relaxation time, and,

ω is the angular frequency.

In studying the properties of a dielectric it is usual to examine its behaviour between two capacitor plates. It was mentioned earlier that the permittivity can be determined experimentally with the use of Eqn. II-2. The permittivity is a temperature dependent quantity for polar molecules since the orientation polarization falls off rapidly with rising temperature. This behaviour occurs because the thermal motion reduces the alignment of the permanent dipoles by the electric field. Also, the permittivity of a material will be higher the greater the polarizability of the molecules.

The molecular polarization is dependent on the frequency of the applied field. At low frequencies the dielectric constant is numerically equal to that obtained when a static field is employed. This value persists as the frequency is increased, until the duration of the field becomes comparable with the relaxation period of the molecular species forming the dielectric. At this point the molecules are no longer able to completely follow the reversals of the electric field. There is no appreciable time lag in the attainment of equilibrium of molecular orientation which leads to a diminuation in the orientation polarizability, and ultimately orientation is undetectable. At this point the molecular polarization is given by the atomic and electronic polarizations. At still higher frequencies the atomic nuclei cease to follow the field, and the dielectric constant is given solely by the electronic polarization.

The static permittivity is related to the polarization by Eqn. II-5:

$$\varepsilon_o = 1 + \frac{4\pi P}{\varepsilon E} \qquad \text{II-5}$$

where P is the polarization,

E is the applied electric field, and

ε is a constant whose value depends on the unit system used.

Permittivity depends on the density of the dielectric material. If the material has a molecular weight M and density ρ then Debye's equation is:

$$\frac{(\varepsilon_o - 1)}{(\varepsilon_o + 2)} \frac{M}{\rho} = 4\pi N(\alpha + \mu^2/3kT)/3 \qquad \text{II-6}$$

where N is Avogadro's number, 6.02257×10^{23} molecules/mole

α is the electronic (α_E) and atomic (α_A) polarizability

$$\alpha = \alpha_E + \alpha_A$$

μ is the dipole moment, and

T is the absolute temperature.

The quantity $(\varepsilon_o - 1)M/(\varepsilon_o + 2)\rho$ is known as the molar polarization. From the Debye Equation II - 6 the following conclusions can be made. For a non-polar material the molar polarizability should be a constant independent of the temperature and pressure. An increase in the density leads to an increase in permittivity. For a polar substance the molar polarizability falls with increasing temperature, because the thermal agitation decreases the dipolar polarization. If a plot of molar polarizability versus the reciprocal of temperature is made, a straight line is obtained, from whose slope the dipole moment of the molecule can be found.

The Clausius-Mossotti-Debye theories give the total polarization (P_T) of a polar molecule in an electric field as:

$$\begin{aligned} P_T &= \frac{4\pi N}{3} \left(\alpha_E + \alpha_A + \frac{\mu^2}{3kT}\right) \\ &= \frac{\varepsilon_o - 1}{\varepsilon_o + 2} \left(\frac{M}{\rho}\right) \end{aligned} \qquad \text{II-7}$$

where k is the Boltzmann constant,

μ is the electric dipole moment,

T is the absolute temperature,

M is the gram molecular weight,

ρ is the density (gm/ml) of the material,

α_E is the electronic polarizability,

α_A is the atomic polarizability, and

N is the Avogadro's number.

The Clausius-Mossotti-Debye theories are applicable to gases, but are often inadequate when applied to polar liquids, due to the inability of the Lorentz field used in these theories to represent adequately the local field in a dipolar dielectric.

In order to give a theory which would extend the relation between permittivity and dipole moment to liquids and solids Onsager's theory was developed. The Onsager theory gives the equation:

$$\frac{(\varepsilon_o - \varepsilon_\infty)(2\varepsilon_o + \varepsilon_\infty)}{\varepsilon_o(\varepsilon_\infty + 2)^2} \frac{M}{\rho} = \frac{4\pi N \mu^2}{9kT} \qquad \text{II-8}$$

where ε_∞ is the very high frequency or optical dielectric constant at very high frequencies when the orientation polarization vanishes.

Equation II-7 then becomes:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \frac{M}{\rho} = \frac{4\pi N}{3} (\alpha_E + \alpha_A) \qquad \text{II-9}$$

Combination of Equations II-7 and II-9 gives the Debye Equation II-10. Equations II-8 and II-10

$$\frac{3(\varepsilon_o - \varepsilon_\infty)}{(\varepsilon_o + 2)(\varepsilon_\infty + 2)} \frac{M}{\rho} = \frac{4\pi N\mu^2}{9kT} \qquad \text{II-10}$$

enable a comparison of the value of μ^2 given by the Onsager and Debye Equations:

$$\frac{\mu^2 \text{ (Onsager)}}{\mu^2 \text{ (Debye)}} = \frac{(2\varepsilon_o + \varepsilon_\infty)(\varepsilon_o + 2)}{3\varepsilon_o (\varepsilon_\infty + 2)} \qquad \text{II-11}$$

For gases at low pressures the Onsager Equation will be reduced to the Debye Equation when ε_o and ε_∞ are practically identical.

In order to study phenomena such as those mentioned in the above discussion the dielectric materials are usually examined between the electrodes of a capacitor. If the capacitor has an applied oscillating electric potential (E), then:

$$E = E_0 \cos \omega t \qquad \text{II-12}$$

where E is the potential at time t,

E_0 is the amplitude of the potential, and

ω is the frequency in radians per second.

With such an experimental set-up an alternating electric field can be applied. If the field alternates at sufficiently low frequencies then the polarization will also alternate. With increasing frequency the polarization will have difficulty in following the electric field and does not have time to attain its full value before the field reverses. At higher frequencies the relative permittivity decreases and there is dielectric loss (ε'') or absorption of electrical energy causing Joule heating in the dielectric.

In the capacitor without the dielectric material the displacement current vector is 90° out of phase with the potential as shown in Fig. II-3. In this case there is a zero component of the current in phase with the potential, and no electrical energy is lost by conversion to heat.

If a polar dielectric material of permittivity ε' and dielectric loss ε'' is placed in a capacitor the displacement current will be slightly less than 90° ahead of the potential as in Fig. II-4. There will now be a small component $E\omega\varepsilon''C$ of the current in phase with the potential causing dielectric heating. The capacitative component $E\omega\varepsilon'C$ is called the charging current.

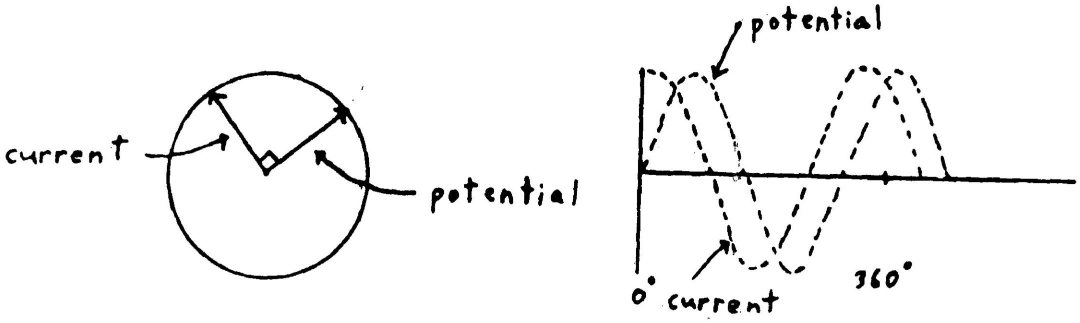


FIGURE II-3: POTENTIAL AND CURRENT VECTORS 90° OUT OF PHASE FOR A LOSS-FREE CAPACITOR IN AN ALTERNATING FIELD.

Fig. II-4 also shows the loss angle δ, which is the lag in the displacement current vector. These parameters are related by the expression:

$$\tan \delta = \frac{\text{loss current}}{\text{charging current}} = \frac{\varepsilon''}{\varepsilon'} \qquad \text{II-13}$$

ε' and ε'' can be combined in the expression:

$$\varepsilon^* = \varepsilon' - j\,\varepsilon'' \qquad \text{II-14}$$

where ε^* is called the complex permittivity.

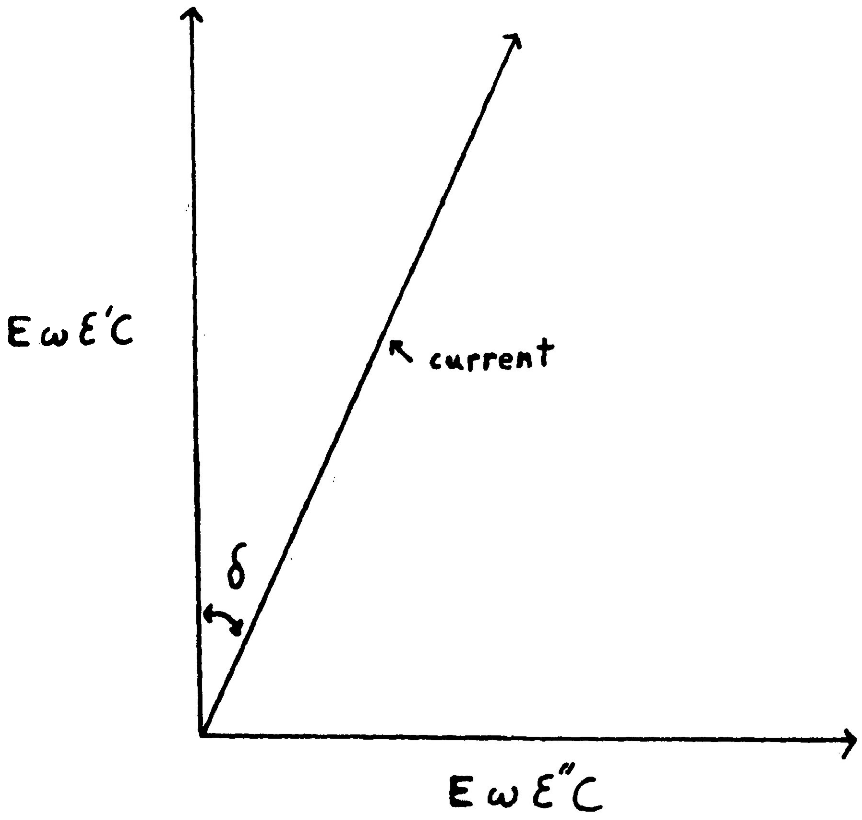


FIGURE II-4: POTENTIAL AND CURRENT VECTORS LESS THAN 90° OUT OF PHASE IN A CAPACITOR WITH LOSS.

The frequency dependence of the relative permittivity ε' and the dielectric loss factor ε'' for the relaxation absorption are described by the Debye Equations[1,2] II-15 and II-16:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + \omega^2 \tau^2} \qquad \text{II-15}$$

$$\varepsilon'' = (\varepsilon_o - \varepsilon_\infty)\frac{\omega\tau}{1 + \omega^2 \tau^2} \qquad \text{II-16}$$

where ε_o and ε_∞ are the relative permittivities below and above the absorption respectively,

$\varepsilon_o - \varepsilon_\infty$ is a factor which is termed the dispersion of the relative permittivity,

ω is the frequency in radians per second, and

τ is the relaxation time of the system.

The relaxation time τ of a system can also be obtained from the position of the frequency maximum in the loss factor curve. τ can be found from the following equations:

$$\omega\tau = 1$$

$$\omega = 2\pi f_m$$

$$\tau = \frac{1}{\omega} = \frac{1}{2\pi f_m} \qquad \text{II-17}$$

where f_m is the frequency maximum of the loss factor curve,

τ obtained from the above method is termed the microscopic or molecular relaxation time.

The Debye Equation can also be written as:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + j\omega\tau} \qquad \text{II-18}$$

Separation of this Equation into its real and imaginary parts gives Eqns. II-15 and II-16. Elimination of $\omega\tau$ from these Equations gives Equation II-19:

$$\left(\varepsilon' - \frac{\varepsilon_o + \varepsilon_\infty}{2}\right)^2 + \varepsilon''^2 = \left(\frac{\varepsilon_o - \varepsilon_\infty}{2}\right)^2 \qquad \text{II-19}$$

This is the Equation of a circle with the centre lying on the abscissa. This function leads to a Cole-Cole plot when ε'' is plotted against ε' at the same frequencies.

Many molecules exhibit a range of relaxation times. Cole and Cole[3] considered the case when there is a symmetrical distribution about the mean relaxation time τ_o, and obtained Equation II-20:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + (j\omega\tau_o)^{1-\alpha}} \qquad \text{II-20}$$

where α is the distribution parameter whose values range $0 \leq \alpha \leq 1$. When $\alpha=0$ the Debye Equation is obtained. When Equation II-20 is separated into real and imaginary parts, then the centre of the semicircle lies below the abscissa.

A number of functions has been considered for non-Debye type of absorption curves. Cole-Davidson have formulated a function which describes right-skewed arcs[4]. The Equation is:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{(1 + j\omega\tau)^\beta} \qquad \text{II-21}$$

where β in the equation is the asymmetric distribution coefficient.

Frohlich, Fuoss, and Kirkwood have considered theories relating to the distribution of relaxation times. Frohlich[2] stated that molecules undergoing relaxation, change their direction by means of jumps over a potential energy barrier. In a particular crystalline solid the energy barriers will be of nearly the same height for all molecules, however, in amorphous solids and liquids the barrier height differs for each molecule. In the last two cases each molecle has a different environment due to the varying arrangement of neighbouring dipoles.

Fuoss and Kirkwood[5] also developed a theory regarding the distribution of relaxation times. These workers found that the dielectric loss of some polymers could be represented by Equation II-22:

$$H(x) = H(0)\ \mathrm{sech}\beta\ x \qquad \text{II-22}$$

where $x = \ln(\frac{\omega}{\omega_m})$,

β is a constant, $0 < \beta < 1$ and $H(0)$ corresponds to $\omega=\omega_m$,

ω_m is the frequency where maximum loss occurs.

For one relaxation time:

$$H(X) = \frac{\omega\tau}{1 + \omega^2\ \tau^2} = H(0)\ \mathrm{sech}\ x \qquad \text{II-23}$$

The β value can be obtained from experimental data by plotting

$$\cosh^{-1}\{\varepsilon''_m\ (2 + 1/\varepsilon'^2_m)/\varepsilon''(2 + 1/\varepsilon'^2)\}$$

against $\ln\omega$ or $\ln f$. By taking the slope of the line from the graph β can be obtained, and the intercept will give the ω_m or f_m value.

A number of models has been suggested to account for the relaxation processes of molecules. Debye has suggested a simple relaxation mechanism[1]. In his theory each dipole has two equilibrium positions

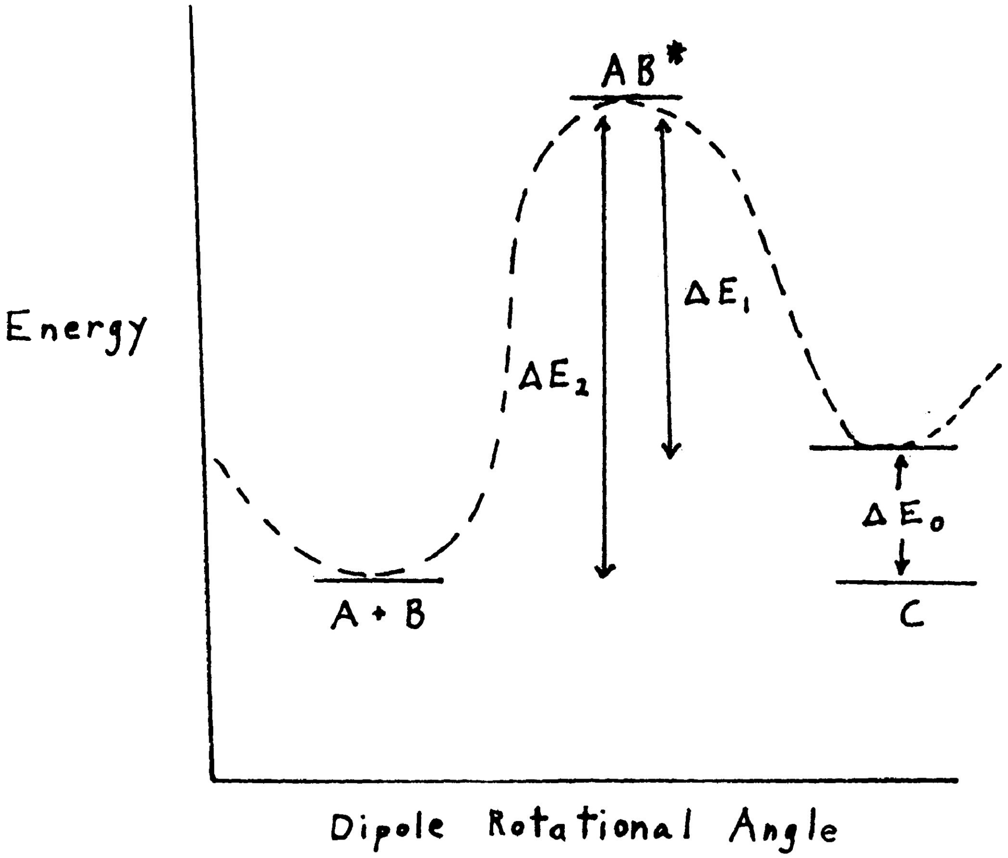


FIGURE II-5: ENERGY BARRIER DIAGRAM FOR A ROTATING DIPOLE.

which are equal in energy and opposite in direction. The two equilibrium positions are separated by an energy barrier, ΔE. In such a situation the dipole will oscillate within the potential minima, and sometimes acquire enough energy to jump the barrier. However, at any instant in time there are equal numbers of dipoles in each equilibrium position in the absence of an external field.

The energy barrier from one equilibrium position to another can be obtained from the dependence of the absorption maximum on the temperature, by use of the equation[6] II-24:

$$f_{max} = \frac{1}{2\pi\tau} = A \exp\left(\frac{-\Delta E}{RT}\right) \qquad \text{II-24}$$

where A is known as the frequency factor,
R is the universal gas constant, and
T is the absolute temperature.

In many molecular systems, particularly solids, the equilibrium positions are unequal as in Fig. II-5.

Eyring has treated dipole rotation by a comparison with chemical rate processes[6]. In his treatment he considers reactants A + B to form an activated complex AB* which then forms product C as in

Fig. II-5. In order to produce C the reactants must acquire sufficient energy to pass over the energy barrier ΔE_2 in Fig. II-5. When this model is applied to dipoles the reaction coordinate must be interpreted as an angular coordinate and the reaction A + B and C as the two equilibrium positions. The activated complex AB* is represented as the activated state in which the dipole has to jump over the energy barrier from one equilibrium position to the other.

From Eyring's theory the following equation was developed:

$$k_1 = \frac{kT}{h} \exp -\Delta G_E/RT \qquad \text{II-25}$$

where k_1 is a rate constant, and

ΔG_E is the free energy of activation, which is the difference of the free energies of the activated and unactivated states, since

$k_1 = \frac{1}{\tau}$ the Eyring equation becomes:

$$\tau = (h/kT) \exp (\Delta G_E/RT)$$

$$= (h/kT) \exp (-\Delta S_E/R) \exp (\Delta H_E/RT) \qquad \text{II-26}$$

where h is the Planch's constant,

ΔS_E is the molar entropy of activation,

ΔH_E is the molar enthalpy of activation,

τ is the microscopic relaxation time,

k is the Boltzmann's constant,

R is the universal gas constant, and

T is the absolute temperature.

It is evident from the above equations that a plot of $\ln(\tau T)$ versus $\frac{1}{T}$ is a straight line. The slope of the line therefore yields the ΔH_E value for the observed relaxation process.

Many molecules exhibit more than one relaxation process. In such molecules there is the possibility of intramolecular as well as molecular rotation. It is then expected that the molecular rotation will be dependent on the viscosity of the medium. Normally, the intramolecular relaxation process will show less viscosity dependence since it causes less disturbance to the surroundings. Also, the intramolecular process is dependent on the magnitude of the potential barriers the molecule must overcome.

Debye[1] in his theory of molecular relaxation states that molecules in the liquid state can be treated as spheres rotating in a continuous viscous medium. The relaxation time for such cases is:

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad \text{II-27}$$

where η is the viscosity,

k is the Boltzmann's constant

a is the radius of the molecule, and

T is the absolute temperature.

Perrin modified Debye's Equation to suit an ellipsoidal molecule, as in Equation II-28:

$$\tau_i = \frac{4\pi\eta f_i abc}{kT} \qquad \text{II-28}$$

where, a, b, and c are the lengths of the semi-axes and

f_i is a numerical factor.

From these theories it is implied that the molecular relaxation process is affected by the viscosity of the medium in which the solute is dispersed.

A case where the viscosity of a solvent is highly increased is in polystyrene matrices. In studies of polystyrene matrices a solute is monomolecularly dispersed in polystyrene, which is considered as a non-polar solvent.

In polystyrene matrices a type of solution is formed in which the solute is trapped in cavities surrounded by chains of polystyrene. Molecules in these cavities find interference in molecular reorientation from the walls of the rigid cage. Anomalous behaviour of the matrix may occur at and above the glass-transition temperature of polystyrene.

Polystyrene is a good matrix solvent since it is almost non-polar and has a low dielectric loss over a wide frequency range. The extent to which the polymer chains are involved in the orientation of the solute is dependent on the size and shape of the solute molecule.

The size and shape of the cavities which form when a solute is molecularly dispersed in polystyrene may influence to an extent the rotation of the solute molecules. Two examples are camphor and tetraphenylcyclopentadienone in polystyrene.[7] The ΔH_E value for camphor in polystyrene was found to be 3.6 ±1.2 kJ mol^{-1}. This observation implies that spherical molecules such as camphor may encounter relatively little difficulty in rotating within the cavities of the matrix.

A large disc-shaped molecule such as tetraphenylcyclopentadienone[7] in polystyrene shows a large ΔH_E value of 520 ±20 kJ mol^{-1}. This large ΔH_E value suggests that tetraphenyclopentadienone encounters considerable hinderance from the polymer during rotation. In this case the molecule may well be undergoing a co-operative type motion with the polystyrene chains.

In polystyrene matrices the activation energy for molecular rotation has been shown to be roughly a linear function of the volume swept out during molecular reorientation (see Chapter V).

Dielectric research with polystyrene matrices show that the permittivity change, $(\Delta\varepsilon') = \varepsilon_o'$ (matrix) - ε_o' (polystyrene) reveals whether there is any dipole reorientation by the polar solute.[7] Values of $\Delta\varepsilon_o' < 0.1$ could have loss values $\varepsilon'' < 50\times10^{-3}$. These quantities imply small dipole activity.[7] Davies and Edwards[7] have calculated the dipole moment of the solute dispersed in polystyrene by the Debye Equation II-29:

$$\varepsilon'' = (\varepsilon' + 2)^2 \frac{\pi N \mu^2 C}{6750kT} \frac{\omega\tau}{1 + \omega^2 \tau^2} \qquad \text{II-29}$$

where, C is the concentration in mole l^{-1},

μ is the dipole moment,

k is the Boltzmann's constant,

T is the absolute temperature, and

N is the Avogadro's number, therefore:

$$\mu^2 = \frac{\Delta\varepsilon' \; 6750kT}{(\varepsilon'_{max} + 2)^2 \pi NC} \qquad \text{II-30}$$

The parameter $\Delta\varepsilon'$ in Equation II-30 is:

$$\Delta\varepsilon' = (\varepsilon_o' - \varepsilon_\infty') = \frac{2\varepsilon''_{max}}{\beta} \qquad \text{II-31}$$

The calculation of the effective dipole moment from the experimental data presented in this thesis is described in Chapter III.

The Fuoss-Kirkwood Equations can also be applied to polystyrene matrix studies. For each measurement temperature, the data of dielectric loss as a function of frequency can be subjected to analysis by the Fuoss-Kirkwood Equation, II-32:

$$\cosh^{-1} \frac{\Delta\varepsilon''_{max}}{\Delta\varepsilon''} = \beta(\ln f_{max} - \ln f) \qquad \text{II-32}$$

Computer analysis can find the value of $\Delta\varepsilon''_{max}$ which provides the best straight line fit to the plot of $\cosh^{-1} \frac{\Delta\varepsilon''_{max}}{\Delta\varepsilon''}$ versus lnf. The value of the distribution parameter, β, can be obtained from the slope of this line, and the frequency of maximum dielectric loss, f_{max}, can be found from the slope and intercept of the line on the $\cosh^{-1}$ axis.

From the above discussions it is evident that much information can be gained by studying dielectric substances in oscillating electric fields. A number of parameters are obtained from such studies, these include the relaxation times at different temperatures, dipole moments, β values, ΔH_E, ΔS_E, and ΔG_E values. Studies of dielectric relaxation have increased in scope by using different environments for the dispersion of solutes, for instance, research has been performed on solutes molecularly dispersed in polystyrene. Further research on polystyrene and other polymer matrices should give more information about the nature of the matrix where the solute acts as a probe of the surroundings, and the Eyring parameters for intramolecular motions in the solute molecule. This thesis concerns itself primarily with relaxation studies of some diaryl molecules in polystyrene matrices, where in addition to molecular relaxation, some of the molecules have been thought to undergo a rather fascinating type of intramolecular motion known as double-internal rotation or coupled ring rotation. One of the prime aims of this work is to make a study of this motion, and to attempt characterize it by means of its Eyring activation parameters.

REFERENCES

1. P. Debye, "Polar Molecules", Chemical Catalogue, New York, U.S.A., (1929).
2. H. Frohlich, "Theory of Dielectrics", Oxford University Press, Amen House, London E.C.4, England, (1949).
3. K. S. Cole and R. H. Cole, J. Chem. Phys., 9, 341 (1941).
4. D. W. Davidson and R. H. Cole, J. Chem. Phys., 19, 1484, (1951).
5. R. M. Fuoss and J. G. Kirkwood, J. Am. Chem. Soc., 63, 385 (1941).
6. S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, U.S.A., (1941).
7. M. Davies and A. Edwards, Trans. Faraday Soc., 63, 2163 (1967).

CHAPTER III

EXPERIMENTAL PROCEDURES

EXPERIMENTAL PROCEDURES

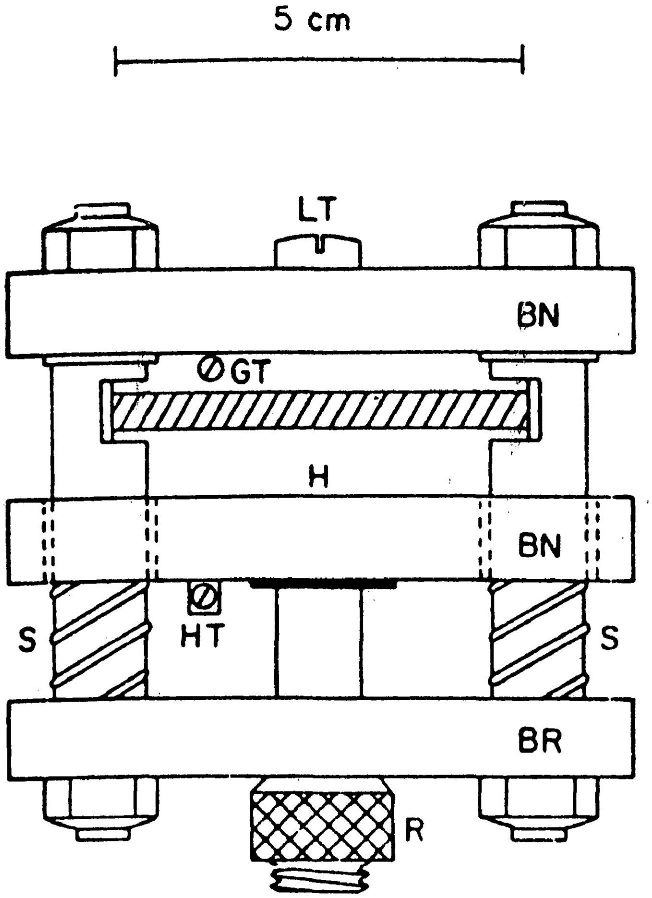
Most of the chemical systems studied in this thesis were experimentally examined as solutes dissolved in polystyrene matrices. The solutes were either polar solids or liquids, which were trapped within cavities in the polymer matrix.

Dielectric measurements of the polystyrene matrices were performed predominantly by the use of a General Radio type 1615A capacitance bridge possessing a frequency range of 50 Hz to 100 kHz. This bridge was used in conjunction with a General Radio Company 1310-B sine wave signal generator, a model 1232-A tuneable amplifier, null detector and an oscilloscope. From the signal generator the signal was split, part going to the capacitance bridge and part going to the horizontal deflection signal of the oscilloscope. On the oscilloscope the pattern was a Lissajous figure whose vertical amplitude reflected the magnitude of the bridge imbalance. Correction of the tilt angle of the pattern enabled balancing to be achieved.

The above bridge was connected to a cell which has a circular parallel-plate capacitor. The cell has three terminals which consist of a guarded 1.45 inch diameter electrode, a lower electrode and a guard ring of 2 inch diameter. The capacitor is mounted in an aluminum air-tight temperature-controlled container equipped with an inlet and outlet for dry nitrogen gas or dry air. Holes in the container enabled placement of a thermocouple connected to a Beckmann /RIIC model TEM-1 temperature controller, as well as a probe for a Hewlett-Packard model 2802A platinum resistance digital thermometer. Dry nitrogen and electrical connections were made by the use of very thin antenna tubing in order to minimize thermal conduction. Temperature control could be made accurate to ±0.1°C by connecting the thermocouple to the nichrome wire heating coil surrounding the cell. The sides of the aluminum container are 0.5 inches thick and there is a flat top with screws enabling easy placement of the disc in the cell by simply unscrewing the top. This top also enables cooling of the cell by conduction from a flat-bottomed styrofoam insulated aluminum container possessing liquid nitrogen.

The temperature range which can be attained with the equipment available is from 77 to 333 K. These extremes are from near the temperature of liquid nitrogen to the glass-transition temperature of polystyrene. With compressed crystalline solid discs the temperature range can be extended for high melting point solids up to about 373 K, which is near the melting point of the styrofoam cell insulation.

The cell container and the liquid nitrogen container were both insulated with 1.5 inch thick sytrofoam. Fig. III-1 shows a cross-section of a cell used in the dielectric measurements.



FigureIII-1: Three-terminal electrode assembly for dielectric measurements on solid disks.

<u>Key</u>:

LT	Low electrode connection terminal
BN	Boron Nitride insulating support plates
GT	Guard ring connection terminal
H	High electrode
HT	High electrode connection terminal
BR	Brass support plate
R	Release nut
S	Steel clamping springs

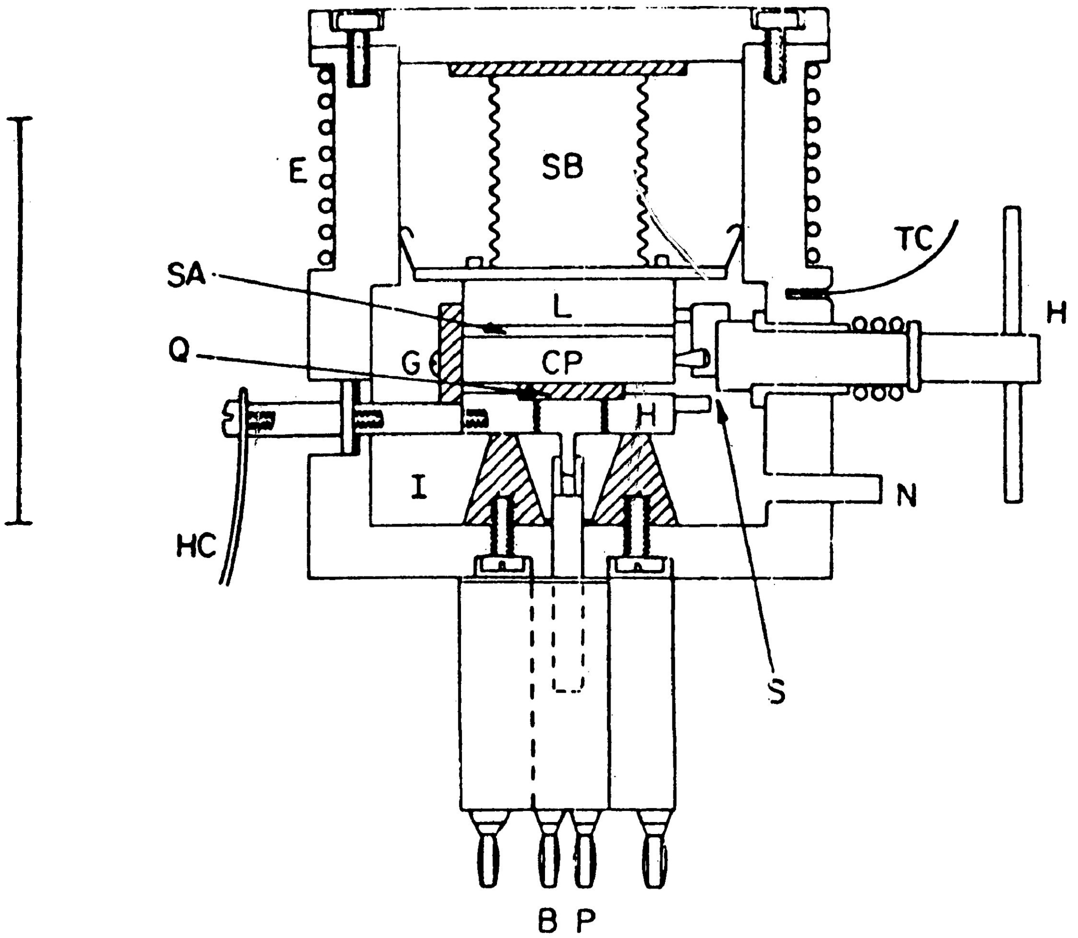
The General Radio bridge enables measurements of the dissipation factor and capacitance. The product of frequency and dissipation factor yields the loss tangent. The General Radio bridge measures the capacitance and conductivity of the capacitor with the matrix sample. Measurements with the General Radio bridge enable calculation of the dielectric permittivity (ε') and the dielectric loss (ε''). The above quantities can be calculated from the following equations:

$$\varepsilon' = \frac{cd_1}{0.2244A} \qquad \text{III-1}$$

$$\varepsilon'' = \frac{\varepsilon' G}{\omega C} \qquad \text{III-2}$$

where C is the capacitance with the sample,
d_1 is the spacing of the capacitor plates,
A is the effective area of the plates,
G is the conductivity of the system, and
ω is the angular frequency of the electric field.

It was possible to extend the frequency range of the dielectric investigations by the use of a Hewlett-Packard Q-meter type HP4342A. This instrument enables dielectric measurements to be made in the frequency range 2.2×10^4 to 5.0×10^7 Hz. The same 2 inch diameter



FigureIII-2: The Morgan tri-electrode cell for Q-meter.
(key on facing page)

Key to Figure III-2 on facing page

SB	Spring bellows
L	Low electrode in contact with case
CP	Centre plate
H	High electrode
I	Insulating supports for high electrode (four)
G	Locating guides for centre plate (three)
TC	Thermocouple in well
H	Handle for operation of switch
N	Nitrogen gas inlet (outlet not shown)
S	Switch assembly
BP	Banana plug connectors for low (case) terminal
HC	High electrode connection strip
Q	Quartz spacer
SA	Sample (2" dia. disk) location
E	Electric heater coil

polystyrene matrix discs as studied with the General Radio bridge could also be studied with the Q-meter. The Q-meter is connected via a model 4342 adapter plate supplied by the Rutherford Research Products Company to a cell designed in this laboratory.

The Q-meter cell whose diagram is shown in Fig. III-2 consists of two capacitors sharing a common plate. One capacitor has the sample between the common plate and the ground while the other has an air gap with a 1 inch diameter quartz disc. The thickness of the air gap can be adjusted by screwing a threaded shaft on which the quartz disc rests. A switch arm is mounted on the common central plate which enables it to be connected to either the low or high side. When the connection is to the low plate the common plate becomes the low plate for the reference capacitor, and so the sample capacitor is removed from the circuit. In the other case when the common plate is connected to the high plate of the reference capacitor, this capacitor is removed from the circuit, and the common plate becomes the high plate of the sample capacitor.

The equation used to determine the dielectric loss (ε'') from the Q-meter is:

$$\varepsilon'' = \frac{\Delta Q}{Q_x} \times \frac{\Delta C_r}{2C_r} \times \frac{d_1}{0.2244A_1} \qquad \text{III-3}$$

where ΔQ is the difference in Q readings for the sample and reference, and x and r refer to measurements made when the switch is connected to either the sample (x) or the reference (r) capacitor,

Q_x is the Q value for the sample capacitor,

ΔC_r is the width of the peak of Q versus C for the reference capacitor, measured at $Q_r\sqrt{2}$,

d_1 is the sample thickness in inches,

A_1 is the area of the cell electrodes in one of the capacitors.

In order to operate the Q-meter the sample disc is placed in the cell and an adjustment of the reference capacitor spacing is made so that both capacitors have the same capacitance. This procedure is performed at room temperature before the actual measurements.

The Q-meter cell is similar to that of the General Radio bridge cell and the temperature control of the cell was accomplished in the same manner. In order to study relaxation processes at low temperatures the cells were cooled with liquid nitrogen. The liquid nitrogen was added to a styrofoam insulated aluminum cylinder with a flat welded bottom. This cylinder was placed on top of the cell, by placing different numbers of sheets of paper between the cell and the cylinder the required temperature could be maintained. The General Radio bridge cell could be cooled down to within a few degrees of liquid nitrogen temperature (77 K). With the Q-meter cell minimum temperatures of about 90 K could be reached.

The majority of compounds studied with the previously mentioned instruments were in the form of polystyrene matrix discs. Preparation of these discs consisted of initially placing the required amount of solute in a pre-weighed, dry, clean,ceramic crucible. Polystyrene (molecular weight = 230,000) pellets were then added to make up a total weight of about four grams of polystyrene and solute. The amount of solute which was used depended on its dipole moment. Solutes with low dipole moments of about one to two Debyes were added to make a 10% solution of solute in solvent. Other solutes which have a high dipole moment of about five Debyes and higher were added to make approximately 5% solutions. Molecules whose dipole moment is between the above limits were studied at about 7% solutions.

Once prepared the polystyrene pellet-solute mixture was dissolved in trans-1,2-dichloroethylene, a non-polar solvent. When the solvent did not dissolve the solute, or was not available other non-polar solvents such as carbon tetrachloride and p-xylene were used. Evaporation of the solute was facilitated by putting the crucible with the mixture in a drying oven at approximately 373 K for about 20 to 30 minutes. At periodic intervals the crucible was removed from the oven and stirred to ensure uniform distribution of the solute. When most of the solvent (e.g., trans-1,2-dichloroethylene) had left the matrix the crucible was placed in a vacuum oven at 358 K to ensure evaporation of nearly all the trans-1,2-dichloroethylene. After about 30 minutes the vacuum was turned off and the crucible was weighed to see whether most of the solvent had been removed from the matrix. A 1% by weight residue of trans-1,2-dichloroethylene could be tolerated in the matrix. If more than this amount was present the sample was returned to the vacuum oven. This procedure was repeated until the tolerance level was reached.

The matrix sample was placed in a stainless steel cylindrical die which has polished tungsten carbide faces and a heating sleeve around the die. Power for the heater came from a controller which sensed the die temperature by a thermocouple. In order to melt the matrix a temperature of 388 K was used. The melting process took about 20 to 30 minutes, after which time the sample was pressed with a pressure 0.8 ton/in^2 to the moving element of the die. Then the heating sleeve was raised and the die cooled by a stream of air from an electric fan. It took about 30 minutes for the die to cool to room temperature. Once the die was disassembled the moving element was removed by application of a pressure of about 0.3 ton/in^2. This produced a disc of 2 inches diameter and about 0.065 inches thick. The disc was then weighed and the thickness determined at six places on the disc with a micrometer, and the average thickness was taken.

The above measurements helped in the calculation of the molar concentration of the solute in the matrix by the following equation:

$$\text{concentration} = \frac{W_s}{M_w} \times \frac{W_d}{W_t} \times \frac{1000}{V_d} \qquad \text{III-4}$$

where W_s is the weight of the solute,

W_d is the weight of the disc,

W_t is the weight of the polystyrene and the solute,

M_w is the molecular weight of the solute, and,

V_d is the volume of the disc in cm^3.

In some cases it was necessary to measure pure compressed solids. This was accomplished by grinding with a mortar and pestle about 5 grams of the solid. The powder was then placed in a stainless steel die and pressed at room temperature with a pressure of 4.7 tons/in^2. All the matrix and compressed solid discs were wrapped in aluminum foil and stored in a desiccator over calcium chloride prior to use.

The data obtained once the polystyrene matrices and compressed solids were studied on the General Radio bridge and Q-meter were analyzed by an IBM 360/70 computer. At each temperature at which dielectric measurements were made on the General Radio bridge readings were taken of the capacitance and dissipation factor (D). The product of D and frequency (f) gave the tan δ:

$$\tan \delta = D \times f \qquad \text{III-5}$$

The General Radio bridge also measures the conductivity of the capacitor with the sample inserted between the capacitor plates. These quantities may be related to the components of the complex dielectric permittivity by Equations III-6 and III-7:

$$\varepsilon'' = C/C_o \qquad \text{III-6}$$

$$\varepsilon'' = G/\omega C_o \qquad \text{III-7}$$

where C is the capacitance of the system,

C_o is the capacitance if the sample is replaced by air,

G is the conductivity of the system, and

$\omega = 2\pi f$ is the angular frequency of the applied field.

Measurements of C_o would require that the electrodes be arranged exactly as they were when they contained the sample, but without the sample this is difficult. Instead, the C_o value may be calculated from Equation III-8:

$$C_o = \frac{0.2244A_1}{d_1}$$

$$C_o = \frac{0.08842A_2}{d_2} \qquad \text{III-8}$$

where A_1 is the effective area of the plates in in.^{2},

A_2 is the effective area in cm.^{2},

d_1 is the spacing of the plates in inches,

d_2 is the spacing in cm., and,

C_o is the capacitance in units of picofarads.

Combination of Equations III-6, III-7, and III-8 leads to Equations III-9 and III-10 which are more convenient for the handling of experimental data:

$$\varepsilon' = \frac{Cd_1}{0.2244A_1} \qquad \text{III-9}$$

$$\varepsilon'' = \varepsilon' G/\omega C \qquad \text{III-10}$$

The values of tan δ along with the capacitance, disc thickness in inches, and cell constant gave the dielectric loss by the use of a computer program, GRDATA, written in the APL language.

With the frequency data, and the dielectric loss corrected for polystyrene, $\Delta\varepsilon'' = \varepsilon''$ (matrix) $- \varepsilon''$ (polystyrene), a computer analysis by the Fuoss-Kirkwood Equation III-11[1] was performed from the following equation along similar lines as indicated by Davies *et al.*[2,3]

$$\cosh^{-1} \frac{\Delta\varepsilon''_{max}}{\Delta\varepsilon''} = \beta \ln \frac{f_{max}}{f} \qquad \text{III-11}$$

The computer program named FUOSSK in the APL language finds the value of $\Delta\varepsilon''_{max}$ which provides the best straight line fit to the plot of:

$$\cosh^{-1} \left(\frac{\Delta\varepsilon''_{max}}{\Delta\varepsilon''}\right) \text{ versus } \ln(f).$$

The slope of the line, the frequency of maximum dielectric loss (f_{max}) and the line's intercept on the $\cosh^{-1}$ axis enable evaluation of the value of the distribution parameter (β). Fig. V-1 (Chapter V) shows a sample plot of Δε'' versus log frequency. The errors in the $\log f_{max}$ are usually ±0.1 or less.

Standard statistical techniques provide a means of estimating errors in fitting a straight line to a set of graph points. In order to minimize the mean square deviation of N experimental points (x_i, y_i) from the best-fit line of the form $Y = ax + b$, the slope and intercept of the calculated line are given by Equations III-12 and III-13:

$$a = \frac{\sum_{i=1}^{N} (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{N} (x_i - \bar{x})^2} \qquad \text{III-12}$$

$$b = \bar{y} - a\,\bar{x} \qquad \text{III-13}$$

where, $\bar{x}$ and $\bar{y}$ are the mean values of x and y, respectively.

The statistical variances S_a^2 and S_b^2 of the slope and intercept, respectively, are given by Equations III-14 and III-15:

$$S_a^2 = \frac{S_E^2}{\sum_{i=i}^{N} (x_i - \bar{x})^2} \qquad \text{III-14}$$

$$S_b^2 = S_E^2 \left[\frac{1}{N} + \frac{\bar{x}^2}{\sum_{i=i}^{N} (x_i - \bar{x})^2} \right] \qquad \text{III-15}$$

where $$S_E^2 = \frac{\sum_{i=i}^{N} (y_i\ (\text{obs}) - y_i\ (\text{calc}))^2}{N - 2}, \text{ and}$$

$$Y_i\ (\text{calc}) = ax_i + b$$

From these variances one may calculate confidence intervals for each slope and intercept as $\pm t\sqrt{S_E^2}$ and $\pm t\sqrt{S_b^2}$, respectively, where t is the value obtained from a "Student t-Table" for the desired level of confidence and (N-2) degrees of freedom. Since two points define a straight line, there are (N-2) degrees of freedom in fitting a line to N experimental points.

Utilization of the above statistical methods allows the β and $\log f_{max}$ values to be assigned 90%, 95%, 98%, and 99% confidence intervals. The experimental errors given in this thesis are quoted from the 90% probability that the true value of the parameters are within that interval centered about the parameter's calculated value.

The ε_∞ value is also determined by computer analysis by a programme named EINF in the APL computer language. The programme makes use of an equation such as III-16, which was developed by Cole and Cole.[4]

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau_0)^{(1-\alpha)}} \qquad \text{III-16}$$

where τ_0 is the mean relaxation time for the whole system, and
α is the distribution parameter which has values from 0 to 1.

Equation III-16 can be separated into real and imaginary parts, as shown in Equations III-17 and III-18:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1 + (\omega\tau_0)^{(1-\alpha)} \sin(\alpha\pi/2)}{1 + 2(\omega\tau_0)^{(1-\alpha)} \sin(\alpha\pi/2) + (\omega\tau_0)^{2(1-\alpha)}} \qquad \text{III-17}$$

$$\frac{\varepsilon''}{\varepsilon_o - \varepsilon_\infty} = \frac{(\omega\tau_o)^{(1-\alpha)} \cos (\alpha\pi/2)}{1 + 2(\omega\tau_o)^{(1-\alpha)} \sin (\alpha\pi/2) + (\omega\tau_o)^{2(1-\alpha)}} \qquad \text{III-18}$$

The Cole-Cole distribution factor α may be obtained from the Fuoss-Kirkwood distribution parameter (β) by means of Equation III-19[5]:

$$\beta = \frac{1 - \alpha}{\sqrt{2} \cos \left(\frac{\pi(1-\alpha)}{4}\right)} \qquad \text{III-19}$$

Use of Equations III-17 and III-19 in conjunction with experimental values of ε' as a function of frequency enable several estimates of ε_∞ to be made by the use of the computer programme EINF in the APL computer language. This programme averages the estimates.

Dipole moments (μ) were also determined by computer analysis using the Debye Equation III-20[6] and the Onsager Equation III-21[7]:

$$\mu^2 = \frac{27000 \text{ kT } (\varepsilon_o - \varepsilon_\infty)}{4\pi NC(\varepsilon_m'+2)^2} \qquad \text{III-20}$$

$$\mu^2 = \frac{9000\ kT\ (2\varepsilon_o + \varepsilon_\infty)(\varepsilon_o - \varepsilon_\infty)}{4\pi NC\varepsilon_o(\varepsilon_\infty+2)^2} \qquad \text{III-21}$$

where $(\varepsilon_o - \varepsilon_\infty) = 2\varepsilon''_{max}/\beta$ (Eqn. II-31),

ε'_m is the permittivity at $\omega_{max} = \frac{1}{\tau_o}$,

ε_o is the static permittivity,

N is Avogadro's number

C is the solute concentration in moles per litre,

k is the Boltzmann constant, 1.39054×10^{-16} erg k^{-1}, and

T is the absolute temperature.

These two equations yield μ in units of e.s.u.—cm. It is more common to express the parameter in Debye units, where 1 D = 1×10^{-18} e.s.u. - cm.

The experimental data also enabled the calculation of dipole moments at temperatures above or below those where loss maxima were observed. This was accomplished by the use of a computer programme named DIPEXT in the APL computer language. The computer extrapolation technique was similar to that used by Davies and Swain.[3]

Energy barriers for the dielectric relaxation processes were calculated by use of the Eyring rate Equation III-22:

$$\tau = \frac{h}{kT} \exp (\Delta G/RT) \qquad \text{III-22}$$

where τ is the relaxation time,

h is Planck's constant,

ΔG is the free energy,

k is the Boltzmann constant,

T is the absolute temperature, and

R is the universal gas constant.

The enthalpy of activation (ΔH_E) and the entropy of activation (ΔS_E) are obtained by the use of Equation III-23:

$$\ln(T\tau) = \frac{\Delta H_E}{RT} - \frac{\Delta S_E}{R} \ln(h/k) \qquad \text{III-23}$$

A computer programme named EYRING in the APL computer language was utilized to make an Eyring plot of $\ln(T\tau)$ versus $(\frac{1}{T})$. From the slope of the stright line, ΔH_E, the enthalpy of activation was determined, and from the intercept the entropy of activation, ΔS_E, was found. The EYRING programme also gave errors for ΔH_E and ΔS_E values.

A programme, VDIFF in APL, enabled the determination of the energy difference V between the two sides of the activation energy barrier. This was accomplished by plots of $\ln(\varepsilon''_{max}T)$ versus $(1/T)$,[8] where:

$$\varepsilon''_{max} = \frac{B}{kT} \exp(-V/RT) \qquad \text{III-24}$$

where B is proportionality constant.

The results of the various analyses are given in Tables in each chapter.

The compounds investigated were all purchased from commercial sources, except for di-p-tolyl sulfide and di-4-pyridyl sulfide which were synthesized. All commercially available compounds were used as they were after suitable storage. Volitile compounds such as t-butyl sulfide and di-allyl sulfide were stored below room temperature. p-Nitrodiphenyl ether was checked for purity by a melting point determination. n-Butyl ether was distilled and properly stored. In Chapter IV the syntheses of di-p-tolyl sulfide and di-4-pyridyl sulfide are discussed.

REFERENCES

1. N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "Dielectric Properties and Molecular Structure", Van Nostrand Reinhold Co., London, England, (1969), p. 292.
2. M. Davies and A. Edwards, Trans. Faraday Soc., 63, (1967), p. 3163.
3. M. Davies and J. Swain, Trans. Faraday Soc., 67, (1971), p. 1637.
4. C. P. Smyth, "Dielectric Behaviour and Structure", McGraw-Hill Book Co. Inc., New York, New York, U.S.A., (1955), p. 68.
5. N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "Dielectric Properties and Molecular Structure", Van Nostrand Reinhold Co., London, England, (1969), p. 235.
6. Ibid., p. 292.
7. C. J. F. Bottcher, "Theory of Electric Polarization", Elsevier Publishing Co., Amsterdam, The Netherlands, (1952), p. 323.
8. R. J. Meakins, Trans. Faraday Soc., 51, (1955), p. 371.

CHAPTER IV

SYNTHETIC STUDIES OF SOME DIARYL SULFIDES

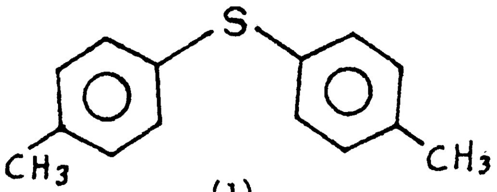
INTRODUCTION

It was mentioned in the third chapter that not all diaryl sulfides used in this study are available commercially. The two aromatic sulfides which were required for dielectric relaxation studies were di-p-tolyl sulfide[1] and di-4-pyridyl sulfide[2]. Synthesis of the first compound was achieved by a study of reduction techniques of diaryl sulfones, while the second one was synthesized by a published[1,2] method.

Although diaryl sulfides can be produced by a number of synthetic methods it was of interest to investigate the problem of reducing diaryl sulfones directly to the corresponding sulfides, since this problem has not received extensive study. The synthesis of di-4-pyridyl sulfide as reported by Jerchal *et al.*[1] was attempted, but did not give good yields and pure product. This synthesis was therefore re-investigated and modified in order to obtain larger quantities of the pure compound.

Synthesis of Diaryl Sulfides

Diaryl sulfides can be synthesized by a number of methods such as, nucleophilic substitution reactions (3) of aryl halides with nucleophiles, such as ArS^-. When a thiol is the reagent the first



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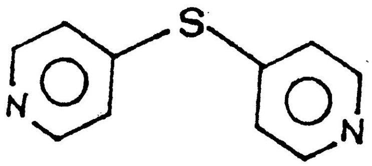

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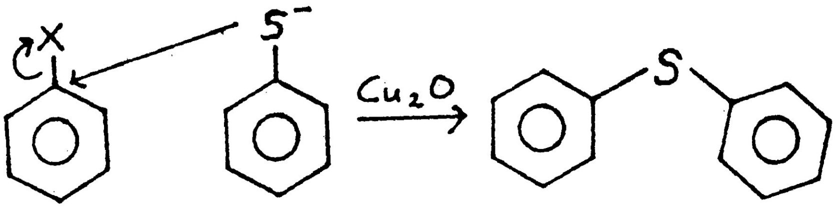

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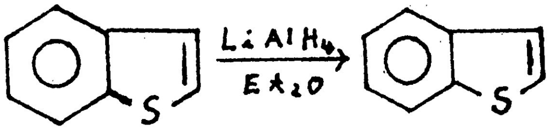

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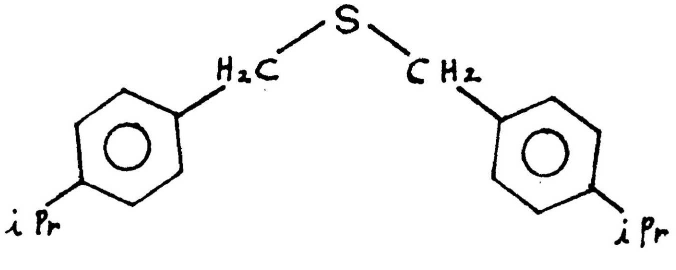

iPr = isopropyl

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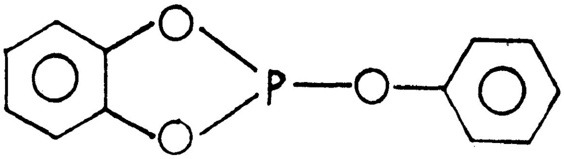

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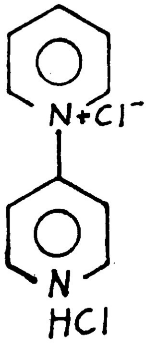

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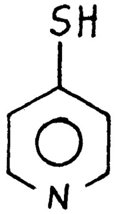

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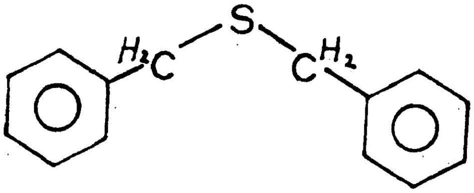

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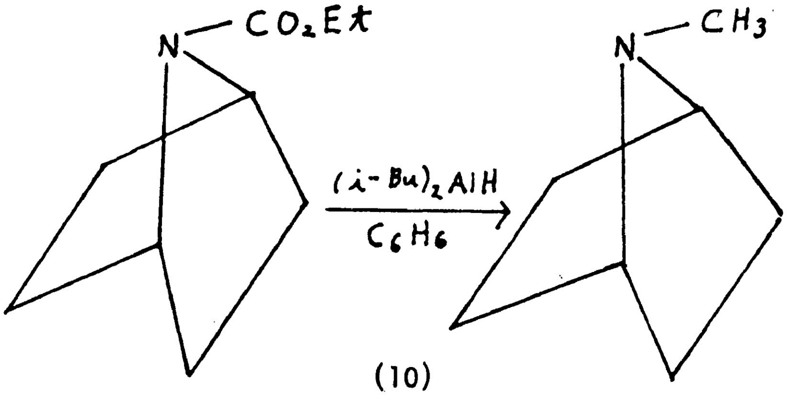

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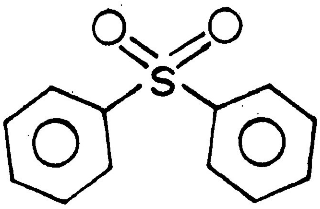

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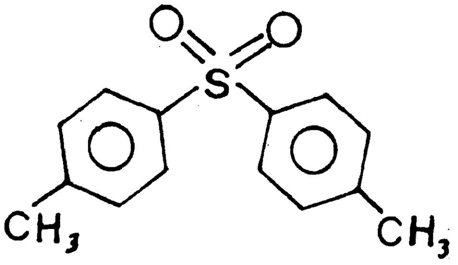

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step is the visible formation of its cuprous salt, CuSR, which then reacts with the halide, and the diaryl sulfide is produced.

Another method of synthesizing diaryl sulfides is from the corresponding disulfides using benzene alkylation conditions. For example, the reaction of $Me_2CHSSCHMe_2$ with benzene in the presence of $AlCl_3$ at 35°C and 80°C gives a mixture which contains $(Me_2CH)_2S$, $PhSCHMe_2$, Me_2CHSH, Ph_2S, thiophene, cumyl sulfide (4), and H_2S.

Besides the above mentioned types of reactions diaryl sulfides can be obtained by the reduction of sulfoxides. Sulfoxides can be reduced to sulfides by a relatively large number of classical and novel reducing agents, such as cyanoborohydrides-crown ether mixtures[3]. The reduction of sulfoxides can also be performed under mild conditions by a new reducing agent, 2-phenoxy-1,3,2-benzodioxaphosphole(5).[4] Reduced iron (Fe^{2+})[5] can also reduce diaryl sulfoxides to the sulfides quantitatively. Catalytic reduction of dimethyl sulfoxide and other sulfoxides with a bromine-hydrobromic acid mixture has been reported.[6]

Sulfoxides have also been reported[7] to be reduced to the sulfides by treatment with titanium chloride. D. Chasar has also reported[8] that a sodium borohydride/cobalt chloride mixture can reduce diphenyl sulfoxide to diphenyl sulfide in an excellent yield. S. Yanagida *et al.*[9] have found that Tin(II) chloride-HCl can reduce diphenyl sulfoxide to the sulfide in good yield.

Since a large number of reducing agents are available for reducing diaryl sulfoxides to the corresponding diaryl sulfides, it is reasonable to investigate whether these reducing agents can also reduce diaryl sulfones. This is particularly interesting since there have been few studies of the reduction of sulfones.

A literature survey has shown that there are few compounds reported which can reduce sulfones. These reducing agents are mostly aluminum hydrides such as lithium aluminum hydride,[10] lithuim-trimethyl aluminum hydride,[11] lithium-t-butoxide aluminum hydride,[10] and diisobutylaluminum hydride.[12] Lithuim aluminum hydride has been used to reduce the cyclic sulfone (6). Lithuim trimethyl aluminum hydride also reduces sulfones but in low yields.[11] A 26% solution of diisobutylaluminum hydride was found[12] to reduce sulfones to sulfides in a 57 to 100% yield. Use of this reducing agent enabled the reduction of dibutyl sulfone and diphenyl sulfone to the sulfides.

Diisobutylaluminum hydride along with a series of other potential reducing agents were tried in attempts to reduce diphenyl sulfone and di-p-tolyl sulfone to the corresponding sulfides, in a reasonably high yield.

In the present study the first attempt to reduce diphenyl sulfone to diphenyl sulfide was with a cobalt chloride hexahydrate-sodium borohydride system, which has been reported[8] to reduce aromatic sulfoxides. Next, nickel chloride hexahydrate-sodium borohydride was tried. The third attempt at reducing diphenyl sulfone was with the classical reducing agent $LiAlH_4$. This seemed reasonable since Brown *et al.*[10] have reported that it reduced alkyl sulfones and some cyclic sulfones to sulfides. In the study presented in this chapter the reaction conditions, such as period of heating, and quantities of reagents were modified in order to observe if the yield of diphenyl sulfide would increase. The yield of diphenyl sulfide, however, was very low (7%) when $LiAlH_4$ was used as the reducing agent.

The reduction of diphenyl sulfone was also attempted with a new organometallic compound[15] which is very easily oxidized. The compound is nickel chloride-tris-triphenyl phosphine, which is very air-sensitive. Since this compound is quite reactive toward oxygen, it was felt that it might be able to remove the oxygen atom(s) from the sulfonyl group of diaryl sulfones. A number of different reaction conditions such as period of heating and ratio of reactants were tried with this compound in order to reduce diphenyl sulfone. Triphenyl phosphene was also tried, as was a nickel chloride/triphenyl phosphine/sodium borohydride mixture. A mixture of nickel chloride/triphenylphosphine was also used in an attempt to reduce diphenyl sulfone. None of the above systems were successful in reducing diphenyl sulfone.

Stannous chloride hexahydrate and also zinc/HCl were studied as possible reducing agents of sulfones. Finally, a 20% solution of diisobutylaluminum hydride in hexane was examined as a reducing agent. This solution was able to reduce diphenyl sulfone to diphenyl sulfide in a 60% yield. This reducing agent was then utilized to reduce di-p-tolyl sulfone to di-p-tolyl sulfide.

Standard analytical techniques, such as column and gas chromatography, thin layer chromatography (t.l.c.), infrared spectroscopy, mass spectroscopy, and elemental analysis were used to identify the products of the reactions.

Preparation of Di-4-pyridyl Sulfide(2)

Di-4-pyridyl sulfide was not commercially available, and thus had to be synthesized. Since di-4-pyridyl sulfoxide and sulfone were also not commercially available the reduction techniques used to obtain di-p-tolyl sulfide could not be used. A method for preparing di-4-pyridyl sulfide was found in the literature.[1]

The synthesis of di-4-pyridyl sulfide was attempted by the reaction of N-(4-pyridyl)pyridinium dichloride(7) with hydrogen sulfide gas.[1] The above reaction failed to produce any noticeable yield of di-4-pyridyl sulfide.

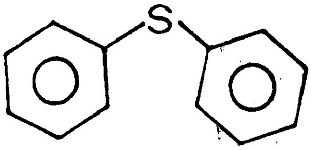
The reaction of 4-mercaptopyridine (8) with N-(4-pyridyl)-pyridinium dichloride prepared according to Jerchel *et al.*[1] resulted in a low yield of di-4-pyridyl sulfide. Once N-(4-pyridyl)pyridinium dichloride was prepared according to the method of Bowden and Green[14], the reaction of N-(4-pyridyl)pyridinium dichloride with 4-mercaptopyridine resulted in a larger yield of di-4-pyridyl sulfide, When the above reactants were mixed and heated at 150°C for 30 minutes a 23% yield of di-4-pyridyl sulfide was obtained.

In order to obtain larger yields of di-4-pyridyl sulfide the period of heating was shortened, and the reaction was carried out in dry nitrogen gas. A reason for shortening the period of heating is that the reactants and products might undergo thermal decomposition with prolonged heating at 150°C. Once the period of heating was shortened to several minutes good yields (94%) of di-4-pyridyl sulfide were obtained.

RESULTS AND DISCUSSION

The Reduction of Diaryl Sulfones

Since a sodium borohydride-cobalt chloride mixture was reported[8] to reduce dibenzyl sulfoxide to dibenzyl sulfide(9) and diphenyl sulfoxide to diphenyl sulfide it seemed worthwhile to



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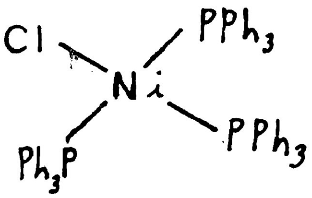

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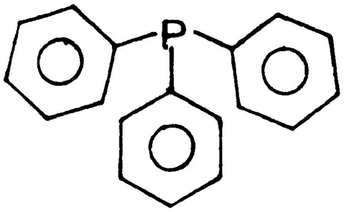

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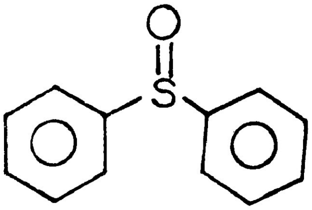

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investigate whether it would reduce diaryl sulfones. Analysis of the reaction mixture showed that the sodium borohydride-cobalt chloride mixture does not reduce diphenyl sulfone.

A second attempt at reducing diphenyl sulfone with a nickel chloride-sodium borohydride complex was equally unsuccessful.

A reduction of diphenyl sulfone with lithuim aluminum hydride was attempted, according to the method of Brown *et al.*[10] Thin layer chromatography of the reaction product indicated one component, which corresponded to diphenyl sulfone. The infrared spectrum and the melting point of the reaction product also indicated that the reaction failed to reduce diphenyl sulfone to diphenyl sulfide in any significant amount.

Gas chromatography with SE-30 liquid phase material indicated the presence of diphenyl sulfide (13), as did a mass spectrum. The yield of diphenyl sulfide, however, was 7%.

A stannous chloride-HCl mixture was used in an attempt to reduce diphenyl sulfone. A t.l.c. (silica gel/benzene) of the reaction mixture indicated the presence of three components. A very small spot near the solvent front corresponded to diphenyl sulfide. This indicates that stannous chloride reduces diphenyl sulfone to diphenyl sulfide (13) in a low yield (20%).

An organometallic compound, nickel chloride tris-triphenyl phosphene (14) was also studied as a potential reducing agent of diphenyl sulfone. The preparation of this compound will be discussed in the experimental section. The melting point (75°C) of the product is close in magnitude to that of diphenyl sulfoxide (16) (70°C) and triphenyl phosphene (15) (77°C). A t.l.c. of the reaction product indicated three components, one of which was near the solvent front. Diphenyl sulfide (13) and triphenyl phosphene both show up near the solvent front. The experimental results of the above reaction are therefore inconclusive.

The above reaction was repeated under more vigorous conditions of heating, and prolongation of reaction time. Negative results were once again observed.

The reduction of diphenyl sulfone was attempted with only triphenyl phosphene as the reducing agent, with a nickel chloride/triphenyl phosphene/sodium brohydride mixture (1:4:6 molar ratio), and with a zinc-HCl mixture. Negative results were obtained from these experiments.

Gardner[12] reported that a 26% diisobutylaluminum hydride

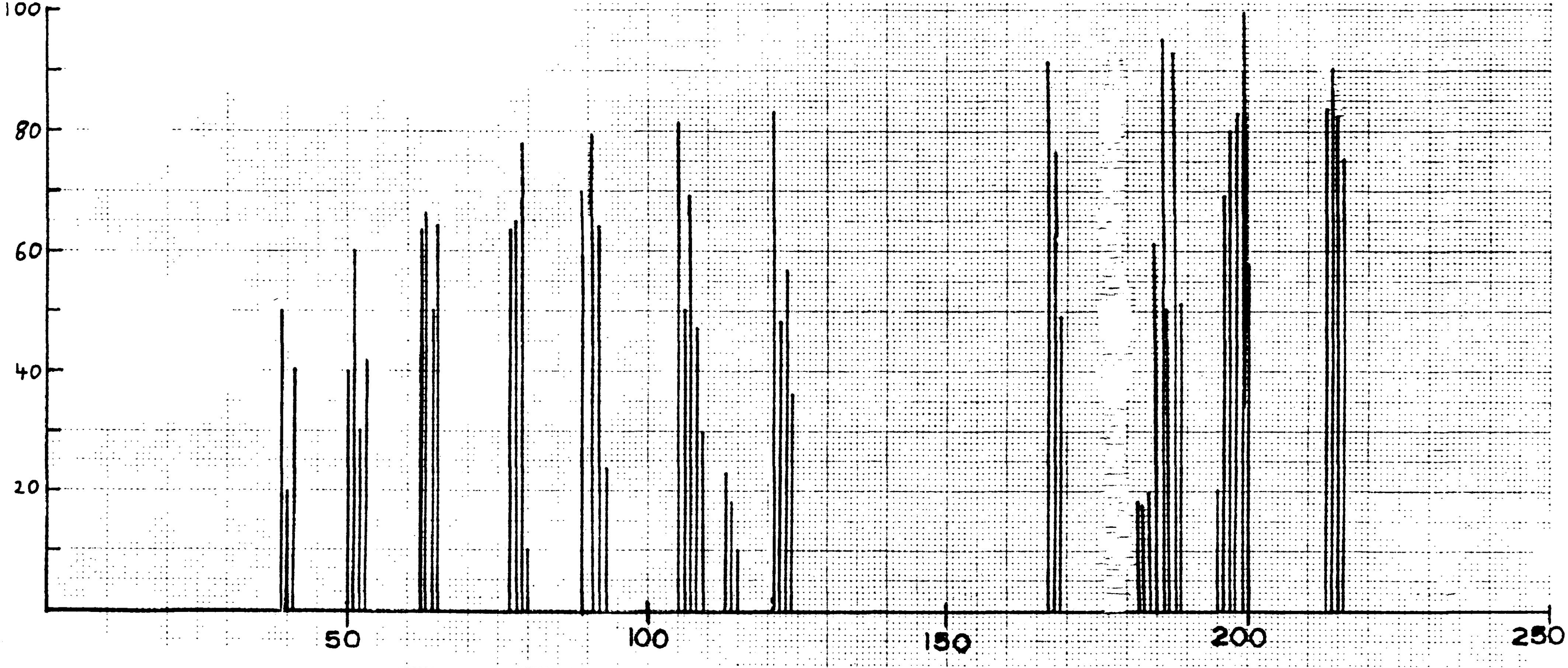


FIGURE IV-1: MASS SPECTRUM OF DI-P-TOLYL SULFIDE

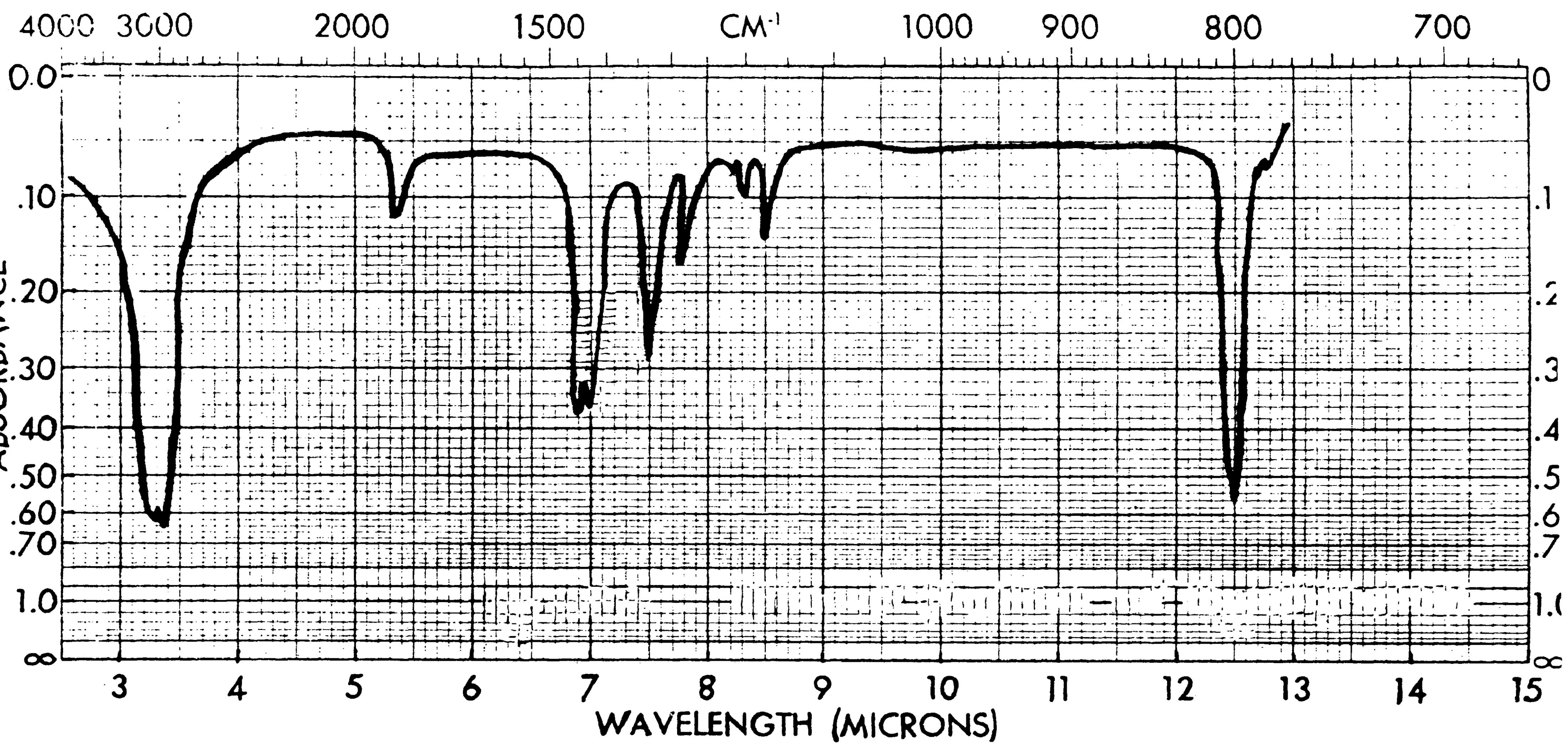
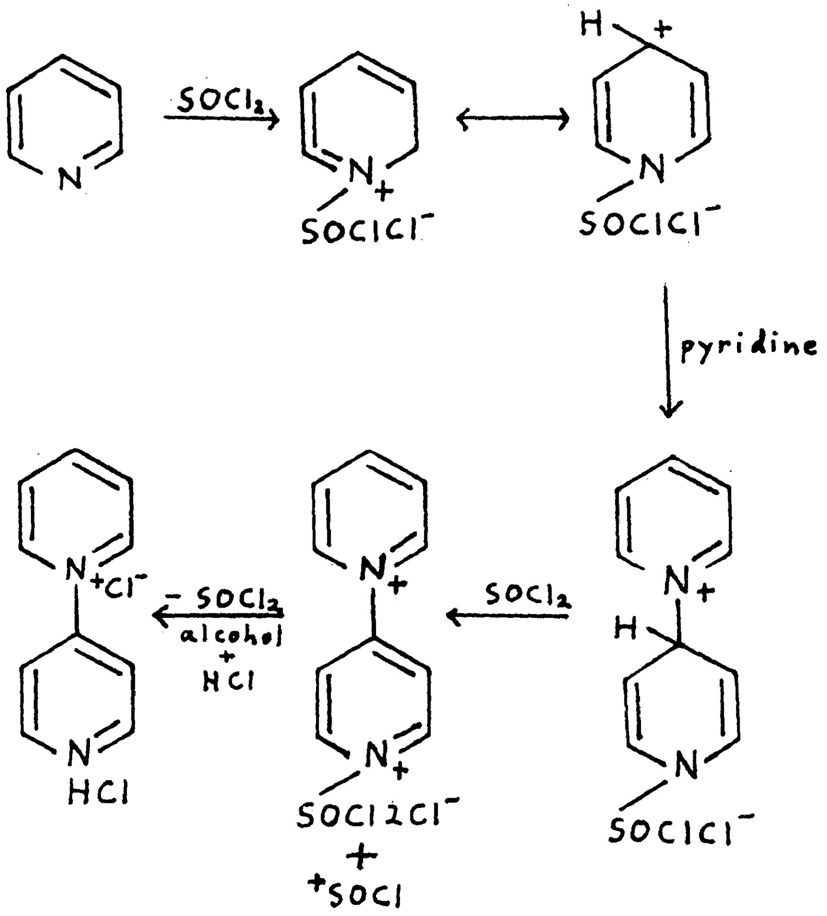


FIGURE IV-2 INFRARED SPECTRUM OF DI-p-TOLYL SULFIDE IN NUJOL solution in hexane reduced dibutyl sulfone in a 57-100% yield. The solution was also found to reduce diphenyl sulfone to diphenyl sulfide. Diisobutylaluminum hydride was also reported[13] to reduce an ethylcarboxy group to a methyl group in the synthesis of N-methyl-7-azanorbornene (10).

A 20% solution of diisobutylaluminium hydride in n-haxane was found to reduce diphenyl sulfone to diphenyl sulfide in a 50% yield. Column chromatography yielded some pure diphenyl sulfide (13) so that the reagent appears potentially suitable for reducing di-p-tolyl sulfone.

It was found that refluxing di-p-tolyl sulfone with the above solution for three days gave the best yield (60%) of di-p-tolyl sulfide, after column chromatography of the crude product. In the mass spectrum (Fig. IV-1) of the pure product the molecular ion of the expected product (1) at m/e 214 is present. In addition to the molecular ion the spectrum displays strong peaks corresponding to the ions $(p\text{-}CH_3Ph)PhS^+$, m/e 199, and Ph_2S^+, at m/e 186. The melting point of the pure product compares well with the literature value (57°C). The infrared spectrum (Fig. IV-2) has a strong band characteristic of a C-S bond at ν_{max} 800 cm^{-1}.

Synthesis of Di-4-pyridyl Sulfide


SOCl₂
SOClCl⁻
H +
SOClCl⁻
pyridine
N+
H
SOClCl⁻
SOCl₂
N+
SOCl2Cl⁻
+
+SOCl
N+Cl⁻
- SOCl₂
alcohol
+
HCl
N
HCl

SCHEME 1

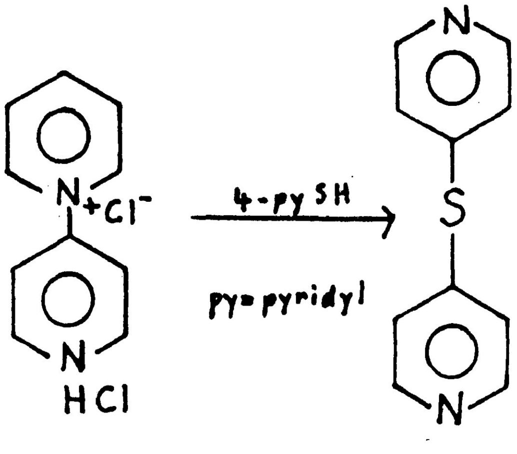
Di-4-pyridyl sulfide was attempted to be prepared according to the procedure of Jerchel *et al.*[1] in which N-(4-pyridyl)pyridinium dichloride was reacted with hydrogen sulfide. N-(4-pyridyl)pyridinium dichloride, however, had to be synthesized separately according to the method of Koenigs and Greiner.[2]

The synthesis of di-4-pyridyl sulfide according to the above procedures was unsuccessful. One reason may have been that the N-(4-pyridyl)pyridinium dichloride prepared by the method of Koenigs and Greiner[2] did not have the properties of the pure compound.[1] An improved preparation of the dichloride was reported by Bowden and Green;[14] this method gave a purer product (scheme 1).

The preparation and purification of N-(4-pyridyl)pyridinium dichloride by the alternative method yielded pale yellow crystals with a melting point of 158°C, which compares well with the literature value[14] (158°C). The pure product was used in the preparation of di-4-pyridyl sulfide according to the procedure of Jerchel *et al.*[1] in which N-(4-pyridyl)pyridinium dichloride was reacted with hydrogen sulfide gas.

The melting point (105-110°C) of the reaction product is too high to be due to di-4-pyridyl sulfide (mp, 68°C). It is also too low to be due to 4-mercaptopyridine (mp, 177°C), which is prepared with reaction conditions similar to those for preparing di-4-pyridyl sulfide.[1] In the mass spectrum the peak corresponding to the molecular ion of 4-mercaptopyridine is absent. The fragmentation pattern suggests that a polysulfide may have been formed. This is supported in part by the infrared spectrum which has a strong band characteristic of the C-S bond.

The original papers from which the experimental procedure for the synthesis of di-4-pyridyl sulfide were obtained were too vague, and not specific as to the experimental reaction conditions, therefore, the method of Jerchel *et al.*[1] was used according to the reaction:



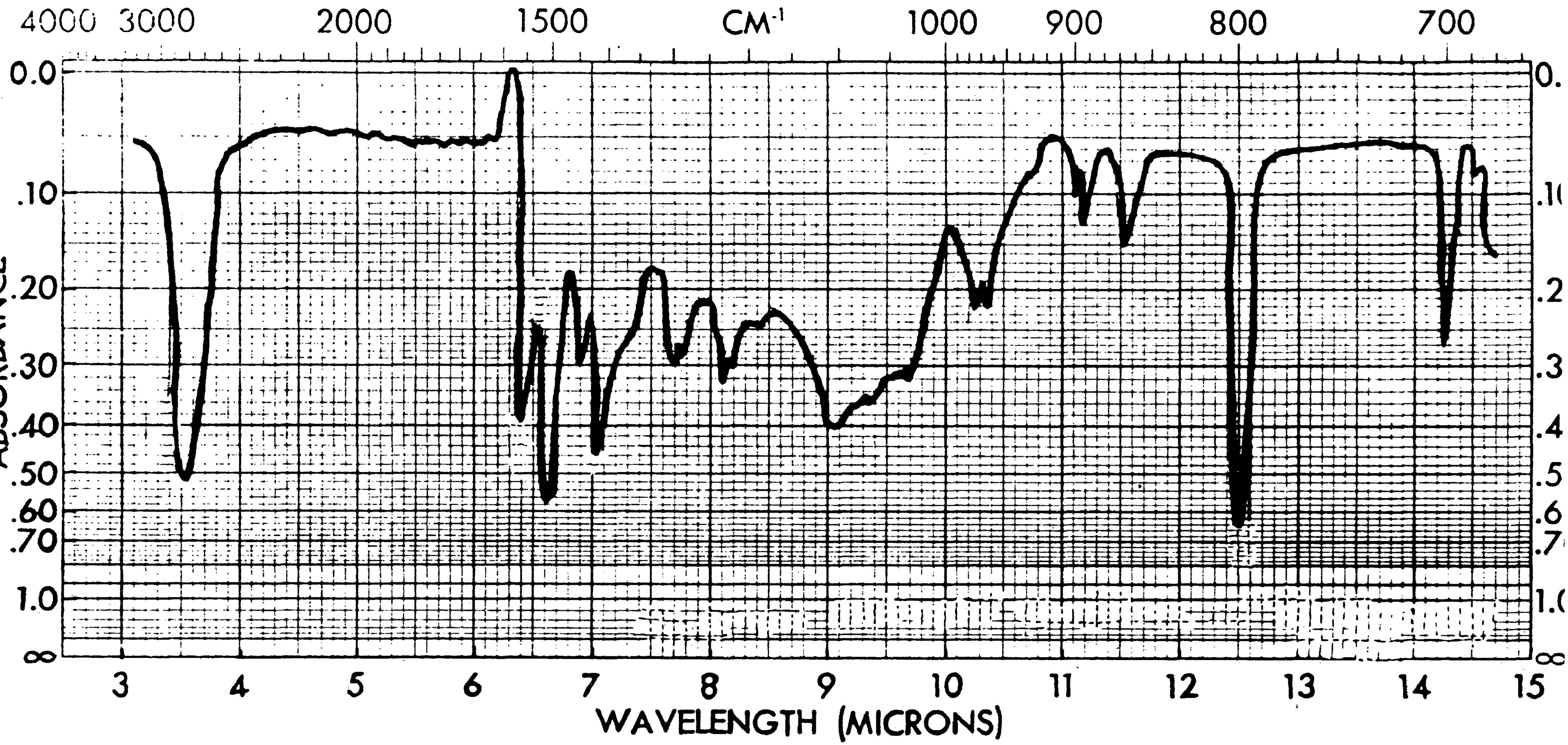


FIGURE IV-3: INFRARED SPECTRUM OF DI-4-PYRIDYL SULFIDE IN NUJOL

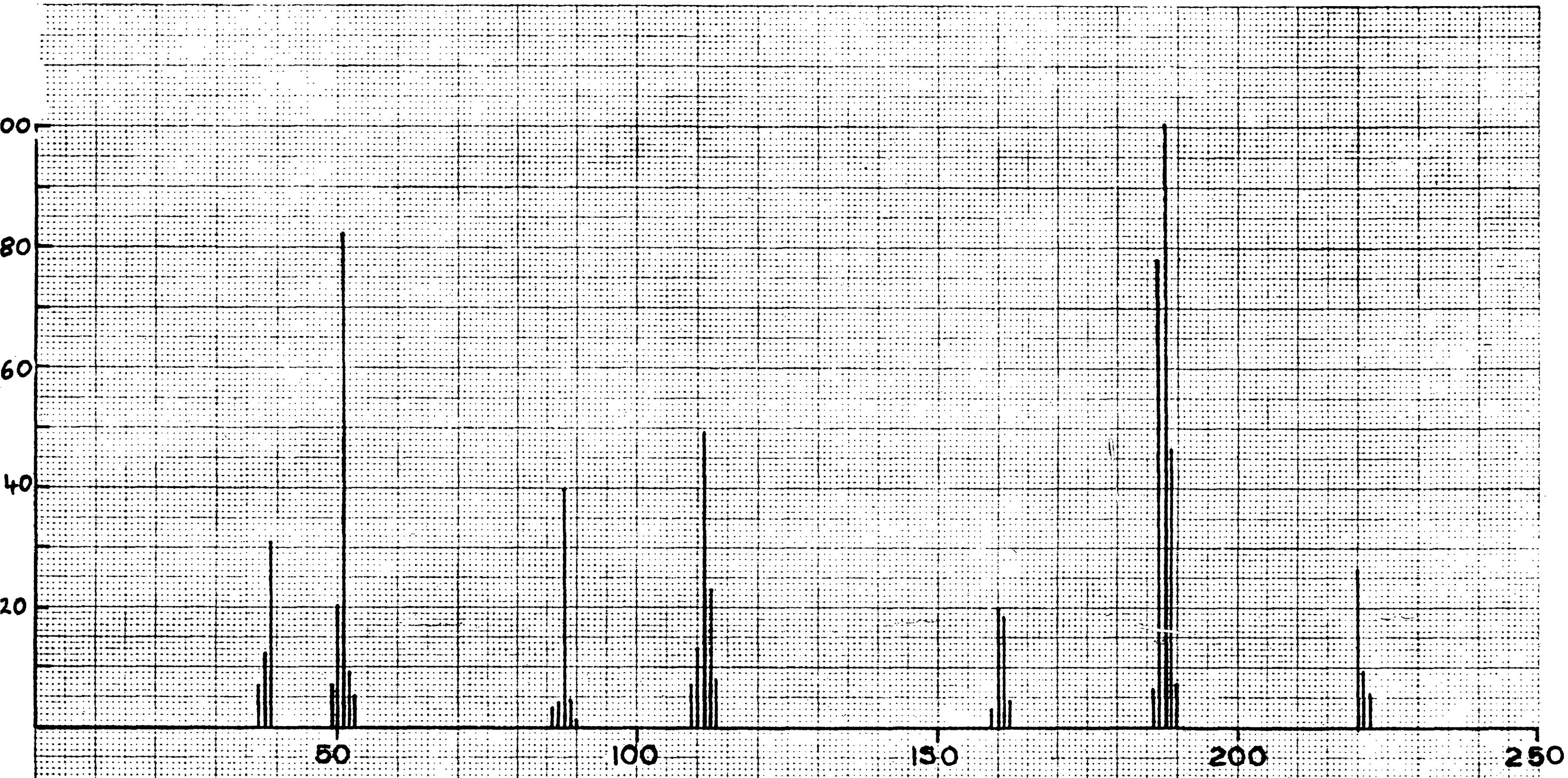


FIGURE IV-4: MASS SPECTRUM OF DI-4-PYRIDYL SULFIDE

Experiments were performed to determine which period of heating at 150°C results in the largest yield of product. The results are shown in Table IV-1. It is noticeable from the Table that a heating period of about 10 minutes results in the largest yield of product (94%). T.l.c.'s were taken of the reaction products with methanol as the eluent, and 4-mercaptopyridine and N-(4-pyridyl)-pyridinium dichloride as standards. The reaction products each showed one spot at the same Rf value. These spots did not correspond to 4-mercaptopyridine or N-(4-pyridyl)pyridinium dichloride. An infrared spectrum of one of the reaction products was taken. It showes a strong peak at 800 cm^{-1} which is due to a C-S bond vibration mode (Fig. IV-3). A mass spectrum (Fig. IV-4) of the product has a major peak at m/e = 188 which was assigned to the molecular ion of di-4-pyridyl sulfide. Other peaks were observed at m/e 111, which was assigned to the molecular ion of 4-mercaptopyridine and at m/e = 220 which was assigned

TABLE IV-1

Wt. of N-(4-pyridyl)-pyridinium dichloride (gm)	Wt. of 4-mercapto-pyridine (gm.)	Period of Heating (min) at 150°C	Wt. of Product (gm.)	Yield (%)
0.60	0.25	30	0.10	23
1.00	0.40	20	0.48	70
0.69	0.28	10	0.43	94

to the molecular ion of di-4-pyridyl disulfide. This molecular ion was expected since a mass spectrum showed that di-4-pyridyl disulfide was present in the 4-mercaptopyridine.

The melting point of the product is 66°C which corresponds well with the melting point (67-68°C) of di-4-pyridyl sulfide. The elemental analysis shows that the reaction product is relatively pure. The di-4-pyridyl sulfide synthesized by the above methods was found to behave as expected during dielectric relaxation measurements (see Chapter VII).

CONCLUSIONS

Synthesis of Di-p-tolyl Sulfide

A conclusion which can be drawn from the preceeding section is that many reducing agents which do reduce sulfoxides do not affect the reduction of diaryl sulfones. Only diisobutylaluminium hydride was found to reduce diphenyl sulfone to diphenyl sulfide in a significant yield (60%). Di-p-tolyl sulfone was reduced to di-p-tolyl sulfide in a 56% yield by diisobutylaluminum hydride.

The cobalt and nickel borohydrides have been found to reduce sulfoxides, however, they are ineffective as reducing agents of diaryl sulfones. $LiAlH_4$ was able to reduce diphenyl sulfone to diphenyl sulfide, but in very low yields (7%), as shown by gas chromatograms. Air-sensitive organometallic compounds such as $NiCl(PPh_3)_3$ did not appear to reduce diphenyl sulfone, but a nickel chloride/triphenyl phosphene/sodium borohydride mixture appeared from a t.l.c., with a diphenyl sulfoxide standard, to reduce in low yield (∿10%) diphenyl sulfone to diphenyl sulfoxide. Zinc was also tried as a reducing agent,but failed to reduce diphenyl sulfone.

A stannous chloride hexahydrate-HCl mixture was found to reduce diphenyl sulfone to diphenyl sulfide in a 20% yield. Since higher yields were necessary and since Gardner[12] had found that diisobutylaluminum hydride reduced dibutyl sulfone, it was found that a 20% hexane solution of diisobutyl aluminum hydride reduced diphenyl sulfone and di-p-tolyl sulfone in 60 and 56% yields repectively. The yield of sulfide was found to increase by increasing the period of refluxing, using a higher boiling point solvent (toluene), and adding an excess of diisobutylaluminum hydride solution. Methanol was found to be a good solvent for recrystallization.

The reasons why diaryl sulfones are difficult to reduce are not clear. Perhaps electronic[17] and steric factors may play a role in the behaviour of diaryl sulfones towards reducing agents.

Considerable information has been gathered with respect to the electronic properties of diaryl molecules.[16,17] Dielectric studies such as those presented in Chapter V ,as well as dipole moment studies[18] of aryl sulfones and ultraviolet spectroscopic studies[19] indicate that there is significant conjugation[19] of the aromatic rings with the bridging groups in aromatic sulfones. Since the exact mechanism by which sulfones are reduced is not clear it is difficult to state the importance of the above factor in reduction.

Another possible explanation of why diaryl sulfones are difficult to reduce may be steric factors. In diaryl sulfones x-ray analysis[17] has shown that the rings are orientated orthogonally, so that they may make it more difficult for a reducing agent to react with the sulfonyl group.

It has been shown[12] that only very powerful reducing agents such as diisobutylaluminum hydride can reduce symmetrical diaryl sulfones, such as diphenyl sulfone and di-p-tolyl sulfone to the sulfides in significant yields. More research is necessary in order to find other reducing agents which can reduce diphenyl sulfone, di-p-tolyl sulfone,and other diaryl sulfones in even larger yields than 60%, one might be di-t-butyl aluminum hydride.

Synthesis of Di-4-pyridyl Sulfide

The synthesis of di-4-pyridyl sulfide was first attempted by the reaction of N-(4-pyridyl)pyridinium dichloride with hydrogen sulfide gas in pyridine and chloroform (scheme 1). This method was chosen since 53% yields of di-4-pyridyl sulfide were reported by Jerchel *et al.*[1]

The N-(4-pyridyl)pyridinium dichloride was also prepared by the method of Jerchel *et al.*[1] as in scheme 1. A t.l.c. and a mass spectrum of the reaction product showed that di-4-pyridyl sulfide was not formed in any significant quantity. Repeated attempts of the above procedure were unsuccessful. N-(4-pyridyl)pyridinium dichloride was prepared by the method of Bowden and Green,[14] yet the reaction of N-(4-pyridyl)pyridinium dichloride with pyridine and hydrogen sulfide was unsuccessful in producing a significant yield of di-4-pyridyl sulfide. A method of obtaining larger yields of di-4-pyridyl sulfide is by the reaction of N-(4-pyridyl)pyridinium dichloride with 4-mercaptopyridine, for ten minutes at 150°C in dry nitrogen gas. Under these conditions a product yield of 94% was obtained. The product, after several recrystallizations, was characterized by infrared, t.l.c., melting point, mass spectral, and elemental analyses. Dielectric studies of the pure product showed that it behaved as would be expected of di-4-pyridyl sulfide (see Chapter VII).

EXPERIMENTAL

Introduction

The physical measurements in this study were performed as specified below, unless otherwise stated.

The infrared spectra were recorded on a Perkin Elmer 137 spectrophotometer for Nujol mixtures and were calibrated with a standard polystyrene film.

The mass spectra were taken on a Hitachi Perkin Elmer RMU-7 double-focussing mass spectrometer using a direct inlet system.

Neutral alumina and silica gel used in chromatography (both thin layer (t.l.c.) and column) were supplied by Woelm.

Melting points were determined with an electrically heated metal block type apparatus and are uncorrected.

Gas chromatographs were obtained on a Perkin Elmer model 800 gas chromatograph. The inert support material used was Gaschrom W and the liquid phase was 5% SE-30. A 3/8 in x 5 ft. glass column was used at a temperature of 200° .

Microanalysis was carried out with a Perkin-Elmer 240 elemental analyzer.

Attempted Reduction of Diphenyl Sulfone (11) with Cobalt Borohydride

To a cold stirred solution of 2.0 g (0.01 mole) of diphenyl sulfone and 4.8 g (0.02 mole) of cobalt chloride hexahydrate in 200 ml of 95% ethanol was added 3.8 g (0.10 mole) of sodium borohydride. The sodium borohydride was added over a period of 10 minutes. The solution was cooled by means of an ice-water bath. After complete addition of the sodium borohydride the cooling bath was removed and the solution was stirred for 2 hours at room temperature. Water (25 ml) was added to the solution. The solution was heated on a steam bath for 10 minutes. After cooling to room temperature the solution was poured into 300 ml of water and the water layer was extracted with two 100 ml portions of benzene. The combined benzene extracts were dried over anhydrous magnesium sulfate, and the drying agent was removed by filtration. The filtrate was flash evaporated to give 1.21 g of (11), mp 120-122° (lit.[10] 123°). An infrared absorption spectrum of the residue was identical with that of (11). The residue on t.l.c. (silica gel/benzene) was identical to (11).

Attempted Reduction of Diphenyl Sulfone (11) with Nickel Borohydride

In the same manner as described in the previous experiment for cobalt chloride hexahydrate 4.80 g (0.02 mole) of nickel chloride hexahydrate was added to a cold stirred solution of 2.0 g (0.01 mole) of diphenyl sulfone and 3.80 g (0.10 mole) of sodium borohydride. After work-up as in the previous experiment 1.51 g of (11) was obtained, mp 120° (lit.[10] 123°). The residue on t.l.c. (silica gel/ benzene) was identical to (11).

Attempted Reduction of Diphenyl Sulfone (11) with Lithium Aluminum Hydride

To a slurry of 0.20 g (5 mmole) of lithium aluminum hydride in 15 ml of tetrahydrofuran was added a solution of 7.19 g (3.33 mmole) of diphenyl sulfone in 5 ml of tetrahydrofuran. After the mixture was stirred at room temperature for several hours in an atmosphere of dry nitrogen it was hyrolyzed with 2 ml of dilute sulfuric acid. The mixture was extracted with four 20 ml portions of ether. The extracts were combined, and removal of the solvent by flash evaporation gave 0.55 g of unchanged starting material (11). An infrared spectrum of the product was identical to that of (11). The residue on t.l.c. (silica gel/benzene) was identical to (11).

In a manner similar to that described above 3.0 g (1.3 mmole) of diphenyl sulfone was added to 3.0 g (0.11 mole) of lithium aluminum hydride in 75 ml of tetrahydrofuran. The reaction mixture was stirred at reflux for several hr. in a dry nitrogen atmosphere, cooled to room temperature, and hydrolyzed with 20 ml of dilute sulfuric acid. The mixture was extracted with four 40 ml portions of ether. The extracts were combined and the solvent was removed by flash evaporation to give 0.74 g of crude material. The crude product was dissolved in benzene and the solution was applied to a column containing 60 g of silica gel packed in benzene. The product was eluted with benzene, and the first 300 ml of eluate was collected and flash evaporated to give 0.14 g of product. Gas chromatography showed a mixture consisting of (11), 93%, and diphenyl sulfide (13), 7%.

Separation of the mixture was accomplished on a 3/8 in. x 5 ft. glass column packed with 5% SE-30 on Gaschrom W. Samples of (11) and (13) were collected from the column for mass spectrometry. Found for (11) $M^+ = 218$ (calculated for $(Ph_2SO_2)^+$, $M^+ = 218$), and for (13) $M^+ = 186$ (calculated for $(Ph_2S)^+$, $M^+ = 186$).

Preparation of Nickel Chloride Tris-triphenyl Phosphene (14)[15,20]

To a stirred solution of 0.7 g (2.68 mmole) of triphenyl phosphene (13) and 1.65 g (4.5 mmole) of nickel chloride hexahydrate in 25 ml of ethanol was added a slurry of 0.16 g (4.5 mmole) of sodium borohydride suspended in 5 ml of ethanol. After the mixture was stirred for three hours at room temperature in a dry nitrogen atmosphere an orange precipitate 0.71 g (75%) of (14) was filtered off.

Attempted Reduction of Diphenyl Sulfone (11) with Nickel Chloride Tris-triphenyl Phosphene

To a solution of 0.71 g (2.0 mmole) of nickel chloride tris-triphenyl phosphene in 20 ml of dry benzene was added 0.03 g (0.14 mmole) of diphenyl sulfone. The reaction mixture was stirred at reflux for 5 minutes, cooled to room temperature,and extracted with three 10 ml portions of anhydrous ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and the filtrate flash evaporated to give a white solid, 0.46 g, mp 75°. The product on a t.l.c. (silica gel/n-hexane) showed a mixture consisting of (11) and triphenyl phosphene (15).

Reaction of Triphenyl Phosphene (15) with Diphenyl Sulfone (11)

To a stirred solution of 1.1 g (.0042 mole) of triphenyl phosphene in 30 ml of dry benzene was added 0.5 g (.0023 mole) of diphenyl sulfone. The reaction mixture was stirred at reflux for two hr., cooled to room temperature,and flash evaporated to give a yellow solid, 1.20 g. The product was dissolved in 30 ml of ethanol, and the solution stirred for several minutes, and filtered. The filtrate was flash evaporated to give 1.10 g of a white solid. The product on a t.l.c. (silica gel/n-hexane) showed two components (11) and (15).

Reaction of a Nickel Chloride/Triphenyl Phosphene (15)/Sodium Borohydride Mixture with Diphenyl Sulfone (11)

To a solution of 0.50 g (0.0023 mole) of diphenyl sulfone, 0.53 g (2.24 mmole) of nickel chloride, and 4.44 g (0.017 mole) of triphenyl phosphene in 200 ml of degased ethanol was slowly added a slurry of 3.66 g (0.10 mole) of sodium borohydride in 30 ml of absolute ethanol. The mixture was stirred at reflux for three hr. in a dry nitrogen atmosphere, cooled to room temperature, and the solvent removed by flash evaporation to give 2.74 g of a white solid. The product on a t.l.c. (silica gel/benzene) showed two components which were identical to (11) and (15).

Reaction of a Nickel Chloride/Triphenyl Phosphene (15) Mixture with Diphenyl Sulfone (11)

A solution containing 0.53 g (2.24 mmole) of nickel chloride, 4.0 g (0.015 mole) of triphenyl phosphene, and 0.50 g (0.0023 mole) of diphenyl sulfone in 200 ml of benzene was stirred at room temperature for several hours. Removal of the solvent by flash evaporation gave 2.96 g of a white solid, mp 105°, which on t.l.c. (silica gel/benzene) proved to be a mixture of (11), (15), and (16).

Reaction of Stannous Chloride with Diphenyl Sulfone (11)

To a slurry of 7.0 g (0.033 mole) of stannous chloride in 15 ml of concentrated HCl was added 2.0 g (0.009 mole) of diphenyl sulfone. The slurry was heated to reflux for 1 hr., cooled to room temperature, and neutralized with a 40% aqueous sodium hydroxide solution (20 ml). The slurry was filtered and the filtrate extracted with three 15 ml portions of benzene. The combined ethereal extracts were dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the filtrate was flash evaporated to give 0.60 g of a white solid, mp 105°. On t.l.c. (silica gel/benzene) the product showed two components which were indentical to diphenyl sulfone and diphenyl sulfide (13) (20%).

Attempted Reduction of Diphenyl Sulfone (11) with Zinc-HCl

To a solution of 0.54 g (0.003 mole) of diphenyl sulfone in 15 ml of a 50% aqueous ethanol solution was added 0.90 g (0.014 g-atom) of zinc dust. A 2 ml portion of concentrated HCl was slowly added, and the resulting suspension was stirred at reflux for one hr., cooled to room temperature, and left to stir for 48 hr. The slurry was made basic with 10 ml of a 15% alcoholic sodium hydroxide solution and extracted with three 10 ml portions of ether. The ethereal extracts were combined, washed with three 5 ml of water, dried over anhydrous magnesium sulfate, filtered, and the filtrate flash evaporated to give 0.20 g of a white solid. On t.l.c. (silica gel/benzene) the product was identical to (11).

Reaction of Diphenyl Sulfone (11) with Diisobutylaluminum Hydride

To a solution of 0.50 g (2 mmole) of diphenyl sulfone in 30 ml of benzene was added slowly 10 ml (14.03 mmole) of a 20% solution of diisolbutylaluminum hydride in n-hexane. The solution was heated to reflux for several hr. in a dry nitrogen atmosphere. After the solution had cooled to room temperature 15 ml of methanol were added, until complete precipitation of aluminum methoxide. The mixture was filtered and the filtrate flash evaporated to give 0.35 g of product. The product on t.l.c. (silica gel/benzene) showed two components, one was identical to (11) and the other to diphenyl sulfide (13). The product was dissolved in benzene and the solution was applied to a column containing 60 g of silica gel packed in benzene. The reaction product was eluted with benzene and the first 200 ml of eluate were collected and flash evaporated to give 0.22 g (60%) of a pale yellow oil. The oil on t.l.c. showed one component, which was identical to diphenyl sulfide (13).

Reaction of Di-p-tolyl Sulfone (12) with Diisobutylaluminum Hydride

To a 1.0 g (0.4 mmole) solution of di-p-tolyl sulfone in 60 ml of toluene was added 50 ml of a 20% solution of diisobutylaluminum hydride in n-hexane. The solution was stirred at reflux for three days in a dry nitrogen atmosphere. After the solution was cooled to room temperature 60 ml of methanol were added and the mixture was filtered and the filtrate was flash evaporated to give 0.77 g of a yellow solid. The solid was dissolved in benzene and the solution was applied to a column containing 60 g of silica gel packed in benzene. The reaction product was eluted with benzene and the first 550 ml of eluate were collected and flash evaporated to give 0.43 g of residue. The residue on t.l.c. (silica gel/benzene) showed one component, which was not identical to di-p-tolyl sulfone.

In a manner similar to the procedure described above 1.0 g (0.4 mmole) of di-p-tolyl sulfone and 60 ml of a 20% solution of diisobutylaluminum hydride in n-hexane were refluxed for 52 hr. After work-up the filtrate was flash evaporated to yield 0.73 g of a white solid. The solid was dissolved in benzene and was applied to a column containing 60 g of silica gel packed in benzene. The reaction product was eluted with benzene and the first 250 ml of eluate was flash evaporated to give 0.56 g of a white solid. The residue on t.l.c. (silica gel/benzene) showed one component at the solvent front, which is where di-p-tolyl sulfide would be expected to show up.

The solid was recrystallized several times from methanol to yield 0.48 g (56%) of di-p-tolyl sulfide, mp 54° (lit. 57°). The mass spectrum of the solid contains the molecular ion peak of di-p-tolyl sulfide at m/e 214. The infrared spectrum has a band at ν_{max} 800 cm^{-1} (C-S).

Anal. calcd for $C_{14}H_{14}S$: C, 78.5; H, 6.54.
Found: C, 78.23; H, 6.89

Preparation of N-(4-pyridyl)pyridinium Dichloride (7)

An 8.0 g (0.10 mole) portion of freshly distilled pyridine was slowly added to 23.9 g (0.20 mole) of freshly distilled thionyl chloride cooled in an ice bath. After complete addition of the pyridine the reaction mixture was left to stand at room temperature for four days. Volatile materials in the reaction were removed by flash evaporation leaving 9.0 g of a dark brown residue. The residue was triturated with two 8 ml portions of absolute ethanol and evaporated to dryness in vacuo. The crude product (4.9 g) was dissolved in 5 ml of water, and 12 g of 2N HCl was added. After the addition of 0.25 g of activated charcoal the solution was boiled for five minutes and filtered. The filtrate was boiled for five minutes with 0.25 g of activated charcoal, filtered, and the filtrate concentrated to 8 ml in vacuo. The filtrate was cooled to 0° and 10 ml of absolute ethanol was added, at which time pale yellow crystals had separated. The solid was washed with 8 ml of absolute ethanol and dried in vacuo to give 4.5 g (40%) of (7), mp 158° (lit.[14] 158°).

Reaction of N-(4-pyridyl)pyridinium Dichloride with Hydrogen Sulfide

A solution of 2.0 g (0.01 mole) of N-(4-pyridyl)pyridinium dichloride in 8 ml of pyridine and 3 ml of chloroform was heated to reflux for 5 hr. Hydrogen sulfide gas was continuously bubbled through the solution. After the solution had been cooled to room temperature it was extracted with three 10 ml portions of ethyl acetate. The extracts were combined and flash evaporated to give 0.35 g of a brown solid. The solid on t.l.c. (silica gel/benzene) showed two components, one of which was identical to N-(4-pyridyl) pyridinium dichloride. An infrared spectrum of the solid contains a band at ν_{max} 800 cm^{-1} (C-S).

Reaction of 4-Mercaptopyridine (8) with N-(4-pyridyl)pyridinium Dichloride (7)

A mixture of 0.40 g (0.004 mole) 4-mercaptopyridine and 1.0 g (0.005 mole) of N-(4-pyridyl)pyridinium dichloride was heated in dry nitrogen gas for 20 minutes at 150°. After cooling to room temperature the reaction mixture was made basic with an aqueous sodium carbonate solution and extracted with three 10 ml portions of ether. The ethereal extracts were combined, dried over anhydrous magnesium sulfate, filtered, and the filtrate flash evaporated to give 0.48 g of an orange solid. The reaction product on t.l.c. (silica gel/methanol) showed one component. The solid was recrystallized several times from benzene to yield 0.40 g (58%) of a yellow solid (2) mp, 67° (lit.[1] 67°). The mass spectrum of the product shows the molecular ion peak of di-4-pyridyl sulfide at m/e 188.

Anal. calcd for $C_{10}H_8N_2S$: C, 63.83; H, 4.26; N, 14.89.

Found: C, 64.05; H, 4.34; N, 14.41.

The procedure described above was repeated 3 times with 10, 20, and 30 minute heating periods respectively. On t.l.c. (silica gel/methanol) the product from each reaction showed only one component. The infrared spectra each show an absorption band at ν_{max} 800 cm^{-1} (C-S). The mass spectra each have the molecular ion peak of di-4-pyridyl sulfide at m/e 188. Yields of di-4-pyridyl sulfide from the experiments were 23, 24, and 94% for respective heating periods of 30, 20, and 10 minutes.

REFERENCES

1. D. Jerchel and H. Fischer, Chem. Ber., 89, 2921 (1956).

2. E. Koenigs and H. Greiner, Ber., 64B, 1049 (1931).

3. Tet. Lett., 1777 (1974).

4. M. Dreux, L. Leroux, and P. Savignou, Synthesis, 7, 506 (1974).

6. T. Aida, N. Furukaua, and S. Aae, Tet. Lett., 39, 3853 (1973).

7. Syn. Commun, 3(1), 37 (1973).

8. D. Chasar, J. Org. Chem., 36(4), 613 (1971).

9. S. Yanagida and S. Komori, Synthesis, 7, 200 (1973).

10. H. C. Brown, P. M. Weissmann, and N. M. Yoon, J. Am. Chem. Soc., 87, 1458 (1966).

11. H. C. Brown and N. M. Yoon, J. Am. Chem. Soc., 87, 5614 (1965).

12. J. Gardner, (Hoffman-La Roche, Inc.) U.S., 3819, 652(Cl. 260-332. 8; Co 7d), 25 Jan. 1974) Appl. 289, 899, 18 Aug. 1972, 3 pp.

13. A. Marchand and R. Allor, J. Org. Chem., 40,(17), 2551 (1975).

14. K. Bowden and P. Green, J. Chem. Soc., 1795 (1954).

15. A. Khan, M.Sc. Thesis, Lakehead University, (1978).

16. C. Cumper, J. Read, A. Vogel, J. Chem. Soc., A, 239 (1966).

17 C. Cumper, J. Read, A. Vogel, J. Chem. Soc., 5860 (1965).

18. Leonard and Sutton, J. Am. Chem. Soc., 70, 1564 (1948).

19. E. Fehnel and M. Carmack, J. Am. Chem. Soc., 71, 231 (1949).

20. D. G. Holah, A. N. Hughes, B. C. Hui, and K. Wright, Can. J. Chem., 52, 2990 (1974).

CHAPTER V

DIELECTRIC RELAXATION STUDIES OF SOME RIGID SYMMETRIC DIARYL MOLECULES

INTRODUCTION

It has been shown[1] that the use of a solute dispersed in a polystyrene matrix may enable the separation of relaxation processes. If a molecule undergoes over-all molecular and intramolecular rotations a study of the molecule in a polystyrene matrix may enable a resolution of the two processes, and therefore, make possible an investigation of the dielectric relaxation parameters for each process.

Dielectric relaxation of polar molecules in solution can occur by over-all molecular rotation, internal flexing motions such as chair-chair configurational changes, as in cyclohexylchloride or by internal rotations, such as by polar groups. The third case normally has shorter relaxation times, and is an important factor in determining the average unresolved relaxation time of a molecule.

A number of factors determine whether a molecule undergoes primarily a molecular or an intramolecular motion. For example, if a molecule has the possibility of internal rotation then electronic and steric factors may determine whether the internal rotation occurs. An example is diphenyl ether in which internal rotation has been postulated, as exemplified by an exceptionally short relaxation time of $4\text{x}10^{-12}$ s at 293 K in benzene.[2] This is a mean relaxation time incorporating both molecular and intramolecular relaxations. 2-Hydroxydiphenyl ether is similar in size and shape to diphenyl ether, but has one ring blocked from rotation, because of the hydrogen-bond formation between the hydrogen of the hydroxyl group and the central oxygen atom.

Maier[24] measured the relaxation time of 2-hydroxydiphenyl ether in benzene and found that there was no anomalously short relaxation time for this molecule. The measured relaxation time was found to be five times that of diphenyl ether. In molecules such as diphenyl ether the relaxation process for intramolecular rotation is relatively insensitive to the viscosity of the solvent medium.[2]

At least five explanations[3] have been presented as to the origin of the internal relaxation mechanism, including one involving a mesomeric charge shift[16,18] accompanying coupled ring rotation about the C-O bonds (see Chapter VII). A similar relaxation process has been found for diphenyl sulfide (see Chapter VII). In diaryl sulfones and sulfoxides the conjugation of the sulfonyl and sulfinyl groups with the phenyl rings should cause an increased electron density in the C-S bonds, and would substantially increase the energy barrier to internal rotation. As a consequence the major contribution to the observed relaxation process may be from molecular rotation.

This chapter deals with dielectric relaxation studies of a series of symmetric diaryl molecules in polystyrene matrices. The term "symmetric diaryl molecules" as used in this thesis refers to those diaryl molecules in which the bridging species has at least two planes of symmetry, and both the phenyl rings have the same structure. These include diaryl sulfoxides, diaryl sulfones, pyridyl ethylenes, and related compounds. An attempt will be made to correlate structural and electronic properties of the molecules, such as rotational volumes and resultant dipole moment with dielectric relaxation parameters, such as enthalpy of activation, entropy of activation, and relaxation time.

Anomalously short relaxation times have been observed for diphenyl ether[4] and diphenyl sulfide.[19] These relaxations have been attributed to internal rotations associated with coupled ring rotations which cause rapid reversal of the net dipole moment direction (see Chapter VII). Ther term "double-internal rotation" has been used in some places to describe these types of internal rotations. It is therefore of interest to investigate similar molecules in order to observe whether rapid intramolecular relaxation processes occur. These include molecules such as diaryl sulfoxides and sulfones.

One important factor which may determine whether internal rotations occur are electronic effects, such as electron densities in the central bridging atom to aromatic ring bonds, conjugation, and mesomeric shifts of charge. In Table V-1 are listed some symmetric diaryl molecules along with their dipole moments and relaxation times. It can be seen from Table V-1 that diphenyl sulfide and 2'2'-ditolyl sulfide have nearly the same relaxation time. Any internal coupled ring rotations must be unimpeded by the ortho methyl groups. The τ value of 8.7 ps at 298 K in benzene[5] is about twice as large as that for diphenyl ether and therefore, implies a smaller contribution from internal rotation. Reasons for this behaviour are given in Chapter VII. The relaxation time of 14.5 ps at 298 K in benzene[5] for diphenyl sulfoxide is larger than that of diphenyl sulfide (8.7 ps at 298 K in benzene)[5], but is still low for a molecule of its size and dipole moment. These imply that the internal relaxation mechanism is still important.

TABLE V-1: Electric Dipole Moments and Relaxation Times of Some Diaryl Sulfur Compounds in Benzene at 298 K[5]

Molecule	$\tau \times 10^{12}$ (s)	μ (D)
Diphenyl Sulfide	8.7	1.50
Diphenyl Sulfoxide	14.5	3.81
Diphenyl Sulfone	24.8	4.85
2,2'-Ditolyl Sulfide	8.4	0.95
2,2'-Ditolyl Sulfone	21.9	4.30
2,2'-Ditolyl Sulfoxide	22.6	3.85

The relative contribution weight for each relaxation process depends on the molecular dipole moment. This is evident from the following equations:

$$C_1 + C_2 = 1 \qquad \text{V-1}$$

where C_1 and C_2 are the relative contribution weights for each relaxation process: C_1 may be considered as the weight contribution for the molecular process and C_2 as that for the intramolecular process:

$$C_2 = \frac{1}{1 + (\frac{\mu_y}{\mu_x})^2} = \frac{1}{1 + (\frac{2\mu_{x-o}}{\mu_m})^2 \cot^2 \theta} \qquad \text{V-2}$$

where μ_x and μ_y are the dipole moment components along the X and Y axes. If $\mu_x >> \mu_y$ in equation V-2 then the last term on the right would be dominant in Equation V-3:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_o - \varepsilon_\infty) \left[\frac{C_1}{1 + i\omega^2\tau_m^2} + \frac{C_2}{1 + i\omega^2\tau_g^2} \right] \qquad \text{V-3}$$

where

$$C_1 = \frac{\mu_y^2}{\mu_x^2 + \mu_y^2}$$

$$C_2 = \frac{\mu_x^2}{\mu_x^2 + \mu_y^2} \qquad \text{V-4}$$

so that the equation:

$$\frac{1}{\tau_o} = \frac{1}{\tau_m} + \frac{1}{\tau_g} \qquad \text{V-5}$$

may govern the relaxation process, where τ_g is the intramolecular relaxation time, τ_m is the molecular relaxation time, and τ_o is the observed relaxation time.

The anomalously short observed relaxation time of diphenyl ether and diphenyl sulfide can be explained in part by use of the above equations. Diphenyl ether is taken as an example. Substitution of $\mu_{c-o} = 0.95$ D $= \mu_m$ and $\Theta = 60°$ in Equation V-2 lead to a C_2 value of 0.75. Such estimates state, that if μ_m and μ_{c-o} are about the same (0.95 D), then C_2 will be about 0.7 D. As a result τ_m can be calculated from Equation V-5 to be 19.0 ps and τ_g to be 7.3 ps, while τ_o is found to be 5.3 ps which is in close agreement with the experimental value of 4.0 ps at 293 K in benzene.

A similar treatment can be performed on diphenyl sulfide, diphenyl sulfone, diphenyl sulfoxide, and related molecules. For instance, diphenyl sulfide has a slightly larger dipole moment of 1.55 D at 298 K in benzene[23], as compared to 1.23 D at 298 K in benzene[23] for diphenyl ether. As a consequence, it can be noted from Equation V-2 that the weight factor for intramolecular rotation will be less than in diphenyl ether. According to the Equation V-2 if μ_{x-o} has the same direction as the mesomeric moment μ_m, and $\mu_{x-o} \leq 1$ D the C_2 becomes almost unity for $\mu_m \approx 1$ D. Consequently, molecules which have dipole moments similar in magnitude and direction as diphenyl ether have a relaxation process similar to that of diphenyl ether.

Diphenyl sulfones and sulfoxides have dipole moments (diphenyl sulfone, $\mu = 5.10$ D in benzene at 298 K,[23] diphenyl sulfoxide, $\mu = 4.10$ D in benzene at 298 K[23]) which are greater than that of diphenyl ether ($\mu = 1.23$ D at 298 K in benzene[23]). In these cases it can be noticed from Equation V-2 that unless the mesomeric moments were improbably high then, $C_1 >> C_2$, which is unlike the case of diphenyl ether.

2,2'-Ditolyl sulfoxide has a relaxation time of 22.6 ps at 298 K in benzene[5], which is significantly larger than the τ_o value of 14.5 ps at 298 K in benzene[5] for diphenyl sulfoxide. This suggests that there are steric interactions between the methyl groups and the aromatic rings which impede any coupled ring rotations. Diphenyl sulfone and 2,2'-ditolyl sulfone both have larger dipole moments and τ_o values than the corresponding sulfoxides.[5] The relaxation times for the sulfones are shorter than those calculated for molecular rotation. These may be explained in part by mesomeric shifts of charge between the sulfonyl group and the aromatic rings. It may be that in sulfones the 3 d orbitals of the sulfur atom are contracted in size by the electonegative oxygen atoms, thereby permitting mesomerism with the π-electrons of the phenyl rings.[5] Some evidence of the mesomerism is provided by dipole moment measurements and ultraviolet absorption spectra.[6,7]

In the ultraviolet spectra of sulfones the 230-245 mμ band has been considered[8] to involve an excited state in which the aromatic rings are linked via the sulfur 3 d orbitals. A similar explanation could hold in sulfoxides and sulfides, though the interaction with the sulfur atom would progressively diminish due to the increased size of the 3 d orbitals. Although there is a significant flow of electronic charge from the phenyl group to the 3 d orbitals in sulfones the effect is to a smaller extent in sulfoxides. Conjugation normally results in hypsochromic shifts, but the effect is greater in the excited states of these molecules, and any interaction between the aromatic rings and the lone-pair orbitals is eliminated in sulfones. Phenyl-phenyl ring conjugation appears to be present in diphenyl sulfone since there are bathochromic shifts between phenyl-methyl sulfone and diphenyl sulfone.[7]

Measurements of the dipole moments of diaryl sulfur compounds are useful in intramolecular relaxation studies. For instance, diphenyl sulfoxide has a dipole moment of 4.07 D at 298 K in benzene[23], which is less than 0.1 D greater than those of alkyl sulfoxides, while diphenyl sulfone has a dipole moment of 5.05 D at 298 K in benzene[23], which is over 0.5 D greater than those of alkyl sulfones. It has been suggested[9] that conjugation of the unoccupied 3 d orbitals of the sulfur atom with the π-electrons of the phenyl rings can increase the net dipole moment. Some workers,[10] however, have stated that highly diffuse 3 d orbitals are unlikely to enter into effective conjugation with the π-electrons of the aromatic rings. In sulfones, however, the presence of two electronegative oxygen atoms could so reduce the size of the 3 d orbitals that conjugation would not be possible. When chlorine atoms are placed at the para positions of the two rings there is a greater mesomeric shift of electrons towards the sulfone group.

The conformation which some substituted and unsubstituted diaryl sulfoxides and sulfones take has been shown by X-ray studies. In crystalline p,p'-dibromodiphenyl sulfone[11] one ring is twisted 90° out of the C-S-C plane, while in diphenyl sulfoxide[12] it is twisted 82° out of the C-S-C plane. These conformations are important factors in determining the volume swept out during molecular rotation, as will be shown later.

Davies and Edwards[13] have shown experimentally that a good correlation exists between the enthalpy of activation of rigid molecules and the local volume required for orientation of the solute molecules in polystyrene. They obtained a linear plot for ΔH_E versus rotational volume for camphor, anthrone, cholest-4-en-3-one, tetracylone, and the molecular process of β-naphthol. However, cholest-4-en-3-one departs from a general linear relation between enthalpy of activation and rotational volume.

A series of molecules of similar size and shape was studied by Pitt and Smyth.[14] They examined three rigid polar ketone molecules, anthrone, fluorenone, and phenanthraquinone in benzene solution. The respective enthalpies of activation were found to be 8.8, 8.4, and 10.9 kJ mol^{-1}. Phenanthraquinone was shown to have the larger ΔH_E value of 10.9 kJ mol^{-1}, which can be attributed to the larger rotational volume swept out during molecular relaxation about the long molecular axis.

The direction of the resultant dipole moment within a molecule determines about which axes rotation will occur, and thus the volume swept out by a molecule. Pitt and Smyth[14] illustrated this fact in a study of two large oblate ellipsoidal molecules of metal free heptachlorophenyl-porphyrazine and ferric octaphenylporphyrazine chloride in benzene solution. It was observed that the relaxation time of the second molecule was 5/2 times that of the first one, although the enthalpy of activation for both cases was about 10.9 kJ mol^{-1}. The difference in relaxation times was attributed to the dipole moment of the chlorporphyrazine lying in the plane of the molecule, while that of the ferric complex is perpendicular to the molecular plane.

Tay and Walker[15] observed in a series of halonaphthalenes dispersed in a polystyrene matrix a linear correlation between the enthalpy of activation and the volumes swept out during molecular rotation. They found that the ΔH_E values for the 1-halonaphthalenes increased only slightly with increase in halogen atom size. However, for the 2-halonaphthalenes there was a significant increase in the ΔH_E with increasing molecular size. In the 1-halonaphthalenes the major contribution to molecular reorientation would be from rotation about the long molecular axis,which would involve a cylindrical barrel-like volume being swept out. The 2-halonaphthalenes have a much smaller contribution from a barrel-like motion, since the square of the dipole moment component perpendicular to the long axis of rotation is reduced by a factor of four (i.e., $\cos^2 60$). As a result the 2-halonaphthalenes could have an appreciable contribution from an end-to-end tumbling motion,which would sweep out considerably more volume. In this case,the molecules would experience more viscous drag from the polymer matrix,and thereby would have larger ΔH_E values. The ΔH_E values for the 2-fluoro, 2-chloro, 2-bromo, 2-iodo naphthalenes were found to be 23.0, 31.8, 34.7, and 40.6 kJ mol^{-1} respectively. The increasing ΔH_E values could be explained by the fact that as the halogen atom increases in size the resistance encountered in rotating in a polystyrene matrix also increases.

Polystyrene matrix studies have shown that there can be a linear relationship between enthalpy of activation and the volumes swept out during rotation of similar types of molecules. As a consequence it seemed worthwhile to examine a series of rigid symmetric diaryl molecules, where in most cases the dipole moment lies along the Y-axis, to see if there is a linear relationship between ΔH_E and rotational volume. These molecules were studied as dispersed solutes in polystyrene matrices.

Besides the linear correlation of ΔH_E with rotational volume, the entropy of activation (ΔS_E) has been shown in some cases of systems of similar character to have a linear dependence upon the corresponding enthalpy of activation (ΔH_E). Davies and Edwards[13] found a linear relationship between ΔS_E and ΔH_E for some polar molecules of various sizes and shapes dispersed in a polystyrene matrix. They examined camphor, anthrone, cholest-4-en-3-one, tetracyclone, and β-naphthol, and obtained an appreciable linear relation from plots of ΔS_E versus ΔH_E. The linear dependence of ΔS_E with ΔH_E is understood if the activation energy is largely needed to displace adjacent solvent molecules or groups, therefore, the larger the energy for rotation the larger the local disorder, and thus, the larger the ΔS_E.

This chapter deals with a series of symmetric, polar diaryl moleucles dispersed in polystyrene matrices. In view of earlier work by other researchers on ΔH_E, ΔS_E, and rotational volume correlations, these types of studies were also performed on the above types of molecules in atactic polystyrene. The present investigation involves molecules of similar shape, but of different sizes in a highly viscous polystyrene solvent. Another aim of this chapter is to show how molecular properties such as conjugation and related electronic factors influence whether internal rotations occur in a series of diaryl sulfones, sulfoxides, pyridyl ethylenes, and related compounds.

EXPERIMENTAL

Dielectric relaxation measurements were made of a series of symmetric, polar diaryl sulfoxides, sulfones, pyridyl ethylenes, dibenzothiophenes, a ketone, an oxadiazole, and an epoxide, molecularly dispersed in polystyrene matrices.

Measurements were made in the frequency range, 10^2-10^5 Hz, with a General Radio 1615A capacitance bridge. Other apparatus and procedures used during the course of dielectric studies of the above compounds, along with the preparation of the polystyrene matrix, have been discussed previously in Chapter III. The methods utilized for the evaluation of relaxation and activation parameters have also been described in Chapter III.

All the compounds studied were purchased commercially from either the Aldrich Chemical Co. or the K & K Laboratory and were dried

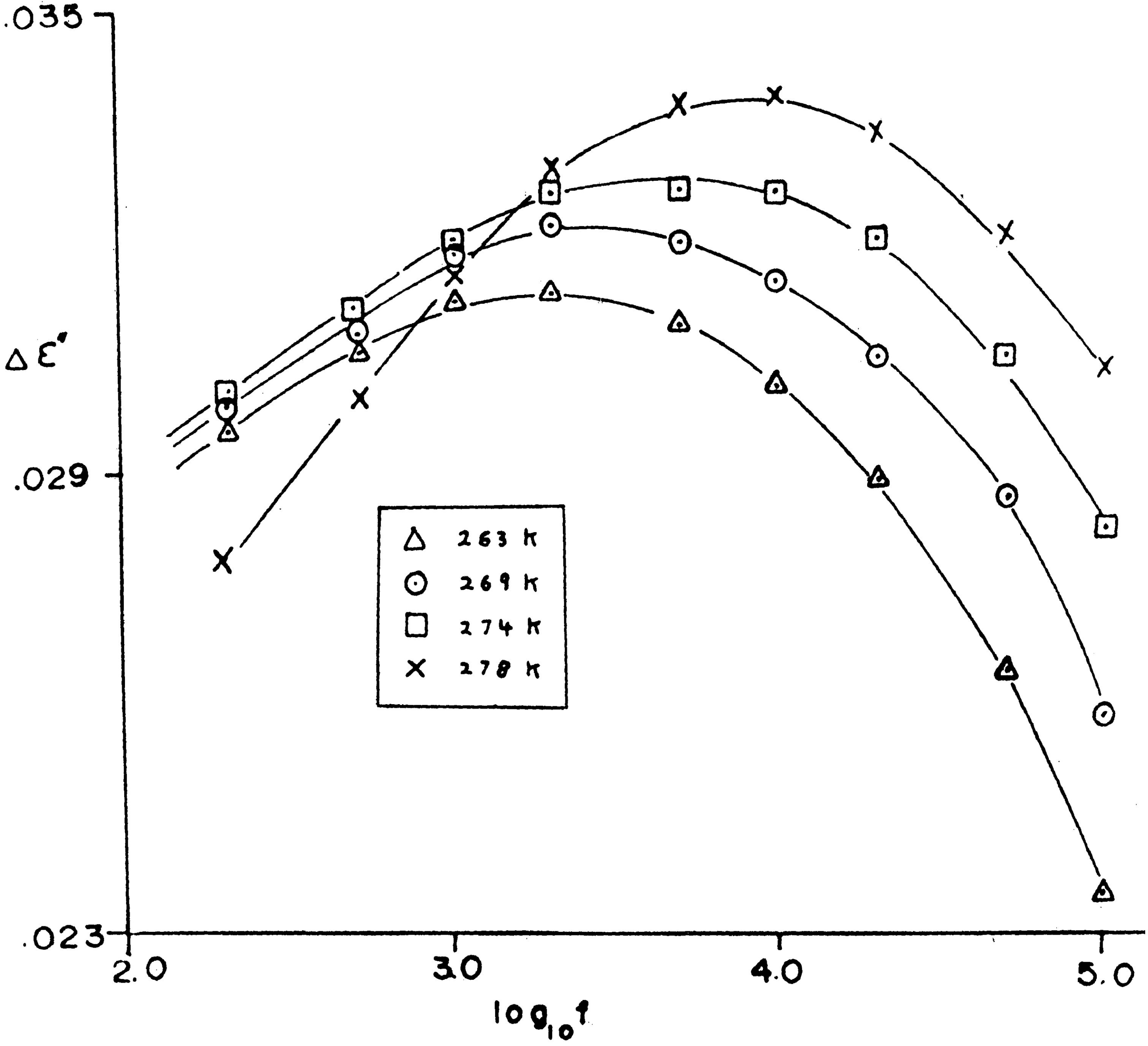


FIG. V-1: Dielectric Absorption of 0.643M Diphenyl Sulfoxide in Polystyrene in the 10^2 - 10^5 Hz range

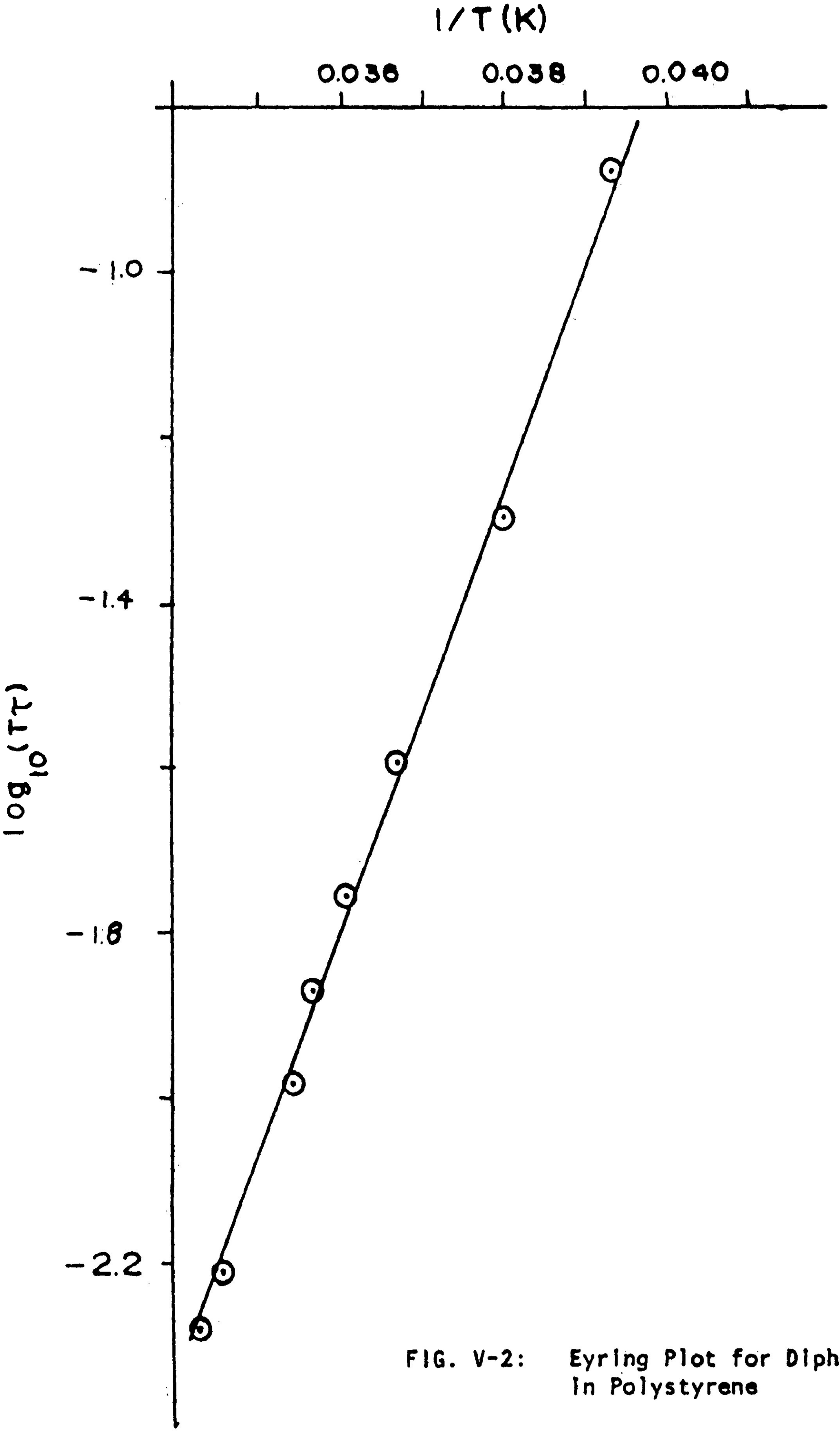


FIG. V-2: Eyring Plot for Diphenyl Sulfoxide In Polystyrene prior to use. The polystyrene matrices were stored in a desiccator overnight prior to use.

The experimental values of τ, $\log_{10}f_m$, β, ε''_{max}, ε_∞, and μ at various temperatures are listed in Table V-8. Table V-3 lists the relaxation and activation parameters for the molecules studied. The confidence interval on all the experimental enthalpies of activation is 90%. This also applies to Chapters VI and VII. A sample plot of dielectric loss ($\varepsilon'' = \varepsilon''_{obs} - \varepsilon''_{polystyrene}$ versus $\log_{10}$ frequency for diphenyl sulfoxide is shown in Fig. V-1. Fig. V-2 also shows the $\log T\tau$ versus $1/T$ plot for diphenyl sulfoxide. The structural diagrams of the molecules studied in this chapter are presented in Table V-9.

DISCUSSION

Since polystyrene is a solvent of much greater viscosity than most organic solvents the relaxation time appreciably increases for rigid molecules in polystyrene matrices as can be seen in Table V-2.

TABLE V-2: Relaxation Times and Enthalpies of Activation for Some Diaryl Sulfur Compounds

Molecule	τ(s) (Benzene at 298 K)	τ(s) (Polystyrene at 200 K)	ΔH (kJ mol^{-1}) (Polystyrene)
Diphenyl sulfide	8.7×10^{-12}	$7.0\times10^{-13*}$	13.6 ± 1.9
Diphenyl sulfoxide	14.5×10^{-12}	3.3×10^{-6}	59.9 ± 4.0
Diphenyl sulfone	24.8×10^{-12}	4.6×10^{-9}	62.0 ± 2.3

*This is a value of τ from a long extrapolation and may be appreciably in error.

Diphenyl sulfide has a lower τ value due to a rapid intramolecular process which has been shown to occur (see Chapter VII), and which is not significantly affected by the solvent viscosity. Diphenyl sulfoxide and diphenyl sulfone have longer τ values in polystyrene than in benzene solution, since the prime contribution to dielectric relaxation may be from molecular tumbling.

Although diphenyl sulfone and sulfoxide are about the same size both are only slightly larger than diphenyl sulfide, and are also about the same size as benzophenone, which has a molecular volume

TABLE V-3: **Dielectric Relaxation and Activation Parameters for Some Diaryl Molecules in Polystyrene**

Molecule	T(K)	τ(s) 150 K	τ(s) 200 K	τ(s) 300 K	ΔG_E(kJ mol^{-1}) 150 K	ΔG_E(kJ mol^{-1}) 200K	ΔG_E(kJ mol^{-1}) 300K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
Dibenzothiophene sulfone	204 - 231	1.1	3.0×10^{-4}	7.0×10^{-4}	36.0	34.8	32.4	39.7 ±2.6	24 ±12
Dibenzothiophene sulfoxide	269 - 300	1.7×10^{2}	5.2×10^{-2}	1.4×10^{-5}	42.3	43.4	45.7	38.9 ±2.6	23 ± 9
Dibenzothiophene	201 - 231	6.0×10^{-1}	2.0×10^{-4}	5.9×10^{-8}	35.2	34.1	31.9	38.5 ±3.1	22 ±14
Diphenyl sulfone	205 - 240	5.6×10^{2}	1.7×10^{-3}	4.6×10^{-9}	43.8	37.7	25.6	62.0 ±2.3	121 ±11
Diphenyl Sulfoxide	251 - 283	1.8×10^{5}	8.2×10^{-1}	3.3×10^{-6}	50.9	48.0	42.0	59.9 ±4.0	60 ±15
Di-p-tolyl sulfone	280 - 300	5.1×10^{7}	2.7×10	1.3×10^{-5}	58.0	53.8	45.4	70.7 ±3.5	84 ±15
Di-p-tolyl sulfoxide	294 - 324	6.0×10^{8}	5.0×10^{2}	3.7×10^{-4}	61.1	58.7	53.8	68.4 ±3.1	49 ±10
P,P'-Dichloro-diphenyl sulfone	306 - 326	1.2×10^{11}	1.5×10	1.5×10^{-3}	67.7	64.3	57.3	78.2 ±5.6	70 ±16
1,2-Bis(2-pyridyl)ethylene	205 - 252	9.5×10^{-2}	1.1×10^{-4}	1.0×10^{-7}	32.9	33.1	33.4	32.5 ±0.9	- 3 ± 4
1,2-Bis(4-pyridyl)ethylene	220 - 253	9.1×10^{-2}	1.3×10^{-4}	1.6×10^{-7}	32.9	33.4	33.5	31.4 ±2.0	- 10 ± 9
1,2-Diphenyl-1,3,4-Oxadiazole	263 - 308	2.4×10^{2}	3.5×10^{-2}	4.4×10^{-6}	42.7	43.0	42.7	43.0 ±3.3	0.9 ±12
1,2-Diphenyl-cyclopropenone	271 - 303	3.4×10^{11}	2.5×10	1.5×10^{-9}	69.0	53.6	22.9	115 ±8.9	30 ±31

TABLE V-4: Distribution Parameters of Some Diaryl Molecules in Polystyrene Matrices

MOLECULE	ΔT (K)	β	RIGID MOLECULE	ΔT (K)	β
diphenyl sulfone	204-231	.22-.34	dibenzothiophene sulfone	205-240	.22-.28
diphenyl sulfoxide	251-283	.16-.19	o-hydroxybenzophenone	256-294	.18-.20
di-p-tolyl sulfone	280-300	.18-.21	dibenzothiophene sulfoxide	270-300	.16-.19
p,p'-chlorodiphenyl sulfone	306-326	.15-.19	dibenzothiophene	201-300	.20-.24
di-p-tolyl sulfoxide	294-324	.11-.16			
1,2-bis(2-pyridyl)-ethylene	205-252	.18-.29			
1,2-bis(4-pyridyl)-ethylene	220-253	.44.59			
1,2-diphenylcyclopropenone	271-303	.06-.02			
2,5-diphenyl-1,3,4-oxadiazole	263-308	.18-.20			

of 170 c.c. mole^{-1} at 333 K.[16] The fact that both molecules have much larger enthalpies of activation than diphenyl sulfide (ΔH_E = 13.6 kJ mol^{-1}) indicates that these molecules most likely undergo a major relaxation contribution from molecular rotation. The ΔH_E values of 59.9 and 61.9 kJ mol^{-1} respectively for diphenyl sulfoxide and diphenyl sulfone are very similar. This reflects the similar sizes of these two molecules. Further evidence of the fact that these molecules undergo primarily molecular reorientation is the good agreement of their ΔH_E values with the ΔH_E value (58.2 kJ mol^{-1}) for o-hydroxybenzophenone, which may be regarded a rigid molecule of similar size and shape to diphenyl sulfone and sulfoxide, where the chelated ring is held together by a strong hydrogen bond.

A fair amount of evidence is available which proves that the rings in many diaryl systems, such as diphenyl sulfone, diphenyl sulfoxide, and o-hyroxybenzophenone are not coplanar, but orthogonal or near orthogonal.[7,17] Dielectric relaxation studies in polystyrene matrices have revealed that for these systems ΔH_E for molecular rotation is about 60 kJ mol^{-1} or larger, as for diphenyl sulfone and sulfoxide (see Table V-3).

The symmetric diaryl molecules studied in polystyrene matrices exhibit low distribution parameters which range 0.06 - 0.29 (Table V-4), in the range 204 - 326 K. These imply a wide range of relaxation times, however, exceptions are diphenyl sulfone where β values range 0.22 - 0.34 in the range 205 - 240 K, and di-4-pyridyl ethylene where β values range 0.44 - 0.59 in the range 220 - 253 K. Davies and Edwards[13] and Davies and Swain[1] observed similar fairly large values of β for a series of rigid molecules.

Diphenyl sulfone has slightly larger β values (0.22 - 0.34) than many of the other molecules studied in this chapter. The β values can be compared with those of dibenzothiophene sulfone (Table V-4), which is a rigid molecule in which the two aromatic rings are linked at the ortho positions. Diphenyl sulfone and dibenzothiophene sulfone are similar in that both have two aromatic rings linked by a sulfonyl group. This fact along with the similar temperature regions 205 - 240 K for diphenyl sulfone, and 204 - 250 K for dibenzothiophene in which loss maxima were observed, enable comparison of β values. For diphenyl sulfone the β values range, 0.22 - 0.34 while for dibenzothiophene sulfone they range 0.22 - 0.28. The similarity in β values and temperature ranges is only one fact which helps to suggest that molecular reorientation may be a major contributor to the dielectric relaxation of diphenyl sulfone. Factors such as electron densities in the sulfonyl-ring bonds which help to explain why molecular rotation is a dominant process, are outlined in the introductory section of the chapter.

Diphenyl sulfoxide has a β value range of 0.16 - 0.19 in the range 250.8 - 283.3 K. These values can be compared with those of o-hydroxybenzophenone. The latter molecule has a β value range of 0.18 - 0.20 in the range 256.3 - 294 K. Since o-hydroxybenzophenone is rigid the β values of diphenyl sulfoxide are one piece of evidence suggestive of a dominant molecular relaxation process.

The temperature range (204 - 326 K) in which the molecules studied in this chapter showed dielectric loss peaks was relatively near or above room temperature as can be seen in Table V-3. Such a temperature range is often indicative of high energy barriers associated with over-all molecular rotation and with co-operative rotation with the polymer chains. Diaryl sulfoxides have absorption maxima at higher temperatures (diphenyl sulfoxide, 251 - 283 K) than corresponding diaryl sulfones, such as diphenyl sulfone (205 - 240 K).

Diphenyl sulfone has a dipole moment along the Y molecular axis (Fig. V-3). The net dipole moment has no component perpendicular to the Y axis, but the resultant dipole moment is perpendicular to the X and Z axes. As a consequence, molecular rotation can occur about the X and Z axes. The large dipole moment of 5.1 D at 298 K in benzene[23] gives a large contribution to molecular rotation, since the contribution to a relaxation process is proportional to the square of the dipole moment component perpendicular to a molecular axis. With substituents such as CH_3 or Cl in each of the para positions the net

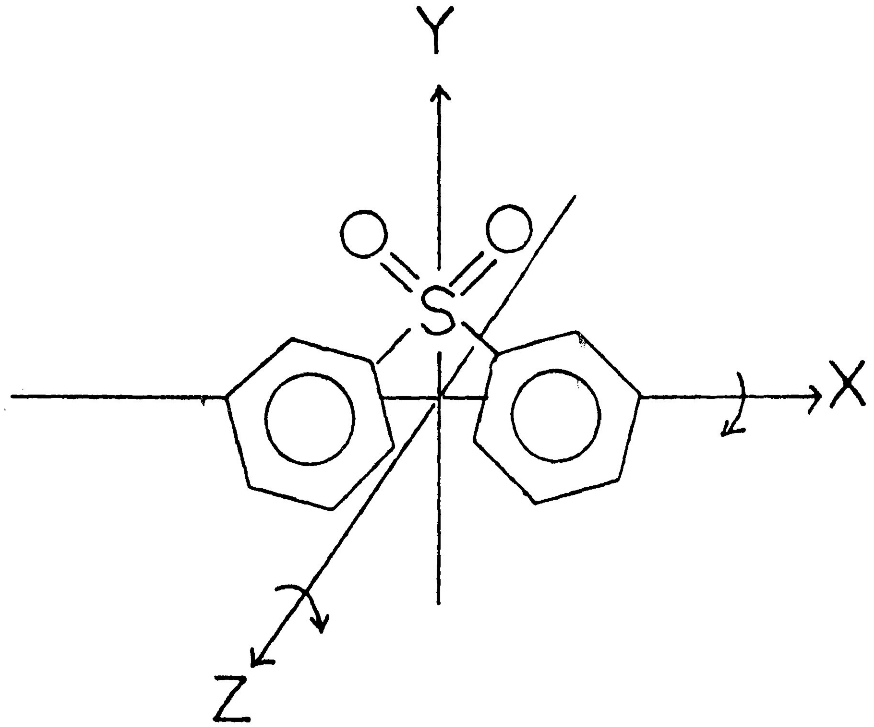


Fig. V-3: Dipole Moment (μm) and Axes of Rotation for Diphenyl Sulfone

dipole moment still lies along the Y axis. Di-p-tolyl sulfone has a dipole moment of 5.54 D at 298 K in benzene[23]. This is expected since the methyl groups exert a +M and a +I effect and therefore direct charge into the rings. p,p'-Dichlorodiphenyl sulfone, however, has a lower dipole moment of 3.30 D (at 298 K in benzene[23]), although the net effect is for the chlorine atoms to get the better share of the valence electrons.

As the size of diaryl sulfones increase so does the enthalpy of activation. This is evident from Table V-3, where the ΔH_E values are 39.7, 61.9, 70.7, and 78.2 kJ mol^{-1}, respectively, for dibenzothiophene sulfone, diphenyl sulfone, di-p-tolyl sulfone, and p,p'-dichlorodiphenyl sulfone. It should be mentioned that di-p-tolyl sulfone and p,p'-dichlorodiphenyl sulfone are nearly the same size. The ΔG_E values at 300 K also increase, for the p,p'-H, p,p'-CH_3, p,p'-Cl diaryl sulfones the values are 25.6, 45.4, and 57.3 kJ mol^{-1} respectively. Relaxation times in polystyrene for these three compounds at 300 K also increase from 4.6×10^{-9} to 1.3×10^{-3} s to 1.5×10^{-3} s for diphenyl sulfone, di-p-tolyl sulfone, and p,p'-dichlorodiphenyl sulfone respectively. These parameters indicate that as molecular volume increases, so do the ΔH_E, ΔG_E, and τ values for these diaryl sulfones. Besides, diphenyl sulfone, the p,p'-Me and p,p'-Cl sulfones also exhibit a large contribution from molecular rotation. The β values for di-p-tolyl sulfone range 0.18 - 0.21 in the range 279.8 - 299.8 K, while for p,p'-dichlorodiphenyl sulfone they range 0.15 - 0.17 in the range 306 - 325 K. These molecules therefore have a wide range of relaxation times with contributions to dielectric relaxation primarily from molecular rotation, with further possible contributions from an intramolecular process, such as coupled ring rotations. Cumper, Read, and Vogel[6] have stated that an internal relaxation process may occur in diphenyl sulfone.

All the diaryl sulfones studied, including dibenzothiophene sulfone, have positive entropy of activation values. For dibenzothiophene sulfone, diphenyl sulfone, di-p-tolyl sulfone, and p-dichlorodiphenyl sulfone in polystyrene the ΔS_E values are 24.3, 121.3, 84.4, and 69.6 J K^{-1} mol^{-1} respectively. Such positive values are often indicative of a molecular relaxation process when the ΔH_E value is greater than 30 kJ mol^{-1}. This is evident from an equation ($\Delta S_E = 2\Delta H_E - 60$) which was developed[20] for solutes exhibiting overall molecular rotation in a polystyrene matrix. The above molecules all have ΔH_E larger than 30 kJ mol^{-1}. Molecules such as benzophenone, the di-alkyl sulfides, and di-benzyl ether have negative ΔS_E values and ΔH_E values less than 30 kJ mol^{-1}. It has been shown (see Chapter VII) that such molecules undergo internal rotation with low ΔH_E values. Davies and Swain[1] found negative ΔS_E values for some flexible molecules, namely, thianthrene, phenoxathiin, diphenylene dioxide, phenothiazine, phenoxazine, and cyclohexyl chloride. ΔS_E values were -134, -180, -170, -54, -42, and -7 J K^{-1} mol^{-1} respectively. Negative ΔS_E values are associated with small ΔH_E values, which is understandable in that an intramolecular motion is likely to involve a minimum molecular reorganization in the polymer medium. Arguments correlating ΔS_E and ΔH_E follow from M. Davies[1] work on polystyrene matrices in which he derived the equation $\Delta S_E = 2.48\ \Delta H_E - 31$ for such intramolecular motions.

Dibenzothiophene sulfone (see Table V-9 for the structure)

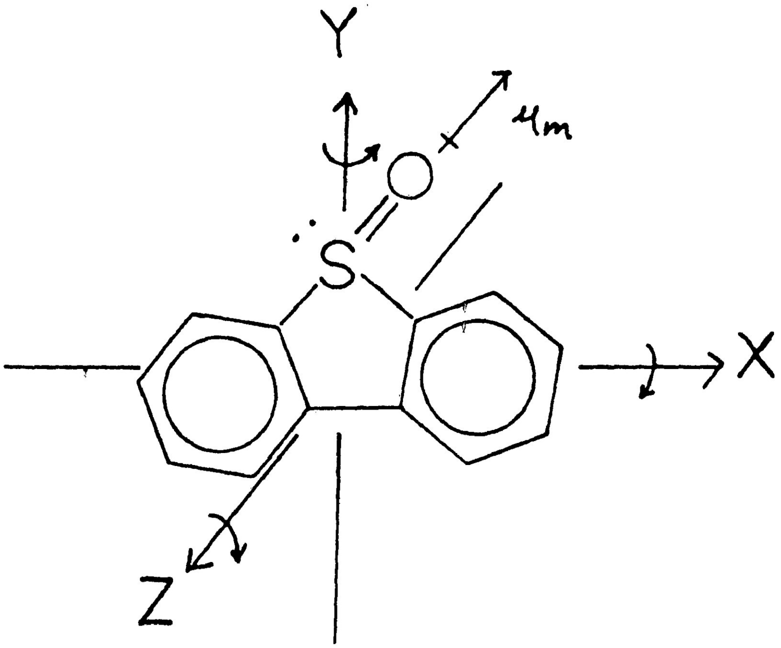


Fig. V-4: Dipole Moment (μm) and Axes of Rotation of Dibenzothiophene Sulfoxide has the two phenyl rings coplanar, thereby sweeping out less volume in its rotations than diaryl sulfones in which the aromatic rings are most likely orthogonal. The smaller molecular volume may account for the low ΔH_E value of 39.7 kJ mol^{-1}. This molecule is essentially disc-shaped as are the other dibenzothiophenes, namely, dibenzothiophene and dibenzothiophene sulfoxide. All these molecules are rigid (see Table V-9) and about the same size, as is reflected in the ΔH_E values of 38.5, 38.9, and 39.7 kJ mol^{-1}, respectively for dibenzothiophene, dibenzothiophene sulfoxide, and dibenzothiophene sulfone in polystyrene. Davies and Edwards[13] also found for fluorenone, a rigid molecule of similar size and shape to dibenzothiophenes, a ΔH_E value of 40 kJ mol^{-1} in polystyrene. This value agrees well with the ΔH_E values of the dibenzothiophenes.

Dibenzothiophene sulfoxide has a net dipole moment of 4.40 D at 298 K in benzene[23] which points out of the molecular plane (Fig. V-4). In diaryl sulfoxides there is a lone-electron pair on the sulfur atom, this as in ammonia causes a pyramidal structure, and as a consequence there are dipole moment components perpendicular to the X, Y, and Z axes. In principle at least, molecular rotation may occur about all three axes which could lead to a wider distribution of relaxation times than for the diaryl sulfones, which can rotate only about the X and Z axes. This behaviour is exemplified in the β values of sulfoxides, which are all less than those of the corresponding sulfones. For the diaryl sulfones the β values range 0.15 - 0.34 in the range 204.4 - 325.5 K, while for the diaryl sulfoxides they range 0.10 - 0.19 in the range 250.8 - 323.6 K.

In Table V-4 the β values of some symmetric diaryl molecules are compared with those of some known rigid diaryl molecules whose loss maxima occur in the same temperature region. It is noticeable from Table V-4 that many of the molecules have β values in reasonable agreement with known rigid diaryl molecules. These values, along with other dielectric data suggest that molecular rotation is the major relaxation process in the sulfones and sulfoxides listed in Table V-3.

All the sulfoxides examined have absorption peaks at temperatures above those for the corresponding sulfones. For example, for diphenyl sulfone the absorption peaks were observed from 204 to 231 K, while for diphenyl sulfoxide they were observed from 251 to 283 K. Similar behaviour was observed for dibenzothiophene sulfoxide and di-p-tolyl sulfoxide. This behaviour could explain why the absorption peaks for p,p'-dichlorodiphenyl sulfoxide could not be observed, since they might occur above the experimentally measureable range (above 325 K). p,p'-Dichlorodiphenyl sulfone has absorption peaks from 306 - 326 K, so that if p,p'-dichlorodiphenyl sulfoxide follows the trend of the other sulfoxides then the loss peaks are above 325 K, as experiments have indicated. However, di-p-tolyl sulfoxide which is about the same size as p,p'-dichlorodiphenyl sulfoxide, does show absorption peaks in the experimentally measureable temperature regions.

Di-p-tolyl sulfoxide, as with the corresponding sulfone, has a larger ΔH_E value than the unsubstitued analogue. This is to be expected because of the larger molecular volume. The diaryl sulfoxides have ΔG_E values which also increase with molecular size. ΔG_E values at 300 K were found to be 38.9, 59.9, and 68.4 kJ mol^{-1}, for the series dibenzothiophene sulfoxide, diphenyl sulfoxide, and di-p-tolyl sulfoxide. These diaryl sulfoxides also have large dipole moments (e.g., 4.10 D at 298 K in benzene[23] for diphenyl sulfoxide) which suggest a large contribution to molecular rotation.

Besides diaryl sulfones and sulfoxides, other related polar symmetric diaryl molecules were studied. The prime intention for studying these was to investigate whether internal rotations such as coupled ring rotations occur. However, since they were found to behave as rigid molecules they were included in this chapter. These molecules include 1,2-diphenylcyclopropenone, 2,5-diphenyl-1,3,4-oxadiazole, trans stilbene oxide, 1,2-bis(2-pyridyl)ethylene and 1,2-bis(4-pyridyl)ethylene. The structures of these molecules are given in Table V-9.

1,2-Diphenylcyclopropenone has a large dipole moment of

5.14 D at 298 K in benzene[23], along the Y axis. It can be seen from the structural diagram (Table V-9) that the molecule is highly conjugated, and thus, may be planar due to resonance stabilization. An infrared spectrum was taken of the molecule in order to gain information concerning the conjugation. A strong peak was found at 1625 cm^{-1} which suggests exceptional conjugation of the carbonyl group with an aromatic ring. From Courtauld models, however, it can be shown that there is steric hinderence between the ortho hydrogen atoms, thereby forcing the rings to be inclined to each other by about 45°. Courtauld models, however, tend to over-emphasize steric effects. This molecule may therefore sweep out large volumes in rotation about the X and Y azes. The volumes swept out, however, are less than those of p,p'-dichlorodiphenyl sulfone and di-p-tolyl sulfone, yet 1,2-diphenylcyclopropenone has a larger ΔH_E of 115 kJ mol^{-1} as compared to 70.7 and 61.9 kJ mol^{-1} for the p,p'-Cl and p,p'-Me diaryl sulfones in polystyrene. Since 1,2-diphenylcyclopropenone has loss peaks in the range 207 - 303 K it is highly probable that it undergoes co-operative motion with the polymer chains. Also, in favour of this is the very large ΔS_E value of 307 J K^{-1} mol^{-1}. Such a large ΔS_E indicates large local disorder as the rotation of the solute disturbs the polymer chains. Davies and Edwards[13] have also observed such large ΔS_E values for tetracyclone, which has a ΔH_E of 546 kJ mol^{-1} and a ΔS_E of 1314 J K^{-1} mol^{-1}. They stated that large local motion of polystyrene units has to occur for the tetracyclone to reorientate.

Another molecule with a large bridging group is 2,5-diphenyl-1,3,4-oxadiazole, whose structure is shown in Table V-9. This molecule has loss maxima from 263 - 308 K, which is about the same temperature range (271 - 308 K) in which 1,2-diphenylcyclopropenone shows loss maxima. Its enthalpy of activation (42.8 kJ mol^{-1}) is much lower than that of the 1,2-diphenylcyclopropenone molecule, as is also the ΔS_E value of 0.9 J K^{-1} mol^{-1}. These two parameters suggest some sort of relaxation process other than co-operative motion with the polymer. The small ΔS_E value suggests that there is little disturbance of the environment.

It can be seen from the molecular structure of 2,5-diphenyl-1,3,4-oxadiazole that the molecule is highly conjugated, particularly if the two aromatic rings are coplanar. Experimental evidence which will be discussed later, relating ΔH_E to rotational volumes favour a coplanar structure for the molecule. This molecule has a ΔH_E value of 42.8 kJ mol^{-1} and a ΔG_E value at 200 K of 42.7 kJ mol^{-1}. These values are larger than the ΔH_E values (39 and 40 kJ mol^{-1}) and $\Delta G_{E(200\ K)}$ values (34.1 and 35.0 kJ mol^{-1}) respectively for dibenzothiophene and dibenzothiophene sulfone, which undergo molecular rotation. Since 2,5-diphenyl-1,3,4-oxadiazole is larger than the other two molecules then the ΔH_E and ΔG_E values should be larger as is observed.

Trans-stilbene oxide was also studied in a polystyrene matrix, however, no absorption peaks were found in the temperature range 83 - 328 K. There was indication from loss curves above room temperatures that absorption peaks may occur above 328 K, which might be expected since this molecule has the two phenyl rings in a trans position, so that it would sweep out a large volume during molecular rotation. Its behaviour might also be similar to that of 1,2-diphenylcyclopropenone in that it could undergo co-operative motion with the polymer.

1,2-Bis(2-pyridyl)ethylene and 1,2-bis(4-pyridyl)ethylene were found to have absorption maxima in the temperature ranges 205 - 252 K, and 220 - 253 K respectively. These are below the glass-transition temperature of the polymer and so are unlikely to be due to co-operative motion with the polymer. The ΔH_E values for 1,2-bis(2-pyridyl) ethylene and 1,2-bis(4-pyridyl) ethylene are 32.5 and 31.4 kJ mol^{-1} respectively. From Courtauld models it can be shown that 1,2-bis-(2-pyridyl)ethylene can adopt planar and non-planar structures. A planar structure would be energetically favoured because of resonance delocalization. The molecular models also show that there is little steric hinderance in a planar structure. Plots of rotational volume versus ΔH_E which will be discussed later suggest that the planar structure sweeps out volumes which correlate linearly with the observed ΔH_E. For the volume swept out by an orthogonal structure a ΔH_E value larger than 32.5 kJ mol^{-1} would be observed.

Courtauld models show that 1,2-bis(2-pyridyl)ethylene has a molecular volume smaller than that of dibenzothiophene, and thus a ΔH_E value of 32.5 kJ mol^{-1}, while for dibenzothiophene a ΔH_E value of 38.5 kJ mol^{-1} is observed. Rotation can occur about the X and Z axes since the resultant dipole moment is along the Y axis in a planar structure. Molecular rotation of a planar molecule with a major contribution to relaxation from a barrel-motion about the X axis could explain the ΔH_E value of 32.5 kJ mol^{-1} for 1,2-bis(2-pyridyl)ethylene. The suggestion that 1,2-bis(2-pyridyl)ethylene undergoes primarily molecular relaxation is substantiated by comparison of the ΔG_E values at 200 K with those for dibenzothiophene and dibenzothiophene sulfone, which are rigid molecules.

These molecules have a resultant dipole moment along the Y axis with a zero dipole moment component along the X and Z axes if the rings are coplanar. The respective ΔG_E values at 200 K for 1,2-bis(2-pyridyl)ethylene, dibenzothiophene and dibenzothiophene sulfone are 33.1, 34.1, and 35.0 kJ mol^{-1}. The respective ΔH_E values are 32.5, 39.0, and 40.0 kJ mol^{-1}.

It may also be argued that this molecule may undergo an intramolecular relaxation process, such as coupled ring rotations. However, the ΔH_E value is larger than that of di-2-pyridyl ketone, and that of benzophenone, both of which have been shown to undergo intramolecular rotations (see Chapter VII). Di-2-pyridyl ketone and benzophenone have ΔH_E values of 21.4 and 27.5 kJ mol^{-1} respectively. It still might be argued that the ΔH_E value of 1,2-bis(2-pyridyl)ethylene is not much higher than that of di-2-pyridyl ketone, but the conjugation in both systems should be similar so that the ΔH_E values would be similar. Another piece of evidence which could favour intramolecular relaxation is the small entropy of activation value (ΔS_E = -3 J K^{-1} mol^{-1}), which indicates a small disturbance of the surrounding medium, as in double-internal rotation. However, from the equation (ΔS_E = 2 ΔH_E - 60)[20] the ΔH_E value must be less than 30 kJ mol^{-1} in order to have a negative ΔS_E value. 1,2-Bis(2-pyridyl)ethylene, however, has a ΔH_E value of 32.5 kJ mol^{-1}. The above equation was developed for the relaxation of rigid molecules below the glass-transition temperature of polystyrene. The above equation fits all the symmetric diaryl molecules studied, with the exceptions of diphenyl sulfone, 1,2-bis(2-pyridyl)ethylene, 1,2-diphenylcyclopropenone, and 2,5-diphenyl-1,3,4-oxadiazole, (Table V-6).

Many workers have shown that for intramolecular rotations such as double-internal rotation to occur the aromatic rings must be orthogonal.[18] Yet, the ΔH_E value correlates well with a planar structure for 1,2-bis(2-pyridyl)ethylene. Since the ΔH_E value for a planar structure undergoing molecular rotation and the ΔH_E value for an intramolecular relaxation process may be close in magnitude it is not possible to reach precise conclusions. Further study of this and similar systems is necessary in order to obtain a clearer insight into their dielectric relaxation behaviour.

1,2-Bis(4-pyridyl)ethylene in contrast to 1,2-bis(2-pyridyl)-ethylene has a narrow distribution of relaxation times, as is reflected in the β range 0.44 ÷ 0.59 from 220 -252 K, whereas 1,2-bis(2-pyridyl)-ethylene has a β range 0.18 - 0.29 in the range 205 - 252 K. This indicates that one major relaxation process predominates in this molecule. Courtauld models of this molecule show that a planar structure is not possible due to steric interactions of the ortho hydrogen atoms. As a result the rings are forced out of plane. If the rings are inclined to each other at about 45° then the observed enthalpy of activation value of 31.4 kJ mol^{-1} can be explained by molecular rotation. Whereas 1,2-bis(2-pyridyl)ethylene has a negative ΔS_E value of -3 J K^{-1} mol^{-1}, 1,2-bis(4-pyridyl)ethylene has a positive ΔS_E value of 30 J K^{-1} mol^{-1}, this supports the idea of a molecular relaxation process.

The possibility that 1,2-bis(4-pyridyl)ethylene undergoes internal rotation as a prime contribution to the observed relaxation process may be slight. One reason is that from Courtauld models it can be shown that the steric interaction between the ortho hydrogen atoms prevents a 360° rotation of the rings, torsional motions however, may be possible. Courtauld models, however, over-emphasize the steric effects of hydrogen atoms. Another reason is that when compared to molecules such as benzophenone, di-2-pyridyl ketone, and even possibly 1,2-bis(2-pyridyl)ethylene there is less interaction between the ring and the bridging group, so that if internal rotation occurred the ΔH_E value would be less than those of these molecules. The large resultant dipole moment of 3.40 D at 298 K in benzene[23] along the Y axis favours rotation about the X and Z axes. A predominant rotation about the X axis would sweep out less volume than that about the Z axis and so could possibly explain the ΔH_E value of 31.4 kJ mol^{-1}. Courtauld models also show that 1,2-bis(4-pyridyl)ethylene is smaller in size than the dibenzothiophene type molecules mentioned earlier. Its ΔH_E value is less than those of the dibenzothiophene type molecules whose ΔH_E values are all about 38 - 39 kJ mol^{-1}. Since intramolecular rotation has not been shown to occur the experimental evidence quoted supports the idea that di-4-pyridyl ethylene undergoes predominantly molecular rotation, as do most of the symmetric diaryl molecules mentioned so far.

It has been shown by other workers that the relaxation time and the enthalpy of activation increase with increasing molecular size, as was noted for halonaphthalenes by Tay and Walker[15]. It is apparent from the values of relaxation times ($\tau_{200\ K}$) and enthalpies of activation for diphenyl sulfone (1.7×10^{-3} s, 62 kJ mol^{-1}), di-p-tolyl sulfone (2.7×10 s, 70.7 kJ mol^{-1}), and p,p'-dichlorodiphenyl sulfone (1.5×10^{4} s, 78.2 kJ mol^{-1}) respectively, that these two parameters are sensitive to the size of the molecule. The increase in size of the molecules would lead to a larger volume being swept out during molecular rotation so that larger molecules such as p,p'-dichlorodiphenyl sulfone show longer relaxation times and larger enthalpies of activation than the smaller molecules.

An increase in the viscosity of the medium in which the solute molecules are dispersed results in much longer molecular relaxation times. This can be seen in the cases of diphenyl sulfone and diphenyl sulfoxide where the relaxation times are 24.8×10^{-12} s and 14.5×10^{-12} s respectively at 298 K in benzene.[5] In a polystyrene matrix however, the relaxation times for diphenyl sulfone and diphenyl sulfoxide at 300 K are 4.6×10^{-9} s and 3.3×10^{-6} s respectively. It can be noted that the increase in relaxation time for symmetric rigid diaryl molecules is significant in going from a low viscosity solvent (benzene) to a high viscosity one such as polystyrene.

Larger molecules sweep out larger volumes and thus have longer molecular relaxation times. When larger volumes are swept out there is greater viscous drag from the surrounding environment, thus, a greater enthalpy of activation is noticed for the relaxation process. Tay and Walker[15] found a linear relationship between enthalpy of activation for molecular reorientation and the volume swept out by some naphthalene molecules dispersed in polystyrene matrices. In view of this correlation it seemed worthwhile to investigate whether there is a similar behaviour for these rigid symmetric diaryl molecules in a polystyrene matrix, where in most cases, the dipole moment lies along the short Y molecular axis.

The molecular axes are represented by X, Y, and Z, as in Fig. V-3, and have lengths in the order X>Y>Z. Since the dipole moments lie along the Y axis as in symmetric sulfones the rotation of the molecule may give rise to two extreme types of swept volume, one involves a large displacement of the surrounding medium corresponding to rotation about the Z axis, while for the other, rotation about the X axis involves less displacement of adjacent molecules. The axes about which rotations occur intercept at the centre of mass, and the volumes of revolution may be treated as cylindrical. With these assumptions and the aid of known radii and lengths of the cylinders the volumes swept out by dipole reorientation about various axes can be determined. Since the exact positions of the centres of mass were not known, rotational volumes were calculated about the centres of volume. The centres of volume were determined from the geometric centres, from Courtauld models.

During rotation about either the centre of mass or the centre of volume two half-cylinders are swept out, the radii of which are the

TABLE V-5: Rotational Volumes About the X (V_x), and Z (V_z) Axes, Mean Volume (V_{mean}), and Enthalpies of Activation for Some Rigid Diaryl Molecules.

Molecule	V_x (Å^3)	V_z (Å^3)	V_{mean} (Å^3)	ΔH_E (kJ mol^{-1})
Diphenyl Sulfone	831	1386	1109	62.0
Di-p-tolyl Sulfone	947	1795	1371	70.7
p,p'-Dichlorodiphenyl sulfone	994	1998	1496	78.2
Diphenyl Sulfoxide	830	1385	1109	59.9
Di-p-tolyl Sulfoxide	947	1795	1371	68.4
p,p'-Dichlorodiphenyl Sulfoxide	994	1998	1496	--
Dibenzothiophene	243	770	507	38.5
Dibenzothiophene sulfone	246	872	559	39.7
Dibenzothiophene Sulfoxide	245	870	556	38.9
1,2-Bis(2-pyridyl)-ethylene (rings orthogonal)	773	1213	993	
1,2-Bis(2-pyridyl)-ethylene (rings coplanar)	219	700	460	32.5
1,2-Bis(4-pyridyl)-ethylene (rings orthogonal)	813	1324	1069	--
1,2-Bis(4-pyridyl)-ethylene (rings inclined 45°)	213	677	445	31.3

TABLE V-5: Rotational Volumes About the X (V_x), and Z (V_z) Axes, Mean Volume (V_{mean}), and Enthalpies of Activation for Some Rigid Diaryl Molecules. continued.....

Molecule	V_x (Å^3)	V_z (Å^3)	V_{mean} (Å^3)	ΔH_E (kJ mol^{-1})
1,2-Diphenylcyclopropenone (rings coplanar)	249	813	531	115.0
1,2-Diphenylcyclopropenone (rings inclined 45°)	794	1310	1051	--
2,5-Diphenyl-1,3,4-oxadiazole (rings coplanar)	284	1068	676	42.8
2,5-Di-phenyl-1,3,4-oxadiazole (rings orthoganol)	784	1786	1285	--

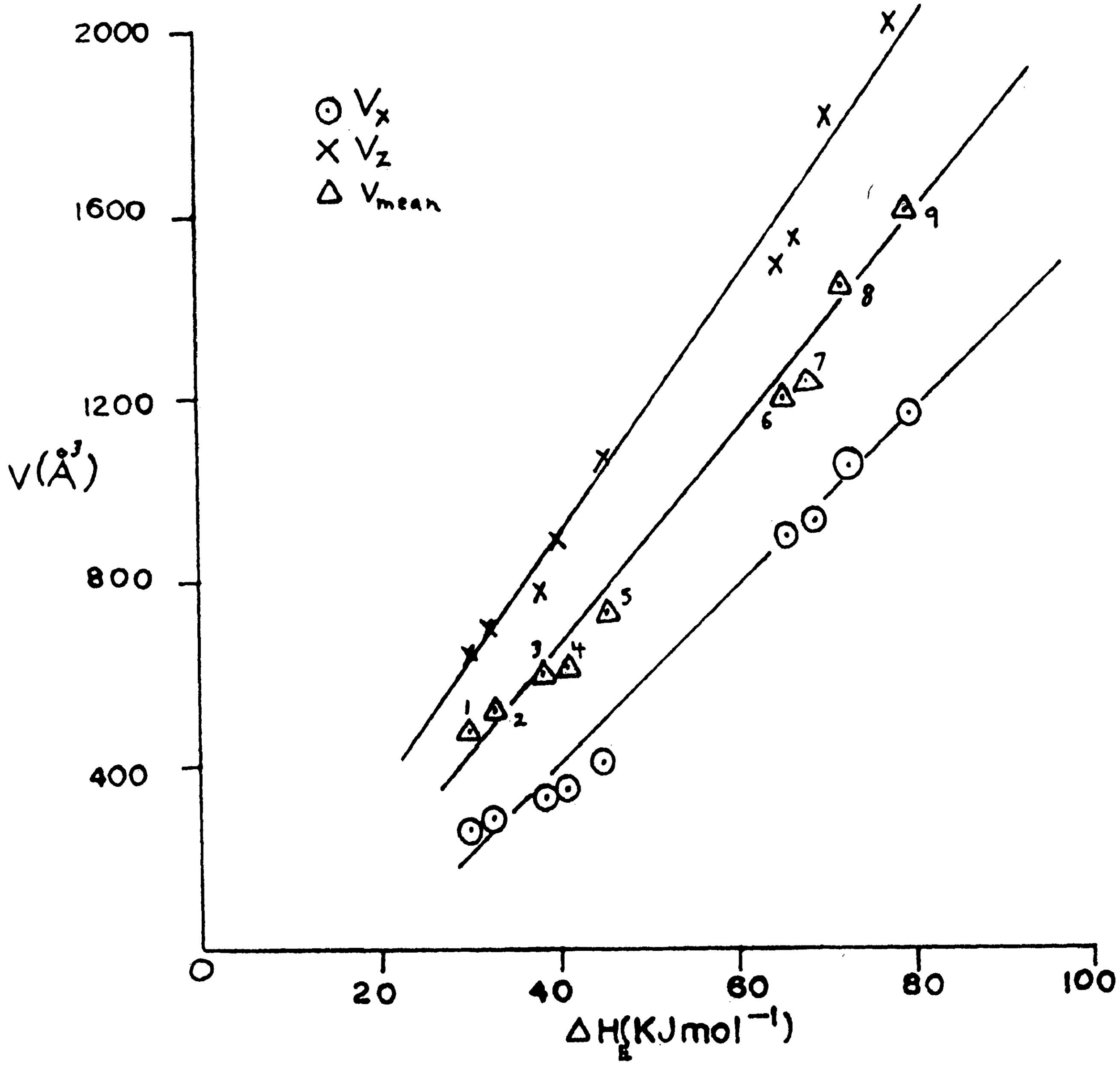


Fig. V-5: Plots of Rotational Volumes about the X Axis (V_x), the Y Axis, (V_y), and the Mean Volume (V_{mean}) for:

1. 1,2-Bis(4-pyridyl)ethylene, 2. 1,2-Bis(2-pyridyl)ethylene,
3. Dibenzothiophene, 4. Dibenzothiophene sulfoxide,
5. 2,5-Diphenyl-1,3,4-oxadiazole, 6. Diphenyl Sulfoxide,
7. Diphenyl Sulfone, 8. Di-p-tolyl sulfone, and,
9. p,p'-dichlorodiphenyl sulfone in polystyrene

maximum **lengths** of the molecule in each direction parallel to the axis of rotation.

The volumes V_x and V_z swept out by rotation about the X and Z axes as well as the mean volume, V_m, are given in Table V-5:

$$V_m = \frac{V_x + V_z}{2} \qquad \text{V-6}$$

These volumes were determined from Courtauld models, with a conversion scale of 0.8" = 1 Å. From Table V-5 it is obvious that for given types of molecules, such as diaryl sulfones the enthalpy of activation and the swept volumes are dependent on the molecular volume. As the molecular volume increases these two parameters also increase. In diaryl sulfones and sulfoxides for example, as the size of the para substituent increases (e.g., H, CH_3, Cl) there is an increase in rotational volume and enthalpy of activation.

Fig. V-5 shows plots of V_x, V_z, and V_{mean} versus enthalpy of activation for a series of rigid symmetric diaryl molecules. It can be observed that the mean volume and swept volumes about the X and Z axes are linearly correlated with ΔH_E. If sources of experimental error during volume determinations are taken into account then the straight lines may pass through the origin as would be theoretically perferable. This is particularly evident from the plots of V_x and V_{mean} versus ΔH_E.

It can be seen from Fig. V-5 that the volume swept out about the Z axis is larger than that about the X axis.

The only molecule which deviates significantly from the plots is 1,2-diphenylcyclopropenone. It was suggested previously that very likely this molecule undergoes co-operative motion with the polymer chains. The fact that this molecule does not lie on the swept volume versus ΔH_E plots is further evidence that the relaxation process which is occurring is different from that of most of the other symmetric diaryl molecules. Davies *et al.*[13] also observed that one molecule, cholest-4-en-3-one did not fit rotational volume versus ΔH_E plots for polystyrene matrices. They found that in a series of molecules of similar shape that a linear correlation exists between rotational volume and enthalpy of activation. Cholest-4-en-3-one departed from the linear relation due to its unusual shape,as compared to four other molecules.

These studies by other workers as well as the study presented in this chapter support the idea that for a series of molecules of similar shape there is a linear dependence between enthalpy of activation and rotational volume for a molecular relaxation process. It can be seen from Table V-5 and Fig. V-5 that, for a given series of molecules, such as sulfones or sulfoxides, as the size of the molecule increases with different para-substituents, the rotational volume and hence, the enthalpy of activation increase . The increase in enthalpy of activation and rotational volume, on passing from p,p'-H to p,p'-CH_3 and p,p'-Cl sulfones and sulfoxides are in the correct sequence.

Plots of rotational volume versus enthalpy of activation can give evidence as to which structures may exist. For example, in the case of 1,2-bis(2-pyridyl)ethylene the most probable resonance and steric conformations are planar, ∿45° ring inclinations, and orthoganal ring structures. From Table V-5 it can be noticed that the respective mean volumes are 993, 460, and 649 $Å^3$. The second rotational volume corresponding to a coplanar ring structure lies on the plot of swept volume versus ΔH_E. This observation and other dielectric parameters mentioned previously support the idea of a coplanar ring structure for 1,2-bis(2-pyridyl)ethylene.

A similar viewpoint can be taken with respect to 1,2-bis-(4-pyridyl)ethylene. It was stated earlier that this molecule can adopt, for steric reasons, a conformation in which the rings are inclined to each other by either about 45° or 90°. The mean rotational volumes given in Table V-5 are 541 and 1069 $Å^3$ for the 45° and 90° ring inclinations structures respectively. The 541 $Å^3$ volume lies on the generated rotational volume versus ΔH_E line, while the volume for the orthogonal case does not. This favours the structure for 1,2-bis(4-pyridyl)ethylene in which the two rings are inclined to each other about 45°.

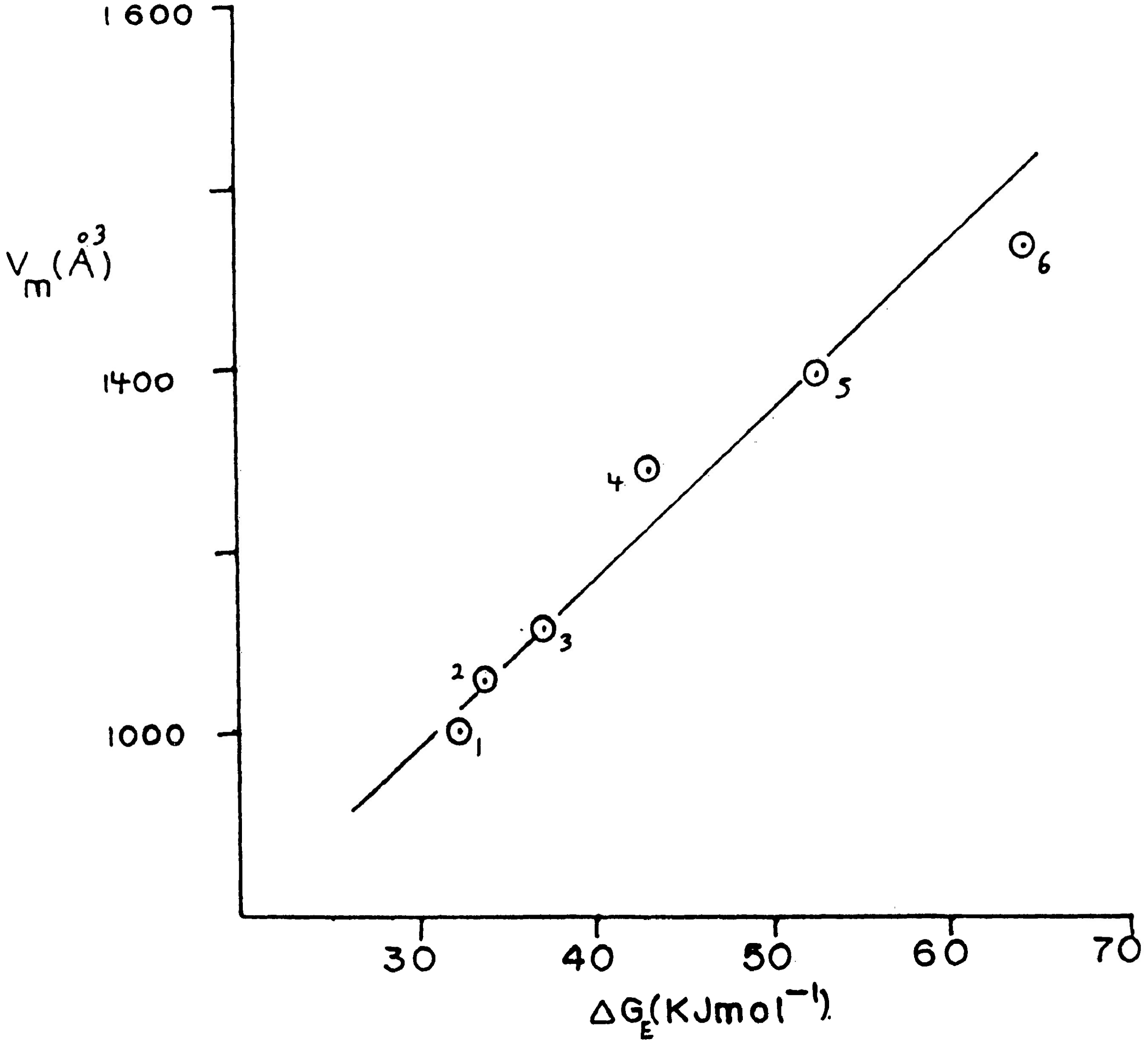


Fig. V-6: Mean Rotational Volume (V_m) versus ΔG_E at 200 K plot for a Series of Rigid Symmetric Diaryl Molecules in Polystyrene:

1. 1,2-Bis(2-pyridyl)ethylene,
2. 1,2-Bis(4-pyridyl)ethylene,
3. Diphenyl sulfone,
4. 2,5-Diphenyl-1,3,4-oxadiazole,
5. Di-p-tolyl sulfone, and,
6. p,p'-Dichlorodiphenyl sulfone in Polystyrene.

2,5-Diphenyl-1,3,4-oxadiazole can adopt either a planar or an orthogonal ring conformation. From Table V-5 it can be seen that the mean rotational volumes are 676 and 1285 $Å^3$ for the planar and orthogonal conformations respectively. The 676 $Å^3$ value lies on the swept volume versus ΔH_E plot. This, therefore, favours that the most probable conformation may be the planar one.

Fig. V-6 shows a plot of the mean rotational volume (V_{mean}) versus ΔG_E at 200 K. A reasonably linear relationship is again seen for some rigid symmetric diaryl molecules.

It is noticeable (see Table V-3) that for molecules which have small enthalpies of activation the corresponding entropies of activation are also small. Higasi[18] found a similar behaviour for 120 substances for which ΔH_E and ΔS_E were available for molecular relaxation processes. He stated, that, "the entropy change, ΔH_E, is zero or has a small negative value if ΔH_E is below 13.4 kJ mol^{-1}." Negative entropies of activation for molecular relaxation are also found elsewhere in the literature, for example, Tay and Walker[15], reported for 1-bromonaphthalene, 2-fluoronaphthalene, and 2-chloronaphthalene in a polystyrene matrix ΔS_E values of -4, -8, and -11 J K^{-1} mol^{-1} respectively. In the present study a negative ΔS_E value has only been observed for 1,2-bis(2-pyridyl)ethylene (-2.8 J K^{-1} mol^{-1}). The entropies of activation for the molecules presented in this chapter range from -3 to 307 J K^{-1} mol^{-1}, as can be seen in Table V-3.

TABLE V-6: Comparison of Calculated and Observed ΔS_E Values for Some Symmetric Diaryl Molecules

(1) $\Delta S_E = 2\ \Delta H_E - 60$ (for molecular rotation below the T_g for polystyrene).

(2) $\Delta S_E = 2.5\ \Delta H_E - 73$ (for co-operative motion of the solute with polystyrene).

*values which agree with the observed ΔS_E, within the error limits

COMPOUND	ΔT (K)	ΔS_E calc ($J\ K^{-1}\ mol^{-1}$) Eqn. 1	$\Delta S_{Ecalc.}$ ($J\ K^{-1}\ mol^{-1}$) Eqn. 2	ΔS_{Eobs} ($J\ K^{-1}\ mol^{-1}$)
Dibenzothiophene sulfone	204-321	19*	26*	24 ±12
Diphenyl sulfone	205-240	79	82	121 ±11
Di-p-tolyl sulfone	280-300	81*	104	84 ±15
p,p'-Dichlorodiphenyl sulfone	306-326	94*	122	70 ±16
Dibenzothiophene	201-231	17*	24*	22 ±15
Dibenzothiophene sulfoxide	269-300	17*	24*	23 ±10
Diphenyl sulfoxide	251-283	59*	77	60 ±15
Di-p-tolyl sulfoxide	294-324	39*	98	49 ±10
1,2-Diphenylcyclopropenone	271-303	107	215	307 ±31
2,5-Diphenyl-1,3,4-oxadiazole	263-308	25	35	1.0 ±12
1,2-Bis(2-pyridyl)ethylene	205-252	5	8	- 3 ±4
1,2-Bis(4-pyridyl)ethylene	220-253	22*	6	30 ±19

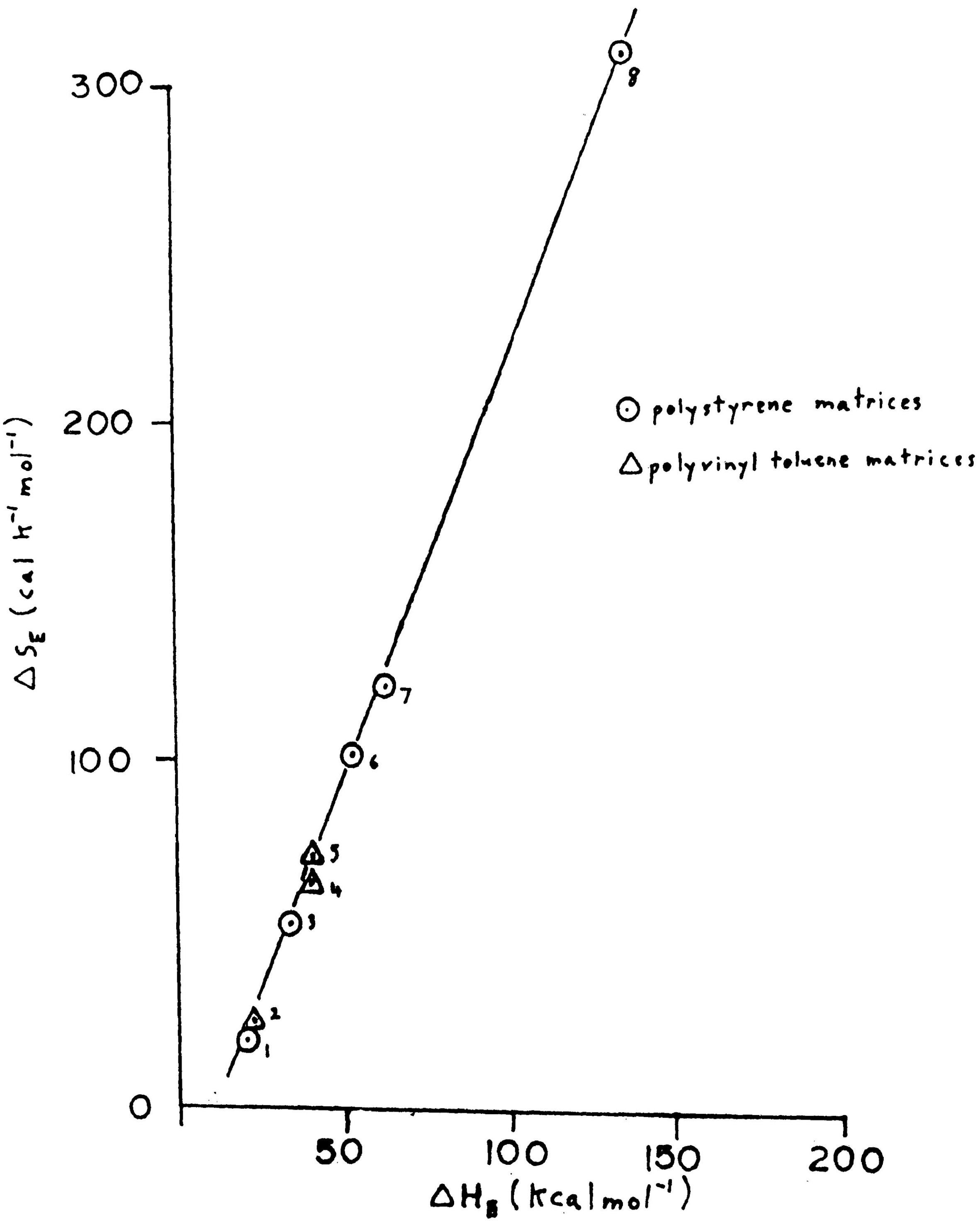


Fig. V-7: Plot of Entropy of Activation (ΔS_E) versus Enthalpy of Activation (ΔH_E) for Some Molecules which Exhibit Co-operative Motion in Polymer Matrices:

1. 4-phenyl pyridine, 2. 2-Nitrobiphenyl,
3. 4-Fluorobiphenyl, 3. 4-Fluorobiphenyl,
4. 2,2'-bipyridine 5. 4-Nitrobiphenyl,
6. Cholest-4-en-3-one, 7. Anthrone, and 8. Tetracyclone

A number of equations have been developed by other workers which correlate linearly ΔS_E and ΔH_E for various kinds of relaxation processes for certain types of molecules. Two such equations[20] are $\Delta S_E = 2\ \Delta H_E - 60$ (V-7), for rigid molecules which have absorption maxima below the glass transition temperature of the matrix and the other is $\Delta S_E = 2.5\ \Delta H_E - 73$ (V-8), for co-operative motion above the glass transition temperature of the matrix.[22] The experimental enthalpies of activation were inserted into these equations for the appropriate cases and the calculated ΔS_E values were compared with the observed entropies of activation, as in Table V-6. Table V-6 shows the results for the equation (V-7), for rigid molecules with absorption maxima. From Table V-6 it can be seen that the $\Delta S_{E(obs)}$ and $\Delta S_{E(calc)}$ values from Eqn. V-7 agree within experimental error for most of the molecules which have absorption maxima below the glass-transition temperature of polystyrene. Exceptions are diphenyl sulfone, 1,2-bis(pyridyl)ethylene, and 2,5-diphenyl-1,3,4-oxadiazole. The ΔH_E values of all the molecules studied in this chapter with absorption maxima above room temperature were put into Eqn. V-8,which was developed for co-operative motion in polymer matrices. The plot of ΔS_E versus ΔH_E for a series of molecules which undergo co-operative motion with polymer chains is shown in Fig.V-7.

The temperature range (205 - 240 K) where absorption maxima were found and the ΔH_E value of 62.0 kJ mol^{-1} for diphenyl sulfone are suggestive of molecular rotation. Other molecules of similar size

TABLE V-7: Free Energy of Activation (ΔG_E) and Free Enthalpy of Activation for Some Diaryl Molecules

Molecule	$\Delta G_{E(200\ K)}$ (kJ mol^{-1})	ΔH_E (kJ mol^{-1})
1,2-Bis(2-pyridyl)ethylene	33.1	32.5
1,2-Bis(4-pyridyl)ethylene	33.4	32
Dibenzothiophene	34.1	39
Dibenzothiophene sulfone	35	40
2,5-Diphenyl-1,3,4-oxadiazole	43	43
Dibenzothiophene sulfoxide	43.4	38.9

and shape to diphenyl sulfone also appear within experimental error limits to obey the equation (see Table V-6) for molecular rotation. Diphenyl sulfoxide has an observed ΔS_E value of 60 J K^{-1} mol^{-1} which agrees well with the calculated ΔS_E value of 59 J K^{-1} mol^{-1} from Eqn. V-7 for molecular rotation. It also has a ΔH_E value of 59.9 kJ mol^{-1}, which corresponds well with the value expected for molecular rotation of molecules with similar structure. For example, diphenyl sulfone has a ΔH_E value of 62.0 kJ mol^{-1}, while 2,5-diphenyl-1,3,4-oxadiazole has a calculated ΔS_E value of 35 J K^{-1} mol^{-1} as calculated from Equation V-8 for co-operative motion.

This ΔS_E value does not agree with the observed ΔS_E value of 1 J K^{-1} mol^{-1}. The value of the calculated ΔS_E (25 J K^{-1} mol^{-1}) from Equation (1) (Table V-6) for molecular rotation also is quite different from the observed ΔS_E value (Table V-6).

An arguement in favour of molecular rotation is that the ΔH_E value (42.7 kJ mol^{-1}) and the ΔG_E value (42.7 kJ mol^{-1}) at 200 K fit the expected pattern for the series of molecules shown in Table V-7. All the molecules listed in Table V-7 are rigid, have a zero dipole moment component along the X and Z axes, and display overall molecular rotation. These molecules are capable of a barrel motion which could predominate and could account for the observed ΔH_E values. Also the ΔG_E values at 200 K (Table V-7) are remarkably similar for these moleules, with the exception of 1,2-diphenyl-1,3,4-oxadiazole (ΔG_E = 43 kJ mol^{-1}).

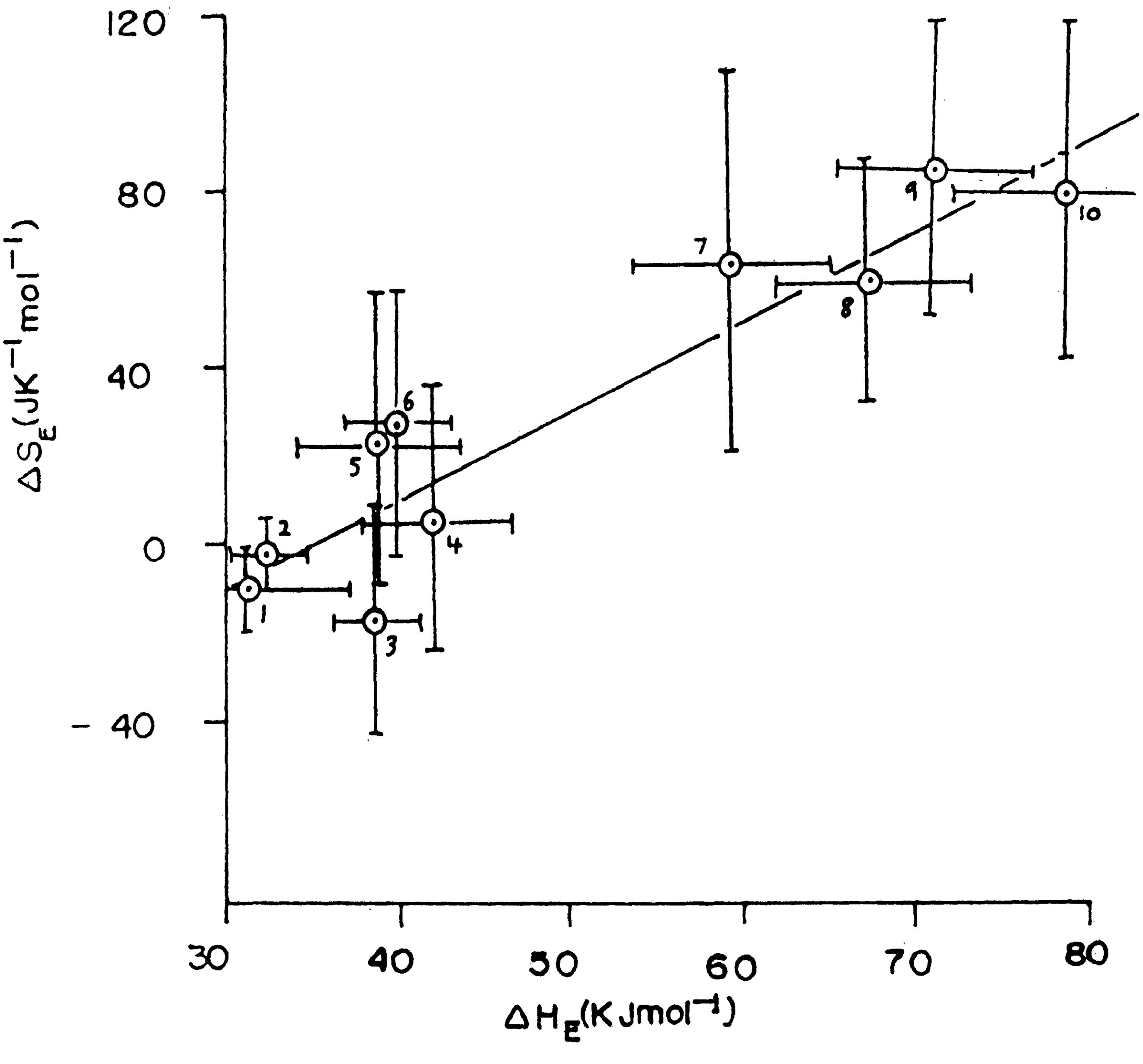


FIG. V-8: Plot of Entropy of Activation (ΔS_E) versus Enthalpy of Activation (ΔH_E) for some Symmetric Diaryl Molecules in Polystyrene:

1. 1,2-Bis(4-pyridyl)ethylene 2. 1,2-Bis(2-pyridyl)ethylene,
3. Dibenzothiophene sulfoxide, 4. 2,5-Diphenyl-1,3,4-oxadiazole,
5. Dibenzothiophene, 6. Dibenzothiophene sulfone, 7. Diphenyl Sulfoxide,
8. Di-p-tolyl sulfoxide, 9. Di-p-tolyl sulfone, and,
10. p,p'-Dichlorodiphenyl sulfone.

The dibenzothiophene, dibenzothiophene sulfone and dibenzothiophene sulfoxide molecules all have a ΔH_E value of about 39 kJ mol^{-1} which is typical for molecular relaxation of this type of molecule. In the two pyridyl ethylenes which are similar in size to the above molecules the angle of inclination of the resultant dipole to the Y axis is different from the dibenzothiophene-type molecules. In the pyridyl ethylene-type molecules the ΔH_E value is about 33 kJ mol^{-1}, and the ΔG_E about 33.5 kJ mol^{-1}. When the size of the molecule is increased as in 2,5-diphenyl-1,3,4-oxadiazole the ΔH_E value increases to 43 kJ mol^{-1} and the ΔG_{E300} value to 43 kJ mol^{-1}. These ΔG_E and ΔH_E values and their modest increase for 2,5-diphenyl-1,3,4-oxadiazole suggest a molecular relaxation process, with a possible large contribution from barrel motion about the X axis.

Fig. V-8 shows a plot of the entropy change of the activation process, ΔS_E versus ΔH_E, for a series of rigid symmetric diaryl molecules. It would appear from Fig. V-8 that within the accuracy of ΔH_E and ΔS_E values, a reasonable linear correlation exists between the enthalpy and entropy of activation for a given type of rigid molecule dispersed in a polystyrene matrix. The increase in ΔS_E values with ΔH_E values for rigid molecules may be attributed to the fact that the larger the molecule the larger the observed ΔH_E for sweeping out a larger volume, and thus, the more the local reorganization of the medium with a corresponding increase in ΔS_E.

CONCLUSION

The experimental data and results obtained during the investigation of a series of symmetric diaryl molecules suggest that within the limitations of this approach most of them appear to be rigid. From other physical evidence symmetric diaryl sulfones and sulfoxides appear to have significant electron densities in the sulfonyl and sulfinyl-ring bonds which may well operate against the occurrence and detection of double internal rotation. This viewpoint is supported by the large ΔH_E values, such as 62.0 and 59.9 kJ mol^{-1} for diphenyl sulfone and diphenyl sulfoxide respectively. When compared to a known rigid molecule such as o-hydroxybenzophenone (ΔH_E = 58.2 kJ mol^{-1}) the ΔH_E values are indicative of molecular rotation. The ΔH_E values for all the molecules in Table V-3 show no signs of any appreciable contribution from a low enthalpy double internal rotation process.

As the size of these rigid molecules increase so do the ΔH_E values. On passing from p,p'-H to p,p'-CH_3 and p,p'-Cl for diaryl sulfones the respective ΔH_E values increase from 67.0 kJ mol^{-1} for the p,p'-H to 70.7 and 78.2 kJ mol^{-1} for the p,p'-CH_3 and p,p'-Cl substituted sulfones. The same pattern with slightly lower ΔH_E values was observed for the corresponding sulfoxides. In the diaryl sulfones and other diaryl molecules presented in this chapter, with the exception of the sulfoxides the resultant dipole moments lie along the Y axis. As a consequence molecular rotation can occur about the X and Z axes. In sulfoxides, however, the resultant dipole moment lies out of the plane of the paper so that rotation can occur about all three molecular axes.

Molecules such as 1,2-diphenylcyclopropenone, 2,5-diphenyl-1,3,4-oxadiazole and 1,2-bis(2-pyridyl)ethylene are significantly conjugated, perhaps having a planar structure. The dielectric parameters, such as ΔH_E, ΔG_E, and ΔS_E suggest, when compared with those for coplanar diaryl molecules, that molecular rotation may be a major contributor to the observed relaxation process of 2,5-diphenyl-1,3,4,-oxadiazole.

1,2-Diphenylcyclopropenone has a ΔH_E value of 115 kJ mol^{-1} and a ΔS_E value of 307 J K^{-1} mol^{-1}, which when compared to other similarly sized and shaped molecules appears to be too large for molecular rotation. This and other data previously given suggest that 1,2-diphenylcyclopropenone may undergo co-operative rotation with the polymer chains.

1,2-Bis(4-pyridyl)ethylene was shown to have a ΔH_E value of 31.4 kJ mol^{-1} which corresponds to the volume swept out by a molecule with ring inclinations of about 45° (Table V-5). Relaxation parameters (Table V-3) for this and most other molecules discussed in this chapter support the idea that the major contribution to dielectric relaxation is from molecular rotation.

It may be concluded that all of the symmetric diaryl molecules presented in this chapter exhibit overall molecular rotation with the exception of 1,2-diphenylcyclopropenone which shows co-operative motion with the polymer chains. Molecules such as dibenzothiophene, dibenzothiophene sulfone, dibenzothiophene sulfoxide, and fluorenone all have ΔH_E values of about 39 kJ mol^{-1}. Such ΔH_E values would be expected for these planar, rigid types of molecules.

1,2-Bis(4-pyridyl)ethylene and 1,2-bis(2-pyridyl)ethylene seem to undergo predominantly overall molecular rotation. In both cases the ΔH_E values are very similar, 32.5 and 31.4 kJ mol^{-1}, for 1,2-bis(2-pyridyl)ethylene and 1,2-bis(4-pyridyl)ethylene respectively. The ΔG_E values, 33.3 and 34.5 kJ mol^{-1}, at 300 K for 1,2-bis(2-pyridyl)-ethylene and 1,2-bis(4-pyridyl)ethylene respectively are also very similar. 1,2-Bis(2-pyridyl)ethylene and 1,2-bis(4-pyridyl)ethylene also showed absorption maxima in similar temperature ranges of 205 - 253 K and 220 - 253 K respectively.

When the size of a molecule is increased over that of the dibenzothiophenes and pyridyl ethylenes as in the case of 1,2-diphenyl-1,3,4-oxadiazole the ΔH_E value increases to 43 kJ mol^{-1} and the ΔG_E value also to 43 kJ mol^{-1}.

Once the plane of one ring in a symmetric diaryl molecule such as diphenyl sulfone becomes orientated perpendicular to the other ring, then the ΔH_E and ΔS_E values considerably increase in comparison to the planar analogues. For example, diphenyl sulfone has a ΔH_E value of 61 kJ mol^{-1} and a ΔS_E value of 121 J K^{-1} mol^{-1}. Dibenzothiophene sulfone, however, has a ΔH_E value of 39 kJ mol^{-1} and a ΔS_E value of 24 J K^{-1} mol^{-1}. This pattern is also apparent with other diaryl sulfones and sulfoxides.

Fig. V-5 also reveals that there is a linear dependence of ΔH_E upon the rotational volume about the X and Z axes. A reasonably good linear plot also exists for the mean volume versus ΔH_E (Table V-5). From a plot of ΔS_E versus ΔH_E for all the symmetric diaryl molecules discussed in this chapter a reasonably linear relationship was observed (Fig. V-8). The equation corresponding to the mean line to all the points was found to be:

$$\Delta S_E = 2.2\ \Delta H_E - 30 \qquad \text{V-9}$$

On the whole, except for diphenyl sulfone and 1,2-diphenylcyclopropenone the symmetric diaryl molecules fitted the above equation.

In view of the above findings it would seem reasonable to carry out further investigations of these types of molecules, such as studying molecules with various substituents at different ring postions, and molecules with other bridging groups.

TABLE V-8: Fuoss-Kirkwood Analysis Parameters of Some Symmetric Diaryl Compounds in Polystyrene Matrices at a Variety of Temperatures

T(K)	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	$\mu(D)$	ε_∞
0.840M Dibenzothiophene in Polystyrene						
201.3	--	2.98	-	7.4	--	--
207.3	85.1	3.27	0.20	3.6	--	2.49
213.7	41.9	3.58	--	3.7	0.47	2.49
219	24.9	3.81	0.47	3.8	0.49	2.49
226.2	13.8	4.06	0.24	3.9	0.47	3.95
230.6	7.0	4.70	0.22	4.0	0.50	4.02
0.359M Dibenzothiophene sulfone in Polystyrene						
204.4	163.7	3.0	0.22	3.2	0.67	0.70
209.9	90.1	3.2	0.21	3.2	0.70	0.67
213.9	64.0	3.4	0.22	3.9	0.71	0.71
218.4	38.7	3.6	0.28	3.9	0.67	0.67
221.3	22.0	3.9	0.22	3.7	0.73	0.74
230.8	12.4	4.1	0.22	3.9	0.78	0.78
0.124M Dibenzothiophene sulfoxide in Polystyrene						
264.6	125.6	3.1	0.10	6.1	2.5	2.51
269.4	96.8	3.2	0.11	6.2	2.4	2.51
275.2	54.7	3.4	0.10	6.3	2.9	2.50
281.9	47.4	3.6	0.10	7.1	5.8	--
288.1	59.1	3.8	0.13	7.9	2.6	2.50
0.643M Diphenyl sulfoxide in Polystyrene						
250.8	478	2.5	0.12	28.7	1.7	2.73
256	205	2.9	0.18	30.1	1.6	2.73
263	119	3.1	0.16	30.8	1.8	2.72
269	63.4	3.4	0.17	31.6	1.8	2.72
271.2	49.4	3.5	0.18	31.8	1.8	2.72
278	22.2	3.9	0.18	33.4	1.8	2.73
283.3	15.1	4.0	0.18	33.8	1.8	2.73

TABLE V-8: continued...

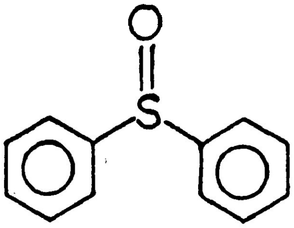
T(K)	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	$\mu(D)$	ε_∞
0.423M Diphenyl sulfone in Polystyrene						
205.4	530.5	2.5	0.22	9.6	1.0	2.72
214.6	44.2	3.6	0.25	9.6	1.0	2.72
220.2	18.8	3.9	0.31	12.9	1.0	2.71
225	16.5	4.0	0.32	13.2	1.0	2.71
231.6	8.3	4.3	0.34	15.0	1.0	2.71
240	2.8	4.8	0.28	15.4	1.2	2.70
0.190M p,p'-Dichlorodiphenyl sulfone						
306.2	365.4	2.3	0.19	18.0	2.5	4.20
309	--	2.4	--	--	--	--
311	191.1	2.5	0.15	15.0	2.5	4.00
316.1	198.4	2.7	0.16	16.0	2.5	4.20
321.1	191.8	2.9	0.19	19.0	2.5	4.30
0.244M Di-p-tolyl sulfoxide in Polystyrene						
310.6	278.6	2.7	0.16	12.1	2.1	2.6
314.3	239.4	2.8	0.16	12,5	2.1	2.6
316.5	158.6	3.0	0.14	13.9	2.4	2.6
322.9	127.3	--	0.14	--	2.5	2.5
325.4	118.3	3.1	0.13	14.5	2.7	2.5
328.3	104.1	3.2	0.11	15.1	2.9	2.5
0.417M Di-p-tolyl sulfone in Polystyrene						
279.8	89.8	3.3	0.20	19.4	1.8	2.50
283.8	68.9	3.4	0.20	20.8	1.8	2.50
288.2	43.3	3.5	0.21	22.2	1.9	2.49
291.8	36.3	3.6	0.20	23.1	1.0	2.48
297.2	17.9	3.9	0.19	24.9	2.1	2.47
299.8	17.0	4.0	0.18	25.3	2.2	2.46

TABLE V-8: continued...

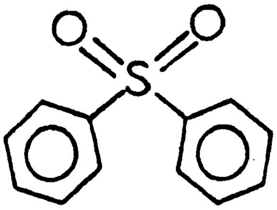
T(K)	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	$\mu(D)$	ε_∞
0.736M 1,2-Bis(2-pyridyl)ethylene in Polystyrene						
204.8	92.7	3.2	0.18	11.4	1.0	2.20
214.5	26.1	3.8	0.20	12.3	1.0	2.20
223.5	11.9	4.1	0.21	13.0	1.0	2.20
230.9	5.5	4.5	0.22	13.6	1.0	2.20
246.4	3.0	4.7	0.26	14.4	1.0	2.23
251.7	1.8	4.9	0.29	14.6	1.0	2.23
0.470M 1,2-Bis(4-pyridyl)ethylene in Polystyrene						
205	188.1	2.9	0.37	2.4	0.4	2.44
212	92.3	3.2	0.35	2.8	1.1	4.60
219.9	25.3	3.8	0.44	3.4	0.4	2.49
253.3	13.4	4.1	0.44	3.5	0.4	2.50
231.2	9.0	4.3	0.50	3.6	0.4	2.50
236.1	6.2	4.4	0.52	3.5	0.4	2.50
241.8	4.2	4.6	0.53	3.5	0.4	2.50
246.3	3.0	4.7	0.54	3.5	0.4	2.30
0.283M 1,2-Diphenylcyclopropenone in Polystyrene						
277.7	40.4	6.4	0.03	44.5	0.2	1.57
282.7	21.0	6.8	0.06	43.8	0.2	1.56
288.2	12.1	7.1	0.05	43.4	0.2	1.56
293.6	7.1	7.4	0.09	42.9	0.2	1.56
299	4.0	7.9	0.14	42.4	0.2	1.55
0.298M 2,5-Diphenyl-1,3,4-oxadiazole in Polystyrene						
263.4	55.6	3.5	0.18	8.1	1.3	2.64
277.7	15.7	4.0	0.18	9.1	1.5	2.64
287.5	9.2	4.2	0.19	9.8	0.5	2.64
292.1	7.0	4.4	0.20	10.3	0.5	2.64
302.3	3.1	4.7	0.19	11.4	1.6	2.63
307.7	2.9	4.7	0.20	11.9	1.7	2.63

TABLE V-9: Structures of Some Rigid Symmetric Diaryl Molecules

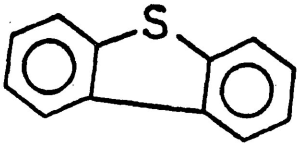
Diphenyl sulfoxide



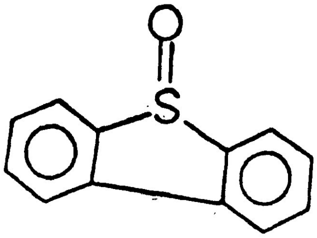
Diphenyl sulfone



Dibenzothiophene



Dibenzothiophene sulfoxide



Dibenzothiophene sulfone

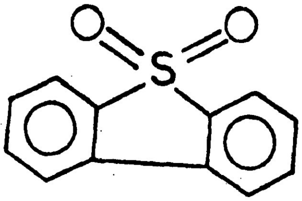
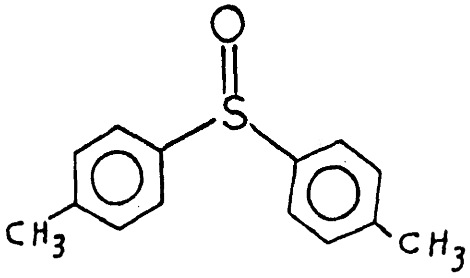
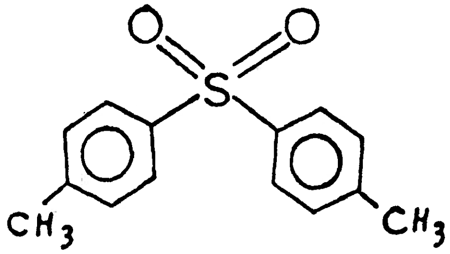


TABLE V-9: continued....

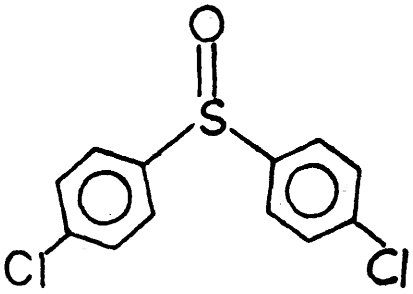
Di-p-tolyl sulfoxide



Di-p-tolyl sulfone



p,p'-Dichlorodiphenyl sulfoxide



p,p'-Dichlorodiphenyl sulfone

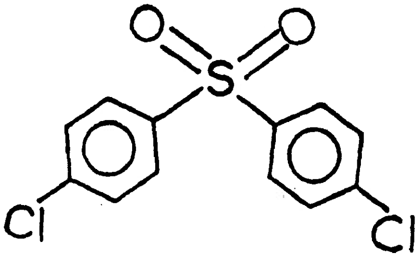
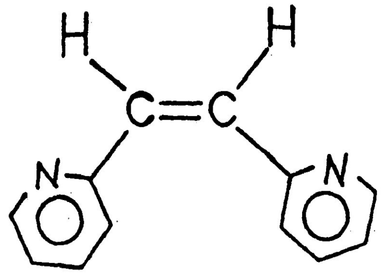
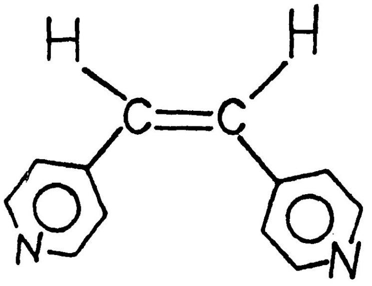


TABLE V-9: continued....

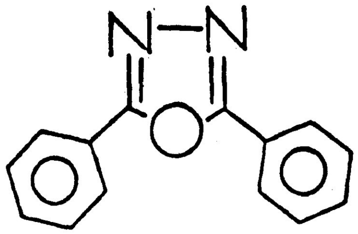
1,2-Bis(2-pyridyl)-ethylene



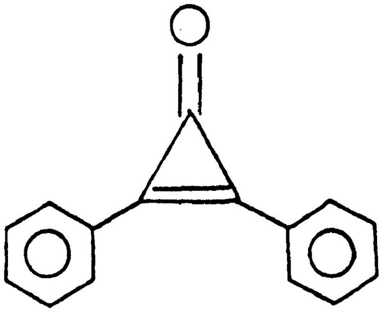
1,2-Bis(4-pyridyl)-ethylene



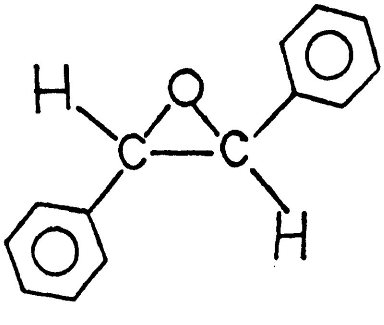
2,5-Diphenyl-1,3,4-oxadiazole



1,2-Diphenylcyclopropenone



1,2,Trans-stilbene oxide



REFERENCES

1. M. Davies and J. Swain, Trans. Frarday Soc., 67, 1637 (1971).
2. D. M. Roberti, O. F. Kalman and C. P. Smyth, J. Am. Chem. Soc., 82, 3523 (1960).
3. F. K. Fonq, J. Chem. Phys., 40, 132 (1964).
4. I. Schneider, J. Chem. Phys., 32, 665 (1960).
5. C. Cumper and R. F. Rossiter, Trans. Faraday Soc., 2900 (1969).
6. C. W. N. Cumper, J. F. Read, and A. I. Vogel, J. Chem. Soc., 5860 (1965).
7. C. W. N. Cumper, J. F. Read and A. I. Vogel, J. Chem. Soc., A, 239 (1966).
8. G. Zeandri, A. Mangini, and R. Passerini, Gazzetta, 84, 3, 73 (1954).
9. H. P. Knoch and W. E. Moffit, Trans. Faraday Soc., 7, 47 (1951).
10. D. W. J. Cruickshank, B. C. Webster, D. F. Mayers, J. Chem. Phys., 40, 3733 (1964).
11. J. Toussaint, Bull. Soc. Chem. Belgic, 54, 319 (1945).
12. S. C. Abrahams, Acta Cryst., 10, 417 (1957).
13. M. Davies and A. Edwards, Trans. Faraday Soc., 67, 1637 (1967).
14. D. A. Pitt and C. P. Smyth, J. Phys. Chem., 63, 582 (1959).
15. S. P. Tay and S. Walker, J. Chem. Phys., 63, 1634 (1975).
16. K. Higasi and C. P. Smyth, J. Am. Chem. Soc., 82, 4759 (1960).
17. Zuccarello *et al.*, J. Phys. Chem., 79, 103 (1972).
18. K. Higasi, "Dielectric Relaxation and Molecular Structure", (Research Institute of Applied Electricity, Hokkaido University, Japan, 1961).

19. E. DiCarlo and C. P. Smyth, J. Am. Chem. Soc., 84, 3638 (1962).

20. H. A. Khwaja, M. A. Mazid, This laboratory, private communication.

21. M. Davies, Quart. Review, 8, 250 (1954).

22. J. Chao, This laboratory, private communication.

23. A. McCellan, "Tables of Experimental Dipole Moments", W. H. Freeman and Co., San Francisco and London (1963).

24. W. Maier, Arch. sci. (Geneva), 12, 20 (1959).

CHAPTER VI

DIELECTRIC RELAXATION OF SOME ASYMMETRIC DIARYL MOLECULES

INTRODUCTION

In the previous chapter it was shown that some symmetric diaryl molecules such as certain sulfoxides, sulfones, and related compounds do not exhibit any noticeable internal relaxation process. Factors which may account for this are the electronic and steric properties of these molecules. If these factors are not significant then some symmetrical diaryl ethers, sulfides, and ketones may display a rapid coupled ring rotation relaxation process (double-internal rotation) (see Chapters I and VII). Since a symmetrical structure appears to be one of the criteria for this type of relaxation process it is of interest to examine whether certain asymmetric diaryl molecules undergo double-internal rotation. A series of asymmetric diaryl ethers, ketones, and one oxazole were studied in polystyrene matrices at frequencies of 200 to 100,000 Hz in the temperature range of 80 to 320 K. The term "asymmetric diaryl molecules" in this thesis refers to those molecules which have a bridging species with two or less planes of symmetry and/or two phenyl rings with different structures.

In symmetric diaryl molecules such as diphenyl ether, rotation is possible about the long X molecular axis as well as the Z axis, (Fig. VI-1) since the net dipole moment is perpendicular to the long molecular axis (X) as well as the Z axis.

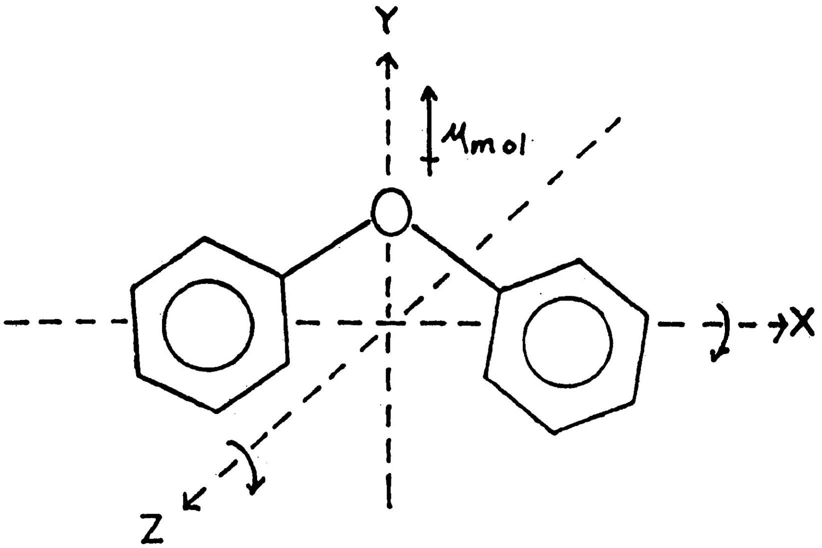


FIG. VI-1: Dipole Moment (μm) Direction and axes of Rotation for Diphenyl Ether

Studies of some asymmetric diaryl molecules[2] have shown that these molecules possess a different predominant mode of dielectric relaxation than do many symmetric diaryl ethers, sulfides, ketones, and related compounds. The dielectric relaxation behaviour of some asymmetric molecules is the subject of this chapter.

One possible reason for the fact that asymmetric diaryl molecules have different dielectric behaviour than do symmetric diaryl molecules is that in the asymmetric molecules the centre of mass is shifted relative to the position in the corresponding symmetric molecules. This may lead to an unbalanced motion and a greater disturbance of the environment. As a result longer relaxation times are observed for the asymmetric diaryl molecules than for the symmetric ones.[1] For example, p-bromodiphenyl ether has a relaxation time of 5.6×10^{-5} s at 300 K in polystyrene, while p,p'-dibromodiphenyl ether has a relaxation time of 2.6×10^{-9} s at 300 K in a polystyrene matrix. These observations could also be accounted for by a contribution to the observed relaxation process from rotation about the third principal axis. In symmetric diaryl molecules the net dipole moment is along the Y molecular axis so that molecular rotation can occur about the X and Z axes. In asymmetric diaryl molecules there are dipole moment components perpendicular to all three principal axes. Consequently, these molecules can rotate about the X, Y, and Z axes.

Most substituted asymmetric diaryl molecules possess motions of greater complexity than do symmetric diaryl molecules. In the para-substituted phenyl ethers there is a component of the dipole moment perpendicular to the plane which bisects the COC valency angle. (Fig. VI-2).

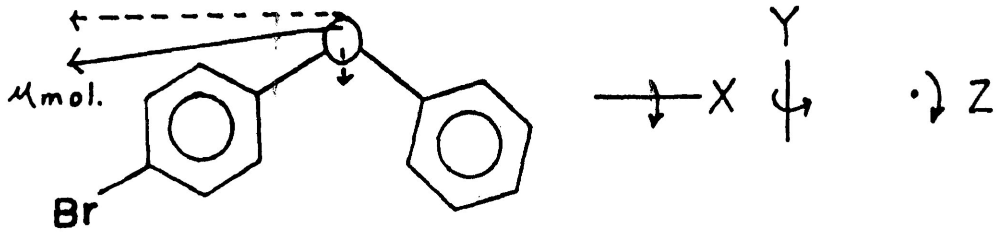
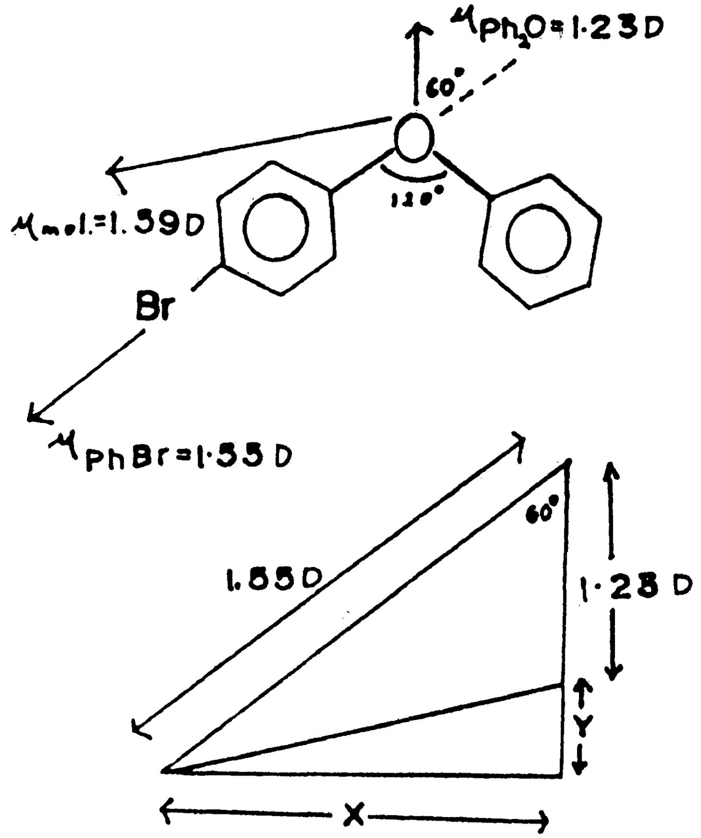


FIG. VI-2: Dipole Moment (μ_{mol}) Components and Possible Axes of Molecular Rotation for p-Bromodiphenyl ether

Because of this fixed dipole component overall rotation about the short Z and Y molecular axes becomes another mode of molecular relaxation. Should the group moment of the para substituent be of the order of 1 or 2 Debyes the resultant dipole moment direction in the molecule will not be far from the perpendicular to the plane bisecting the COC angle. As a consequence, molecular relaxation will be predominantly about the short molecular X and Z axes. A sample calculation for p-bromodiphenyl ether illustrating the above behaviour is shown in Fig. VI-3.



$$X = \sin 60^\circ (1.55) = 1.34$$

$$Y = \cos 60^\circ (1.55) - 1.23 = {}^{-}0.46$$

FIG. VI-3: Dipole Moment Components of p-Bromodiphenyl Ether p-Bromodiphenyl ether[2] was found to have a relaxation time of 72.0×10^{-12} s in dilute benzene solution at 293 K. This value appears long when compared to relaxation times found for corresponding symmetric molecules. For example, p,p'-dibromodiphenyl ether[3] has a relaxation time of 8.7×10^{-12} s in Nujol (viscosity = 197 c.p. at 295 K)[11] at 293 K, and p,p'-dibromodiphenyl sulfide[14] has a relaxation time of 8.2×10^{-12} s at 293 K in Nujol.

It is evident from the above calculations that the two dipole moment components of p-bromodiphenyl ether are -0.46 and 1.34 D along the Y and X axes respectively. These components illustrate that the resultant dipole moment direction is about 7° from being perpendicular to the plane which is perpendicular to the plane of the paper and bisects the COC angle. A phenyl substituent in the para-postion of one ring, however, has little effect on the resultant dipole moment. Consequently, a molecule such as 4-biphenylyl phenyl ether[2] exhibits an unusually short relaxation time of 9.4×10^{-12} s at 293 K in dilute benzene solution, even though the molecule is larger than p-bromodiphenyl ether. Since 4-biphenylyl phenyl ether is asymmetric the centre of mass is shifted relative to the position in diphenyl ether. As a consequence simultaneous coupled ring rotation may not be possible, since a torque must be applied to provide a balanced motion. Since a torque is required for double-internal rotation to occur in this molecule (see Chapter VII) there would be no conservation of angular momentum. However, the short relaxation time of this molecule is suggestive of an intramolecular rotation process such as phenoxy group rotation.

A factor which influences the experimentally observed relaxation time is that when the internal and overall molecular rotation modes have different paths between the same initial and final states, the observed relaxation time is related to the relaxation times τ_1 and τ_2 for the individual processes by Equation VI-1, if the alternate paths have equal probabilities.[5,6,7,8]

$$\tau_o = \frac{\tau_1\tau_2}{(\tau_1 + \tau_2)} \qquad \text{VI-1}$$

For example, the short coupled ring rotations (Fig. VII-11, Chapter VII) in diphenyl ether in combination with overall molecular rotation give a calculated relaxation time which is in accordance with the observed relaxation time.[15] This observation is noticed if τ_1 is taken as 20×10^{-12} s and τ_2 as 6×10^{-12} s. If values twice as large are taken for 4-biphenylyl phenyl ether the calculated relaxation time is found to be 9×10^{-12} s.

For rigid molecules of the size of diphenyl ether, having dipole moments along the short Y axis of the molecule, one would expect

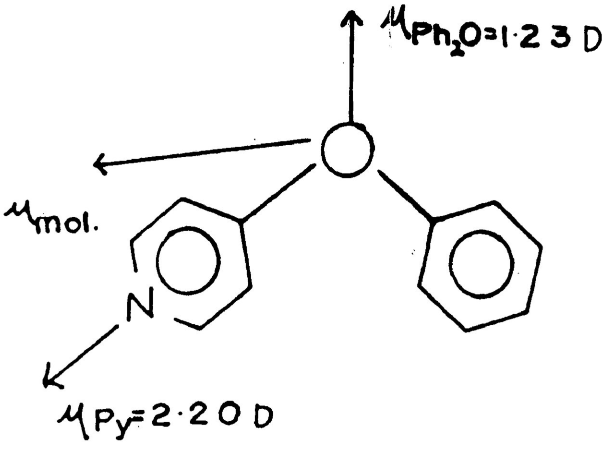
TABLE VI-1: Observed Relaxation Times of Some Asymmetric Diaryl Molecules

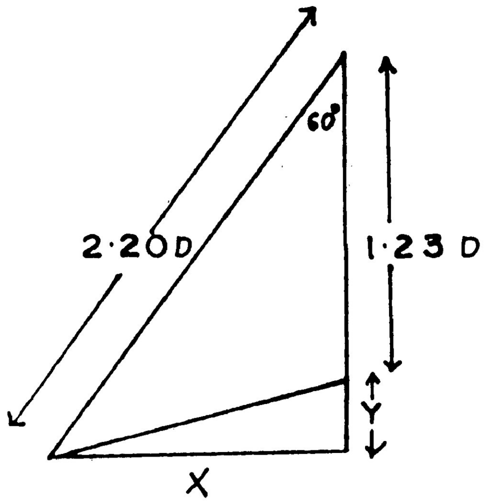
Compound	Solvent	Temp (°C)	τ_o (ps)	Reference
p-Nitrophenyl phenyl ether	Benzene	20	41	2
4-Bromophenyl phenyl ether	Benzene	20	72	2
4-Biphenylyl phenyl ether	Benzene	20	9.4	2
4-Benzoyl pyridine	p-Xylene	25	38	10
o-Pyridyl phenyl ether	Benzene	20	17.7	4
p-Pyridyl phenyl ether	Benzene	20	52.2	4
2-Methyl diphenyl ether	Benzene	20	6.6	15

to find relaxation times of the order of $\tau_1 = 20\times10^{-12}$ s in dilute benzene solution at 293 K.[2] Because of uncertainties arising from differences in shape among various molecules, only relaxation times less than 15×10^{-12} s can be taken as indicative of some internal contribution to relaxation.

Previous studies have also been made of asymmetric diaryl ethers in liquid solution at microwave frequencies (Table VI-1). When some of the molecules listed in Table VI-1 are compared with the symmetric analogues in Table VII-1 it becomes obvious that the relaxation times for asymmetric molecules are longer. For example, 4-bromodiphenyl ether has a relaxation time of 72.0 ps in benzene, (viscosity = 0.65 cp) at 293 K while bis(p-bromophenyl) ether at 293 K in Nujol (viscosity = 197 cp) has a τ value of 8.7 ps. It can also be seen in Table VI-1 and Table VII-1 that molecules which have nearly the same symmetry as the symmetric molecules have longer relaxation times. For instance, o-pyridyl phenyl ether[4] and p-pyridyl phenyl ether[4] in benzene solution at 293 K have relaxation times of 17.7 and 52.2 ps respectively as compared to 4.0 ps for diphenyl ether in benzene solution at 293 K. It is clear from these values that the pyridyl phenyl ethers must be undergoing predominantly overall molecular rotation, whereas diphenyl ether undergoes a very fast intramolecular relaxation process. The fact that ortho and para pyridyl phenyl ethers have a large difference in τ values may be attributed to the direction of the dipole moment

I: Dipole Moment Components of p-Pyridyl Phenyl Ether





$X = \sin 60^\circ (2.2) = 1.9$

$Y = \cos 60^\circ (2.2) - 1.23 = {}^{-}0.13$

The Dipole Moment Components of p-Pyridyl Phenyl Ether is 1.9 D Along the X Axis and -0.13 D Along the Y axis.

FIGURE VI-4

II: Dipole Moment Components in o-Pyridyl Phenyl Ether with a Coplanar Ring Structure

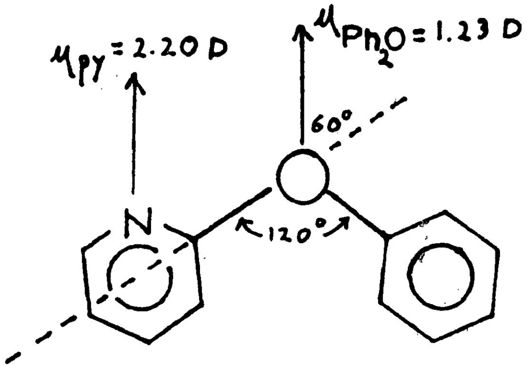


FIG. VI-5

Since μ_{Ph_2O} and μ_{py} are parallel then $\mu_{mol} = 2.20 + 1.23 = 3.43$. The Dipole Moment Components are Perpendicular to the X and Z Axes so that Molecular Rotation can Occur About These Axes.

III: Dipole moment components of o-pyridyl phenyl ether with rings positioned orthogonally.

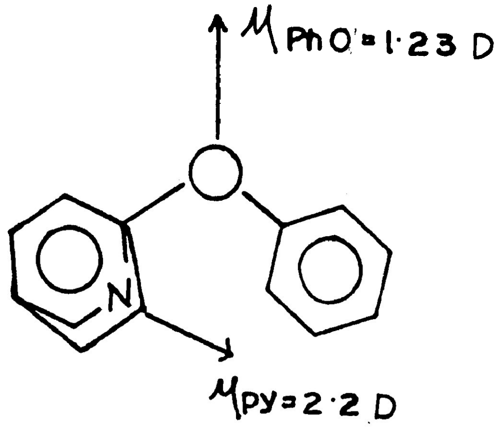


FIG. VI-6

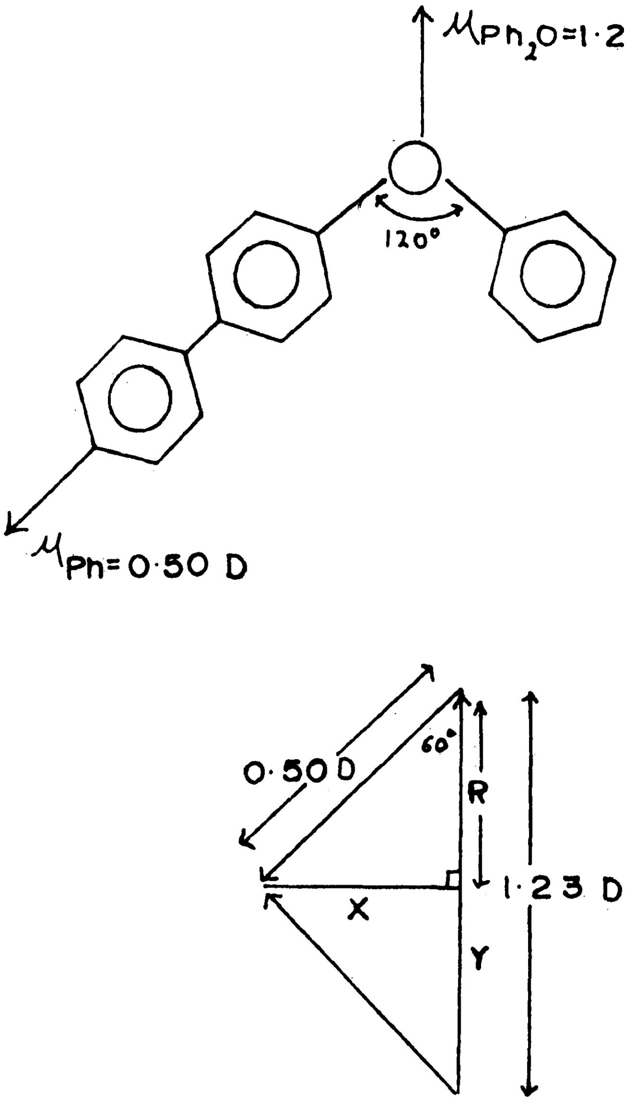
In this case it is difficult to calculate the dipole moment components since the resultant dipole is out of the plane of the oxygen valency angle. There are therefore dipole moment components perpendicular to all three molecular axes.

components (Fig. VI-4) (Fig. VI-6).

If the molecule is planar (see Fig. VI-5) then the dipole moment situation is similar to the case of benzophenone, where τ is 20.4 ps in a benzene solution at 293 K. If the rings are orthogonal, however, then the resultant dipole is out of the plane of the paper and a complicated situation arises where the dipole moment has components perpendicular to all three molecular axes so that molecular rotation is feasible about all three principal axes (Fig. VI-6). p-Pyridyl phenyl ether, however, has dipole moment components perpendicular to the short molecular Y, Z, and X, axes, and therefore, rotates about these axes sweeping out a greater volume than that by rotation about only the long molecular X axis. The dipole moment components and their magnitudes for p-pyridyl and o-pyridyl ether are shown in Figs. VI-4, VI-5, and VI-6.

Relative to diphenyl ether, p-pyridyl phenyl ether has a smaller shift of centre of mass than does 4-biphenylyl phenyl ether. Yet, 4-biphenylyl phenyl ether has a shorter relaxation time[2] of 9.4×10^{-12} s at 293 K in benzene, as compared to 52.2×10^{-12} s for p-pyridyl phenyl ether at 293 K in benzene. A key factor in explaining the difference may be the angle the molecular dipole moment makes with the Y axis (see Fig. VI-4). For example, p-pyridyl phenyl does not appear to undergo double-internal rotation as suggested in part by

IV: Dipole moment components of 4-biphenylyl phenyl ether



$X = \sin 60^{\circ}\ (.5) = 0.43$

$R - \cos 60^{\circ}\ (.5) - 0.25$

$Y = 1.23 - 0.25 = 0.98$

FIG. VI-7

It can be seen from these calculations that the dipole moment of 4-biphenylyl phenyl ether is not far from being parallel to the Y axis.

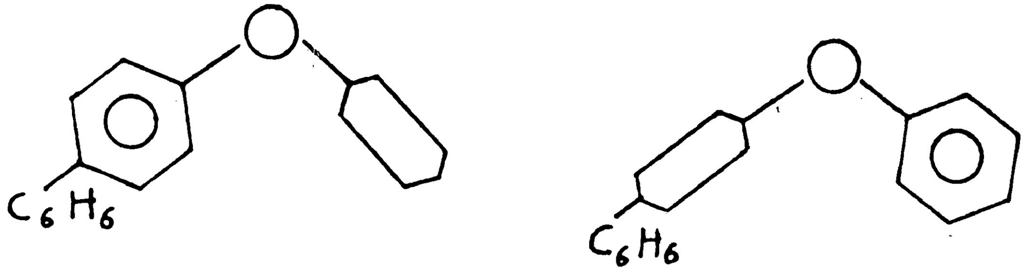


FIG. VI-8

Molecular Configurations of 4-Biphenylyl Phenyl Ether

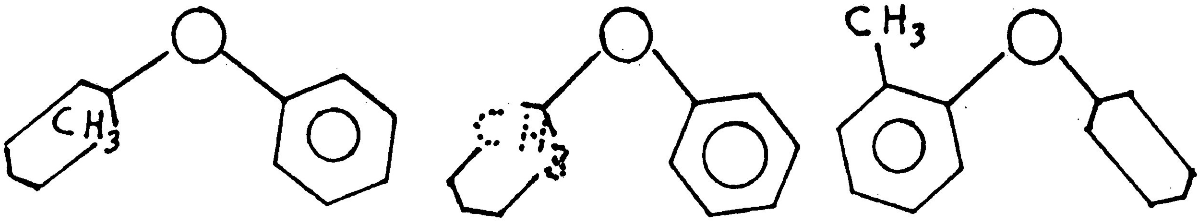


FIG. VI-9

Molecular Configurations of o-Methylphenyl Phenyl Ether the relaxation time of 52.2 ps in benzene solution at 293 K. Fig. VI-4 shows the dipole moment components of p-pyridyl phenyl ether. It can be seen that the dipole moment component about the X axis is 1.9 D, while along the Y axis it is 0.13 D. Consequently, the resultant dipole moment is not far from perpendicular to the Y axis. The major contribution to the relaxation process of this molecule will be rotation about the Y and Z axes. p-Pyridyl phenyl ether, unlike molecules such as 4-biphenylyl phenyl ether and o-methyl phenyl ether, does not have a small dipole moment of the order of that of diphenyl ether, along or very close to the Y axis. The size and angle of the resultant dipole moment may therefore be an important factor in determining whether internal rotation will be a dominant relaxation process.

Both 4-biphenylyl phenyl ether (Fig. VI-7) and 2-methyl phenyl phenyl ether have relaxation times of 9.4 ps and 6.6 ps at 298 K in benzene, respectively (see Table VI-1). The size and direction of the dipole moments are very close to that of diphenyl ether (μ = 1.23 D at 298 K in benzene[12]). If the molecular configurations given in Fig. VI-8 and Fig. VI-9 are possible and the dipole moments of the phenyl and methyl groups are small, then the same treatment as for diphenyl ether may be possible (see Chapter VII).

If $\tau_m = 18$ ps and $\tau_g = 4$ ps are assumed for 2-methyl phenyl phenyl ether then Equation VI-2:

$$\frac{1}{\tau_o} = \frac{1}{\tau_m} + \frac{1}{\tau_g} \qquad \text{VI-2}$$

where τ_m is the molecular relaxation time and τ_g is the intramolecular relaxation times, gives $\tau_o = 6.0$ ps.

The discussion part of this chapter deals with a study of some asymmetric diaryl ethers and ketones dispersed in polystyrene matrices.

EXPERIMENTAL

The study of the dielectric relaxation behaviour of some asymmetric diaryl molecules was performed primarily with the solutes dispersed in polystyrene matrices. The preparation and storage of these matrices is outlined in Chapter III. In this chapter the molecules which are discussed are p-bromodiphenyl ether, p-nitrodiphenyl ether, 4-biphenylyl phenyl ether, o-hydroxybenzophenone, 2-benzoyl pyridine, p-fluorobenzophenone, p-chlorobenzophenone, and 2,5-diphenyl oxazole. All these compounds were purchased from commercial sources and the polystyrene matrix samples were dried by storing them in a desiccator over calcium chloride prior to use. A melting point determination was performed on a sample of p-nitrodiphenyl ether in order to determine its purity. The melting point was found to be 54°C, which is in good agreement with the literature value of 56°C.

Measurements and analysis of the data were as discussed in Chapter III. Experimental values of τ, $\log_{10}f_m$, β, ε''_{max}, ε_∞, and μ at various temperatures, obtained for a series of asymmetric diaryl ethers and ketones, are listed in Table VI-5. Table VI-2 shows the values of ΔH_E, ΔS_E, ΔG_E, and τ values at 150 K, 200 K, and 300 K for each molecule. The structural diagrams of the molecules studied in this chapter are presented in Table VI-6.

DISCUSSION

An examination of Tables VI-2 and VII-8 reveals that the enthalpy of activation values for the asymmetric molecules are larger than those for the corresponding symmetric molecules. Relaxation times also behave in the above manner. ΔH_E values were determined from straight line computer generated Eyring plots (Fig. VI-10). Other relaxation parameters such as $\log f_m$, ε''_{max}, ε_o, ε_∞, etc., were determined from computer analysis of dielectric loss (ε'') = (ε'' polystyrene matrix plus solute - ε'' polystyrene) versus log frequency plots, (Fig. VI-11) and (Fig. VI-12).

TABLE VI-2; Dielectric Relaxation and Activation Parameters for Some Diaryl Molecules in Polystyrene

Molecule	$\Delta T(K)$	$\tau(s)$ 150K	200K	300K	ΔG_E(kJ mol^{-1}) 150 K	200 K	300 K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
o-Hydroxybenzophenone	256-294	5.6×10^{4}	3.7×10^{-1}	2.1×10^{-6}	49.5	46.6	40.9	58.2 ±1.0	58 ± 4
2-Benzoylpyridine	249-295	3.9×10^{8}	2.8×10^{0}	5.1×10^{-7}	56.4	50.0	37.3	75.4 ±8.9	127 ±34
p-Fluorobenzophenone	295-322	7.9×10^{10}	1.5×10^{3}	2.7×10^{-5}	67.2	60.5	47.2	87.2 ±9.4	133 ±30
p-Chlorobenzophenone	300-325	1.0×10^{10}	1.4×10^{3}	1.8×10^{-4}	64.4	60.4	51.9	77.3 ±4.3	85 ±16
p-Bromodiphenyl ether	289-319	2.4×10^{11}	3.9×10^{3}	5.6×10^{-5}	68.5	62.0	49.0	88.0 ±6.3	130 ±21
p-Nitrodiphenyl ether	304-329	2.7×10^{11}	1.1×10^{4}	4.3×10^{-4}	68.7	63.8	54.2	88.2 ±8.3	97 ±26
4-Biphenylyl phenyl ether	263-301	7.4×10^{-3}	2.0×10^{-4}	4.7×10^{-7}	29.7	34.1	42.9	16.6 ±2.4	- 84 ± 9

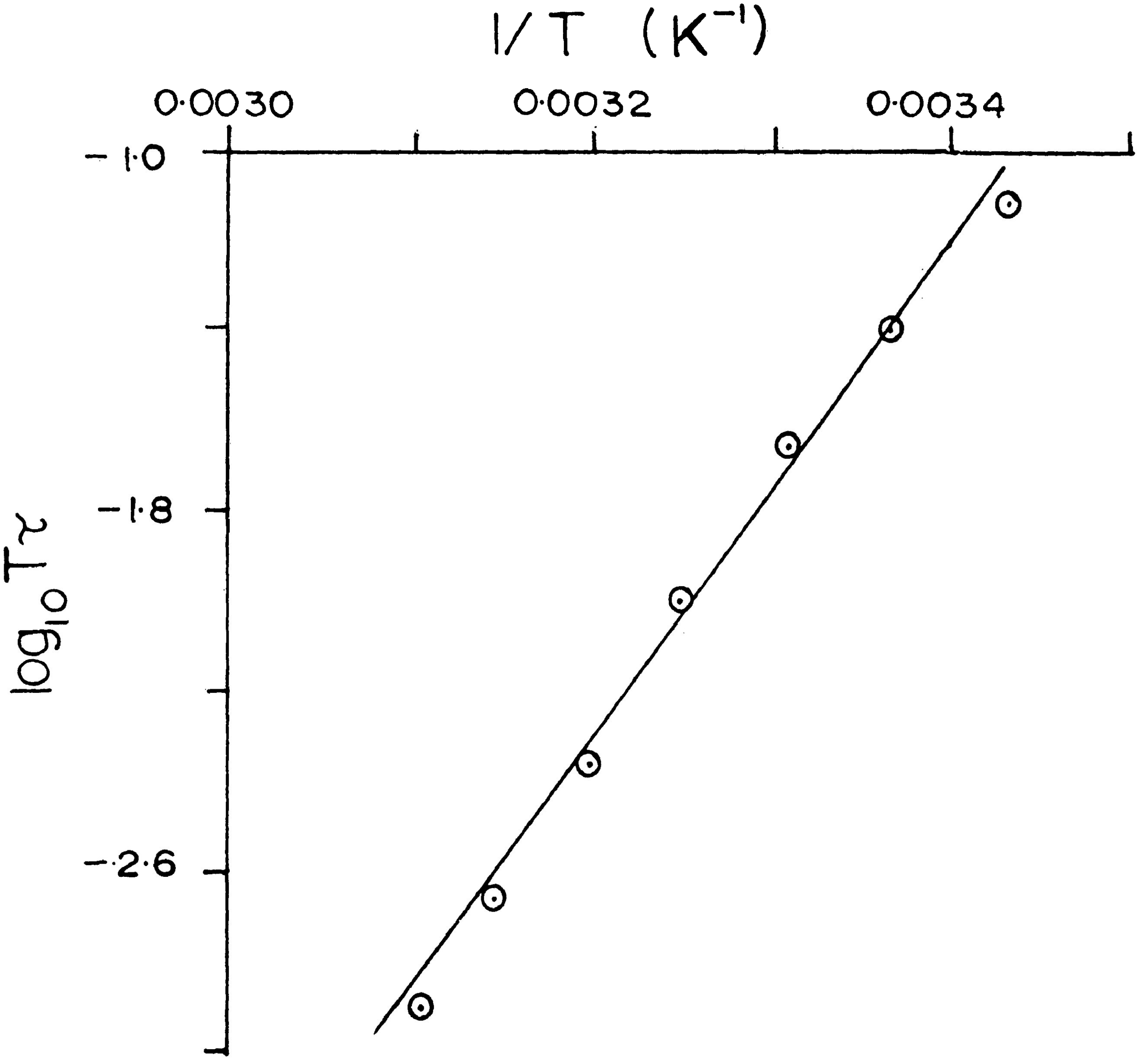


FIG. VI-10: Eyring Plot for p-Nitrophenyl Ether in Polystyrene

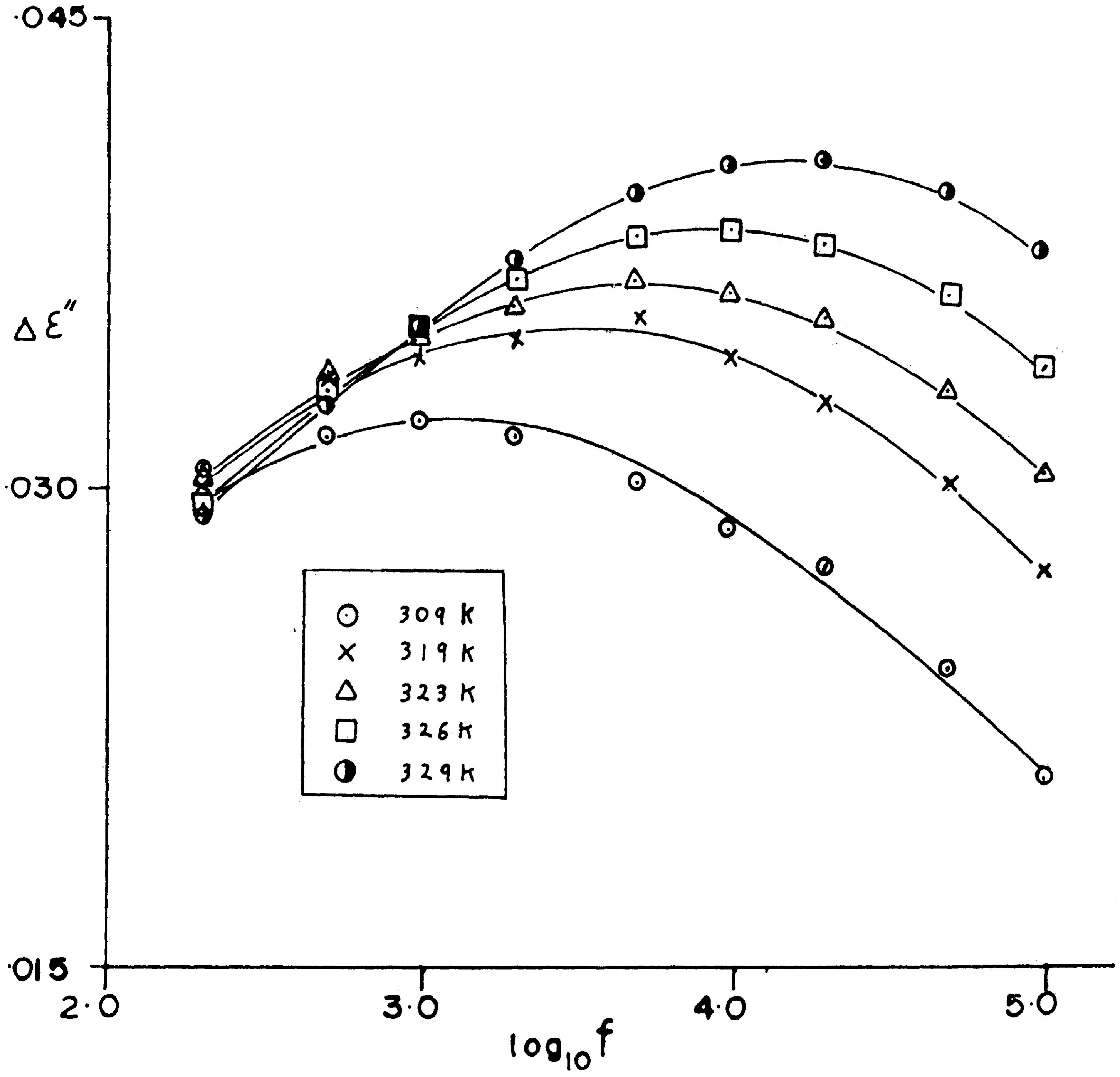


FIG. VI-11: Dielectric Absorption of 0.314 M p-Nitrodiphenyl Ether in Polystyrene in the 10^2 - 10^5 Hz Range.

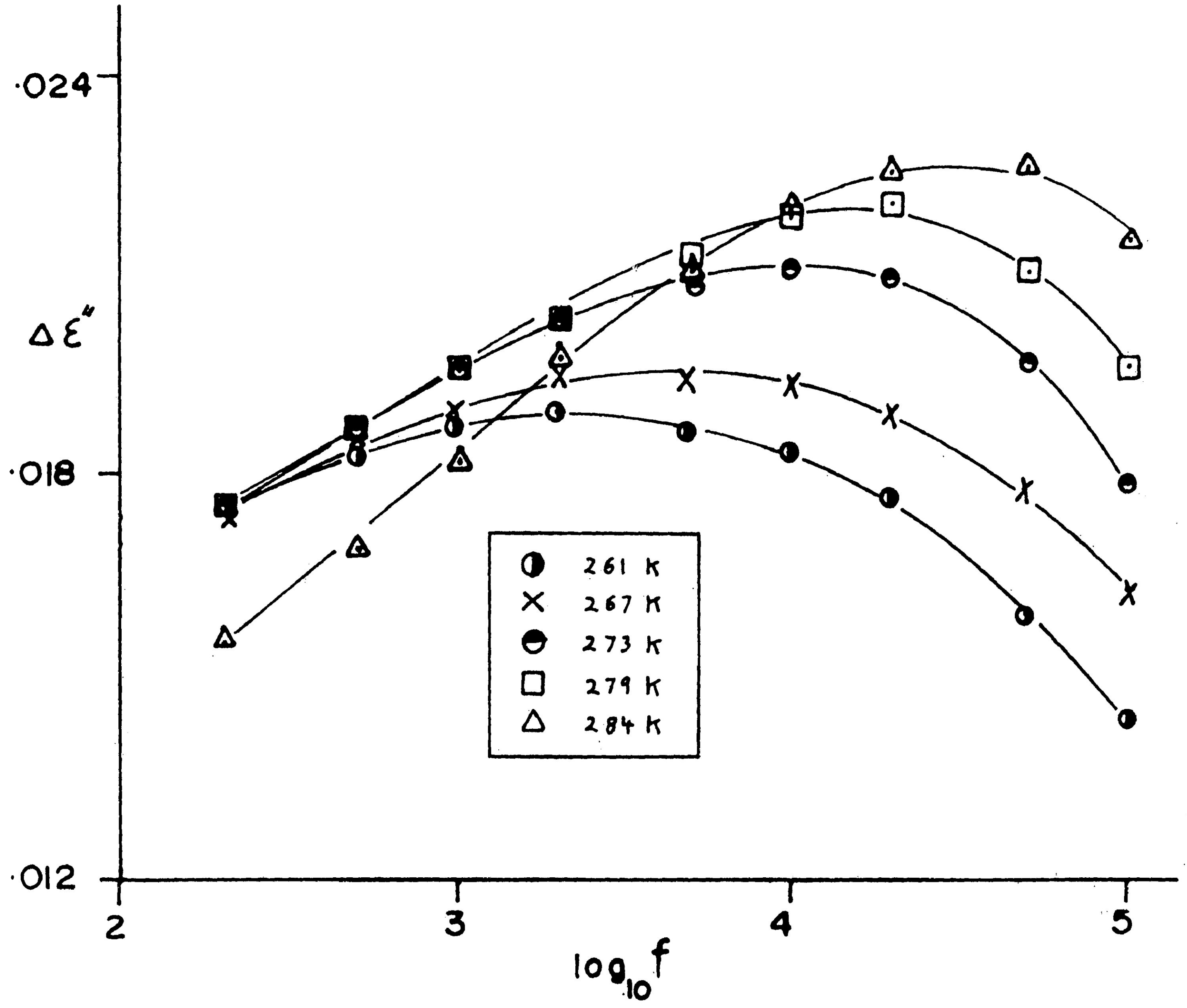


FIG. VI-12: Dielectric Absorption of 0.396M o-Hydroxybenzophenone in Polystyrene in the 10^2 - 10^5 Hz Range.

It was mentioned in the introduction to this chapter that p,p'-dibromodiphenyl and p-bromodiphenyl ethers have different relaxation times,as can be seen from solution studies in the microwave region. When these two molecules were studied in polystyrene matrices a similar behaviour was observed. The former molecule was found to have a ΔH_E value of 63.0 kJ mol^{-1}, while the second one has an enthalpy of activation value of 88.0 kJ mol^{-1}. Both these values are far too large to have arisen from intramolecular relaxation processes.

The p,p'-Bromodiphenyl ether and p-bromodiphenyl ether have β ranges of 0.27 - 0.30 from 288 - 319 K and 0.22 - 0.23 from 205 - 233 K respectively. In the case of p,p'-dibromodiphenyl ether the β values are relatively large and indicate a narrow distribution of relaxation times. It is shown (see Chapter VII) that this molecule undergoes double-internal rotation. The major contribution to dielectric relaxation at the above specified temperature region would be molecular rotation about the X and Z axes. One reason is that at near liquid nitrogen temperatures double-internal rotation was observed, therefore, in the temperature range 288 - 319 K it is likely that a molecular reorientation process is occurring, as is reflected in the ΔH_E value of 63.0 kJ mol^{-1}. p-Bromodiphenyl ether has a wider distribution of relaxation times, which might result in part from the fact that molecular rotation can occur about all three molecular axes. Whereas it is known that symmetric diaryl molecules orientate about the long X axis and the Z axis, asymmetric molecules can rotate about the X and Z axes as well as the short molecular Y axis. The reason is that asymmetric diaryl molecules possess dipole moment components perpendicular to all three principal axes (Fig. VI-13).

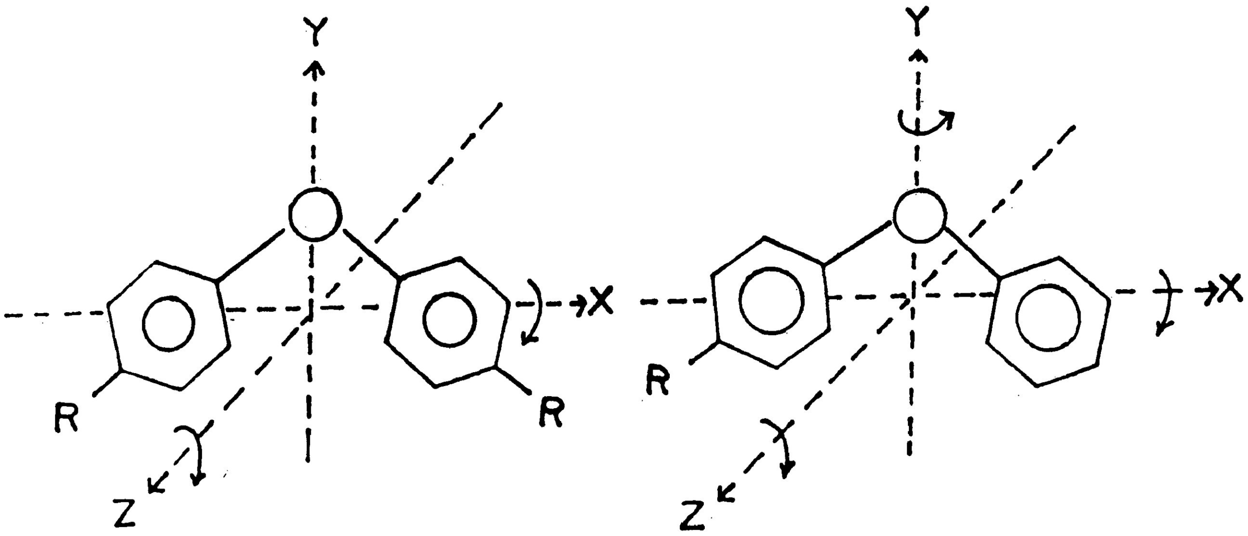


FIG. VI-13: Rotation about Molecular Axes in Symmetric and Asymmetric Diaryl Molecules.

Other relaxation parameters also suggest the above mentioned types of relaxation. For example, the ΔS_E value for p-bromodiphenyl ether is 130 J K^{-1} mol^{-1}, while for p,p'-dibromodiphenyl ether it is 129 J K^{-1} mol^{-1}. Such a large positive ΔS_E suggests a molecular reorientation process. Molecules which exhibit intramolecular relaxation processes such as symmetric diaryl molecules usually possess negative ΔS_E values, as for example benzophenone, which has a ΔS_E value of -14 J K^{-1} mol^{-1}. Small negative ΔS_E values result when there is a small disturbance to the surrounding medium. For example, during double-internal rotation the molecule almost rotates within its own volume so that there is little disturbance of the surrounding polymer chains.

The relaxation time of 5.6×10^{-5} s at 300 K for p-bromodiphenyl ether is appreciably longer than that for p,p'-dibromodiphenyl ether ($\tau = 2.6\times10^{-9}$ s at 300 K),this observation indicates a higher energy process in the case of p-bromodiphenyl ether. The ΔG_E values further substantiate the idea of rotation about the molecular X, Y, and Z axes for para substituted asymmetric diaryl molecules. For example, the ΔG_E at 250 K is 62.0 kJ mol^{-1} for p-bromodiphenyl ether, while for p,p'-dibromodiphenyl ether the ΔG_E value at 250 K is 37.0 kJ mol^{-1}.

Another asymmetric molecule which behaves similarly to p-bromodiphenyl ether is p-nitrodiphenyl ether. The dielectric loss curves for p-nitrodiphenyl ether are shown in Fig. VI-11 and the Eyring plot in Fig. VI-10. From Courtauld models it can be seen that a bromine atom has a van der Waals volume of 27.7 $Å^3$ and the nitro group a van der Waals volume of 25.8 $Å^3$.[13] It is therefore not surprising to see that both molecules have nearly equal enthalpies of activation, 88.0 kJ mol^{-1} for p-bromodiphenyl ether and 88.2 kJ mol^{-1} for p-nitrodiphenyl ether. p-Nitrodiphenyl ether therefore appears to undergo molecular rotation about the three molecular axes. It has a dipole moment of 2.80 D at 298 K in benzene[12] which suggests a considerable contribution from molecular relaxation. In support of the above statements are the β values of 0.19 to 0.21 and the positive ΔS_E value of 97 J K^{-1} mol^{-1}. It's temperature range of maximum dielectric loss is from 304 - 329 K, which is close to that of p-bromodiphenyl ether (288 to 319 K).

p-Nitrodiphenyl ether as with other asymmetric diaryl molecules has a centre of mass which is shifted away from the position in the analogous symmetric diaryl molecule. As a consequence, angular momentum is no longer conserved, so that a double-internal rotation type of mechanism is not observed.

Phenoxy group rotation is another possible relaxation process for the molecule. The ΔH_E value however, seems to be too large for phenoxy group rotation. The nitro group can take part in a resonance structure in which there is a partial double-bond character in the C_{aryl}—O bond due to mutual conjugation (Fig. VI-14). This would tend to increase any barrier for phenoxy group rotation. However, the observed ΔH_E value is too large even for this situation.

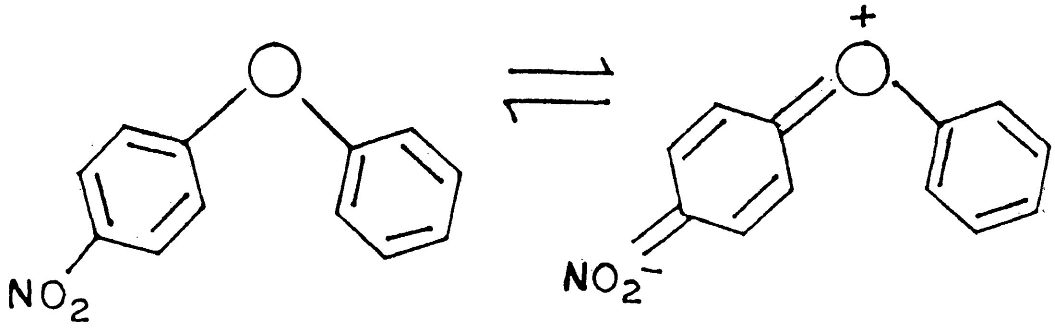


FIG. VI-14: Resonance Structures of p-Nitrodiphenyl Ether

In the case of 4-biphenylyl phenyl ether the observed ΔH_E value of 16.6 kJ mol^{-1} might be due to phenoxy group rotation. The ΔH_E value, however, appears to be much too low for overall molecular rotation of a large molecule such as 4-biphenylyl phenyl ether. Another explanation of the ΔH_E value is that double-internal rotation is being observed. This statement, however, is contrary to the conclusion derived in Chapter VII, that symmetry is a prerequisite for double-internal rotation. Also, in this case angular momentum would not be conserved. Anderson and Smyth[2] have stated that if the molecule has contributions from both molecular and intramolecular rotations then use of τ_1 = 40 ps and τ_2 = 12 ps in Equation VI-1 gives the observed relaxation time of 9.4 ps at 293 K. Anderson and Smyth favour phenoxy group rotation as the observed relaxation process in 4-biphenylyl phenyl ether on the basis of the observed relaxation time of 9.4 ps at 293 K, and the dipole moment components (see Fig. VI-7). Only one set of absorption peaks was found for 4-biphenylyl phenyl ether in the temperature range 263 to 301 K. These were found in the $\log_{10}$ frequency range 4.06 to 4.54. The negative ΔS_E value of -87 J K^{-1} mol^{-1} and the computer extrapolated dipole moments of 0.48 and 0.43 D at 300 and 330 K respectively favour an intramolecular relaxation process. The ΔG_E value at 200 K is 34.1 kJ mol^{-1}, which is lower than that of other asymmetric molecules such as p-nitrodiphenyl ether, where ΔG_E at 200 K is 63.8 kJ mol^{-1}. ΔG_E values at other temperatures show the same pattern.

The fact that 4-biphenylyl phenyl ether has a smaller dipole moment of 1.10 D at 298 K in benzene[12] is one factor along with the aromatic structure, dipole moment components, (Fig. VI-7), and relaxation parameters, which suggest that a possible mesormeric effect as in diphenyl ether may play a part in the relaxation process of the molecule. An intramolecular process such as double-internal rotation however, may be offset by the fact that angular momentum may not be conserved in the coupled intramolecular ring rotation of an asymmetric structure. Since the β values range from 0.27 to 0.38 there are contributions to dielectric relaxation from more than one process. It is evident from Table VI-2 that 4-biphenylyl phenyl ether and 1,2-diphenylcyclopropenone have absorption maxima at nearly similar temperature ranges of 269 - 301 K and 271 - 303 K respectively. 4-Biphenylyl phenyl ether, however, has a β value range of 0.27 - 0.38 as compared to 0.06 - 0.02 for 1,2-diphenylcyclopropenone. Since 1,2-diphenylcyclopropenone is a rigid molecule the difference in β values as compared to 4-biphenylyl phenyl ether is one fact which suggests that the ether undergoes a process different from molecular rotation. This fact, along with other dielectric parameters, favour an intramolecular rotation involving the phenoxy group.

Another series of compounds which show similar behaviour to the asymmetric ethers are the asymmetric diaryl ketones. One of these is o-hydroxybenzophenone in which one ring is strongly hydrogen bonded to the carbonyl group. In o-hydroxyacetophenone the strength of the hydrogen bond has been found to be about 30 kJ mol^{-1}.[10] Since in o-hydroxybenzophenone the two aromatic rings are most likely orthogonal[11] then electronic shift of charge into the carbonyl group from the unsubstituted phenyl ring should be negligable. There would be no overlap of the π orbitals of the phenyl ring with those of the carbonyl group. It would consequently be expected that the hydrogen bond strength in o-hydroxybenzophenone would not be much different from that of o-hydroxyacetophenone, and so would be about 30 kJ mol^{-1}. The dielectric loss curves for o-hydroxybenzophenone are shown in Fig. VI-12. The aromatic rings in o-hydroxybenzophenone are orthogonal, with dipole moment components perpendicular to all the molecular axes. As a consequence, it is possible for the molecule to rotate about all three molecular axes. The large dipole moment of 3.0 D at 298 K in benzene[12] for o-hydroxybenzophenone is one reason why molecular reorientation is a predominant process. The molecule is held rigid by the hydrogen bond so that intramolecular coupled ring rotation is not possible,as is also the case in o-hydroxydiphenyl ether.[15] Also, in support of molecular relaxation is the temperature range (256 - 294 K) where absorption maxima occur. This is where many molecular relaxation processes are observed, such as for diaryl ethers, sulfides, sulfones, sulfoxides, and ketones. A specific example is diphenyl sulfoxide which shows loss peaks from 251 to 283 K, and 2-benzoylpyridine which shows dielectric loss peaks from 249 to 295 K. The $\log_{10}$ frequency maximum range is 3.08 to 4.64 and the β range is 0.18 - 0.20 for o-hydroxybenzophenone. These β values although low suggest molecular rotation, since beta values for most molecular processes are small if the temperature is not high. The beta range is similar to that for diphenyl sulfoxide (0.16 - 0.19) from 251 - 283 K.

TABLE VI-3: Comparison of Beta Values for Asymmetric and Rigid Diaryl Molecules at Similar Temperature Ranges

Asymmetric Molecule	ΔT(K)	β	Rigid Molecule	ΔT(K)	β
2-benzoyl pyridine	249.1-294.5	.10-.21	o-hydroxy benzophenone	256.3-294	0.18-.20
p-fluoro-benzophenone	295.4-321.9	.11-.14	p,p'-dichloro-diphenyl sulfone	306.2-325.5	0.15-0.19
p-chloro-benzophenone	300.3-325.4	.17-.19	p,p'-dichloro-diphenyl sulfone	306.2-325.5	0.15-0.19
p-bromo-diphenyl ether	288.8-315.6	.22-.23	p,p'-ditolyl sulfone	294.2-337.6	0.10-0.16
p-nitro-diphenyl ether	303.6-329.3	.2-.22	p,p'-dichloro-diphenyl sulfoxide	306.2-325.5	0.15-0.20
p-biphenylyl-phenyl ether	263.1-301.4	.27-.38	1,2,-diphenyl cyclo-propenone	276.8-303.4	0.2-.06

Since diphenyl sulfoxide, which behaves as a rigid molecule (see Chapter V) has similar temperature and beta ranges to those for o-hydroxybenzophenone, then molecular rotation is favoured for o-hydroxybenzophenone (see Table VI-3). The molecular relaxation processes can include molecular rotation about the long molecular X axis and the Y, and Z axes. Support for the above statement is the large ΔH_E value of 58.2 kJ mol^{-1} and the positive ΔS_E value of 58 J K^{-1} mol^{-1}.

o-Hydroxybenzophenone is a good standard molecule for comparing molecular rotations of diphenyl ether type molecules since it is of nearly the same size and shape as diphenyl ethers, ketones, sulfides, sulfoxides, and sulfones. For example, the ΔH_E of diphenyl sulfoxide is 60.0 kJ mol^{-1} as compared to 58.2 kJ mol^{-1} for o-hydroxybenzophenone. Also the ΔS_E values for o-hydroxybenzophenone and diphenyl sulfoxide are 58 and 60 J K^{-1} mol^{-1} respectively. Diphenyl sulfoxide also has a large dipole moment of 4.10 D at 298 K in benzene[12] and a τ value of 3.3×10^{-6} s at 300 K in polystyrene. Similarly o-hydroxybenzophenone has a large dipole moment of 3.0 D and a τ value of 2.1×10^{-6} s at 300 K in polystyrene. These and other molecules of similar size and shape undergo similar molecular relaxation processes.

2-Benzoyl pyridine is a good example of how slight changes in structure can affect relaxation processes. In this case the ΔH_E value

TABLE VI-4: Comparison of Calculated and Observed ΔS_E values for Some Asymmetric Diaryl Molecules

$$\Delta S_{E(calc)} = 2.5\ \Delta H_E - 73$$

Molecule	ΔT (K)	$\Delta S_{E(calc)}$ ($J\ K^{-1}\ mol^{-1}$)	$\Delta S_{E(obs)}$ ($J\ K^{-1}\ mol^{-1}$)
o-Hydroxybenzophenone	256 - 294	72	58 ± 4
2-Benzoyl pyridine	249 - 295	116	127 ±34
p-Fluorobenzophenone	295 - 322	145	133 ±30
p-Chlorobenzophenone	300 - 325	120	85 ±16
p-Nitrobenzophenone	304 - 329	148	97 ±26
p-Bromodiphenyl ether	289 - 319	147	130 ±21
4-Biphenylyl phenyl ether	263 - 301	- 31	- 87 ± 9

is 75.0 kJ mol^{-1}, which is larger than would be expected if the molecule underwent an intramolecular relaxation process. This can be seen when it is compared to benzophenone and di-2-pyridyl ketone. These two molecules have ΔH_E values of 21.0 and 28.0 kJ mol^{-1} respectively. Also, when 2-benzoyl pyridine is compared with o-hydroxybenzophenone or diphenyl sulfone it becomes obvious that 2-benzoyl pyridine possesses an additional mode of molecular relaxation. Molecular rotation appears to be the predominant relaxation process for 2-benzoyl pyridine.

The loss peaks were observed from 249.1 to 294.5 in the $\log_{10}$ frequency maximum range of 2.7 to 4.8. Such a temperature range is where molecular rotations would be expected to be found. 2-Benzoyl pyridine also has a relatively large literature dipole moment value of 2.95 D at 298 K in benzene[12], which would contribute to molecular rotation. The beta values of 0.10 to 0.21 indicate a wide distribution of relaxation times. From Table VI-3 it is evident that 2-benzoyl pyridine and o-hydroxybenzophenone have absorption maxima at nearly similar temperature ranges of 249 - 295 K and 256 - 294 K respectively. These molecules have beta ranges of 0.10 - 0.21 for 2-benzoyl pyridine and 0.18 - 0.20 for o-hydroxybenzophenone. Since o-hydroxybenzophenone is a rigid molecule, and since the beta values in both cases are similar, then this fact along with other dielectric data point to molecular, or possibly co-operative motion as a likely relaxation process for 2-benzoyl pyridine (Table VI-4).

Further evidence which is in support of co-operative motion for 2-benzoyl pyridine is that the observed ΔS_E value of 127 J K^{-1} mol^{-1} is relatively close in value to that of the calculated ΔS_E of 115 J K^{-1} mol^{-1} from Eqn. VI-3:

$$\Delta S_E = 2.5\ \Delta H_E - 73 \qquad \text{VI-3}$$

Equation VI-3 was developed[17] from a plot of ΔS_E versus ΔH_E for a number of molecules which exhibit co-operative with the polymer chains. The ΔH_E was obtained from the slope of the line and the ΔS_E from the intercept. The units for ΔH_E are in kJ mol^{-1} and those for ΔS_E are in J K^{-1} mol^{-1}. The plot of ΔS_E versus ΔH_E is shown in Fig. V-7.

The fact that asymmetric molecules such as 2-benzoyl pyridine only exhibit molecular or co-operative motion with the polymer supports the idea that symmetry is an important factor in determining whether double-internal rotation relaxation processes occur. Even slight changes in symmetry can affect double-internal rotation motions. Slight changes in the structure of one ring can affect internal rotation, as in the case of 2-benzoyl pyridine as compared to benzophenone. Although 2-benzoyl pyridine and benzophenone are very similar in terms of size, shape, and mass there is in 2-benzoyl pyridine an inclination of the net dipole moment direction to the principal axes. In 2-benzoyl pyridine the resultant dipole moment has components perpendicular to all three axes. As a consequence the molecule can rotate about all three principal axes. In benzophenone, however, the resultant dipole is along the Y axis and so molecular rotation can occur about the X and Z axes.

The behaviour of both molecules can be noticed in a comparison of their relaxation parameters in a polystyrene matrix. Benzophenone has a small ΔH_E value of 21.0 kJ mol^{-1} which can be attributed to an intramolecular relaxation process (see Chapter VII), while 2-benzoyl pyridine has a ΔH_E value of 75.0 kJ mol^{-1} which is the result of molecular rotation. Also, benzophenone has a τ value of 5.0×10^{-9} s at 300 K while 2-benzoyl pyridine has a τ value of 5.1×10^{-7} s at the same temperature. The ΔG_E value at 200 K for benzophenone is 24.2 kJ mol^{-1}, while for 2-benzoyl pyridine at 200 K it is about twice as large, being 50.0 kJ mol^{-1}. These values imply that benzophenone undergoes a relatively low energy intramolecular relaxation process, while 2-benzoyl pyridine undergoes molecular relaxation. It may be that a key factor in determining whether double-internal rotation occurs is the inclination of the dipole moment to the principal axes. Asymmetric diaryl molecules which have inclined dipole moments do not exhibit any double-internal rotation.

p-Fluorobenzophenone was studied in the frequency range 200 to 100,000 Hz on the General Radio capacitance bridge. Two sets of absorption peaks were observed in the above frequency range. One set was found from 295 to 322 K to give a ΔH_E value of 87.0 kJ mol^{-1} (Table VI-2). This ΔH_E value seems indicative of a molecular relaxation process, as does the ΔG_E value of 47.2 kJ mol^{-1} at 300 K, however, they could also be indicative of co-operative motion with the polymer. ΔS_E values for asymmetric diaryl ethers and ketones which were suspected of undergoing predominantly co-operative motion with the polymer chains were found to obey within error limits Equation VI-3 (see Table VI-4).

This equation was developed for co-operative motion of rigid molecules in polymer matrices in which there is a linear relationship between ΔS_E and ΔH_E. As the size of a rigid molecule increases so does the ΔH_E for molecular rotation, as does also the ΔS_E. The reason why the entropy of activation also increases is that many large molecules cause large disorder of the local medium, as they rotate. Co-operative motion of the solute with a polymer solvent occurs when the solute causes lowering of the glass-transition state of the polymer. As a result the polymer chains become more flexible and cause greater difficulty for the rotation of the solute molecules. The ΔH_E value of 87.0 kJ mol^{-1} for p-fluorobenzophenone may be too large for molecular rotation of the molecule when compared with the ΔH_E value of 58.0 kJ mol^{-1} for o-hydroxybenzopheone, which is of similar size and shape to p-fluorobenzophenone. Some asymmetric molecules such as p-chlorobenzophenone, p-nitrodiphenyl ether, 4-biphenylyl phenyl ether and o-hydroxybenzophenone do not follow within experimental error (see

Table VI-4) Equation VI-3 .

Another set of absorption peaks for p-fluorobenzophenone was found from 168 to 184 K in the frequency range 0.2 to 100 KHz. In this case, however, there are double absorption peaks. The overlap is such that full peaks cannot be resolved. It is quite possible that the peaks might be the result of overall molecular rotation, or of benzoyl group rotation. The study of p-fluorobenzophenone also shows how slight changes in structure affect relaxation processes. For instance, when a hydrogen atom at the para position in benzophenone is replaced by an atom of nearly the same size double-internal rotation is eliminated. Although the size of hydrogen and fluorine atoms are very similar having van der Waals volumes of 5.2 $Å^3$ and 8.6 $Å^3$ respectively their masses are different, being 1 a.m.u. for hydrogen and 18 a.m.u. for fluorine. Since the volumes of p-fluorobenzophenone and benzophenone are very similar it appears that not volume but net dipole inclination to the principal axes could determine which relaxation process is predominant, as does symmetry. Because the mass of one ring in p-fluorobenzophenone is larger than the other the centre of mass is shifted thereby eliminating double-internal rotation as a predominant process. Instead molecular rotation about the three principal molecular axes may occur.

Another asymmetric compound which was studied was p-chlorobenzophenone in a polystyrene matrix. It also was examined with a General Radio capacitance bridge from 83 to 330 K in the frequency range 0.2 to 100 KHz. In the temperature and frequency range scanned only one set of dielectric loss peaks was observed. The peaks occurred from 300 to 325 K in the log f_m range 2.65 to 4.09. Since this molecule is asymmetric it would be expected to show one set of peaks resulting from overall molecular rotation. The p-chlorobenzophenone molecule is larger than 2-benzoyl pyridine, but smaller than p-bromodiphenyl ether and p-nitrodiphenyl ether, and so would be expected to have a ΔH_E value larger than 2-benzoyl pyridine and lower than the two ethers. This is indeed what is observed, the ΔH_E value being 77.3 kJ mol^{-1} as compared to 75.4 kJ mol^{-1} for 2-benzoyl pyridine and 88.0 and 88.2 kJ mol^{-1} for p-bromodiphenyl ether and and p-nitrodiphenyl ether respectively.

The literature dipole moment of 2.95 D at 298 K in benzene[12] and the experimentally calculated dipole moment of 1.26 D at 300 K favour a molecular reorientation process for p-chlorobenzophenone. Further support of this conclusion is the relatively large positive ΔS_E value of 85 J K^{-1} mol^{-1}. Also, in agreement with the conclusion is the ΔG_E value at 300 K of 51.9 kJ mol^{-1}, which is close to the ΔG_E values of 49.0 and 54.2 kJ mol^{-1} for p-bromodiphenyl and p-nitrodiphenyl ethers.

Another parameter which adds to the idea of molecular rotation is the τ value at 300 K. At this temperature τ is 1.8×10^{-4} s for p-chlorobenzophenone, whereas benzophenone at 300 K has a τ value of 4.6×10^{-9} s. The long relaxation time for p-chlorobenzophenone substantiates a molecular relaxation process about all three principal molecular axes because of the dipole moment components prependicular to the X, Y, and Z axes. p-Chlorobenzophenone has a beta value range of 0.17 - 0.19 from 300 - 325 K as compared to 0.15 - 0.19 from 306 - 326 K for p-dichlorodiphenyl sulfone which behaves as a rigid molecule (see Chapter V). This fact along with other dielectric data suggests that p-chlorobenzophenone undergoes molecular rotation as the major contribuiton to the observed dielectric relaxation.

An alternative theory for the relaxation behaviour of some asymmetric molecules such as 2-benzoyl pyridine and p-fluorobenzophenone is that the absorption peaks above room temperature indicate co-operative relaxation with the polystyrene. Such a relaxation process would account for the large ΔH_E and τ values at 300 K. In support of such a conclusion is that the above molecules obey the Equation VI-3 for co-operative motion with the polymer chains.

One last compound which was studied was 1,2-diphenyl oxazole in a polystyrene matrix. This compound was studied from 88 to 312 K on the General Radio capacitance bridge in the frequency range 0.2 to 100 KHz. No sets of peaks were found in these temperature and frequency ranges. The analogous symmetric compound with two nitrogen atoms on the oxazole ring has a set of loss peaks from 263 to 308 K at frequencies of 0.2 to 100 KHz which are due to molecular rotation. The structures and names of some less well known molecules are given in Table VI-6.

The fact that 1,2-diphenyl oxazole does not show any dielectric loss peaks below room temperature indicates that they could occur above room temperature. This is what would be expected, since if this molecule behaves as do the other asymmetric molecules it could relax about the three principal axes of the molecule and so would have a larger ΔH_E value than the symmetric analogue which has a ΔH_E value of 42.7 kJ mol^{-1}.

CONCLUSION

The above discussion on asymmetric diaryl molecules gives further insight into understanding the relaxation behaviour of diaryl molecules. One of the major conclusions is that these molecules relax primarily by overall molecular relaxation. Since substituents are in the para position of one ring molecular relaxation becomes possible by rotation about the short Y molecular axis as well as the X and Z axes.

Rigid molecules of about the size of o-hydroxybenzophenone have ΔH_E values of about 60 kJ mol^{-1} for overall molecular rotation. As an example diphenyl sulfone and diphenyl sulfoxide have ΔH_E values of 61.9 and 59.9 kJ mol^{-1} respectively.

Once a substituent, such as a halogen atom, or a nitro group is placed in the para position of one ring the enthalpy of activation values increase substantially above 60 kJ mol^{-1}. For example, p-bromodiphenyl and p-nitrodiphenyl ethers have ΔH_E values of 88.0 and 88.2 kJ mol^{-1} respectively. Since a bromine atom and the nitro group are both similar in dimensions they have similar energy barriers for molecular rotations. In the para mono-substituted diaryl molecules there is a component of the dipole moment perpendicular to the plane which bisects the bridging atom or group valency angle. Consequently, rotation about all three molecular axes occurs. From Courtauld models it can be seen that rotation about the short molecular axes sweeps out a larger volume, so that larger ΔH_E and τ values are found for asymmetric diaryl molecules than for the symmetric molecules which can rotate only about the X and Z principal axes.

It was also observed in the study of asymmetric diaryl molecules that slight changes in the structure of a symmetric diaryl molecule could change the relaxation modes of the molecule. For example, benzophenone was found to undergo a double-internal rotation type of relaxation process with a ΔH_E value of 21.4 kJ mol^{-1}. However, once one of the carbon atoms in one ring was substitued with a nitrogen atom which is about the same mass (14 a.m.u.) as a CH group (13 a.m.u.) the double-internal rotation process is not observed. The ΔH_E for 2-benzoyl pyridine was found to be 75.4 kJ mol^{-1} as compared to the symmetric analogue 2-pyridyl ketone which has ΔH_E as 27.5 kJ mol^{-1}. 4-Biphenylyl phenyl ether was observed to behave differently from the other asymmetric ethers. For example, its ΔH_E is 16.6 kJ mol^{-1}, which is much lower than that of the other asymmetric molecules studied (see Table VI-2). The origin of the process resulting in the relatively small ΔH_E value is difficult to determine, however, the dielectric relaxation parameters indicate that phenoxy group rotation is the most likely relaxation process.

It may therefore be concluded that both slight and large changes in certain molecular properties such as symmetry, centre of mass, and resultant dipole moment direction, can influence whether a double-internal rotation type of relaxation process occurs. When such factors are present so that the situation as is found in symmetric diaryl ethers, sulfides, and ketones is altered, then a contribution to the observed relaxation process from a double-internal relaxation process cannot be inferred from the evidence considered here. In asymmetric diaryl ethers and ketones, it has been shown that relaxation data may be accounted for by molecular relaxation about the permissible principal axes.

TABLE VI-5: Fuoss-Kirkwood Analysis Parameters of Several Asymmetric Diaryl Ethers and Ketones in Polystyrene Matrices at a Variety of Temperatures

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	μ(D)	ε_∞
0.39M o-Hydroxybenzophenone in Polystyrene						
256.3	130.7	3.09	0.18	18.4	1.72	2.51
260.8	82.9	3.28	0.18	18.8	1.78	2.50
266.6	44.4	3.55	0.18	19.5	1.84	2.50
273.2	21.4	3.87	0.18	-	-	-
279.1	12.6	4.10	0.20	-	-	-
284.3	8.1	4.29	0.20	22.0	1.91	2.49
289.0	5.4	4.47	0.20	22.5	1.97	2.48
294.0	3.5	4.66	0.20	22.9	2.01	2.47
0.54 M 2-Benzoyl pyridine in Polystyrene						
294.5	2.99	4.72	0.21	19.54	1.52	2.56
290.3	2.58	4.79	0.16	19.53	2.26	2.53
284.1	2.86	4.75	0.14	19.16	-	2.51
276.8	4.93	4.51	0.12	18.52	1.89	2.49
263.2	44.40	3.55	0.11	17.37	1.89	2.49
255.4	101.0	3.19	0.11	17.12	1.83	2.49
249.1	300.0	2.70	0.10	16.87	1.85	2.49
0.43M p-Chlorobenzophenone in Polystyrene						
293.3	354.0	2.65	0.19	9.45	1.26	2.53
299.7	171.0	2.97	0.19	9.50	1.29	2.52
304.9	109.0	3.16	0.19	9.76	1.31	2.52
310.3	63.4	3.40	0.18	10.05	1.37	2.51
315.5	40.8	3.59	0.18	10.51	1.41	2.51
320.2	23.6	3.83	0.17	10.70	1.49	2.50
325.4	12.7	4.10	0.17	11.28	1.56	2.50
0.45M p-Fluorobenzophenone in Polystyrene						
295.4	81.7	3.29	0.11	11.21	1.75	2.61
301.1	24.9	3.80	0.10	11.41	1.82	2.60
306.6	11.9	4.12	0.12	11.79	1.75	2.60
310.7	6.86	4.36	0.11	12.03	1.80	2.60
314.3	3.64	4.64	0.11	12.41	1.85	2.59
317.7	3.61	4.64	0.14	13.08	1.72	2.62
321.9	2.40	4.82	0.14	13.74	1.75	2.61

TABLE VI-5: continued.....

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\epsilon''_{max}$	μ(D)	ϵ_∞
0.53M p-Bromodiphenyl ether in Polystyrene						
288.8	201	2.90	0.23	9.89	1.01	2.69
295.1	99.2	3.20	0.22	10.24	1.07	2.69
301	57.8	3.44	0.22	9.44	1.05	2.60
306.6	29.6	3.73	0.21	9.80	1.09	2.62
312.9	12.6	4.10	0.22	8.46	1.08	2.30
318.6	6.03	4.42	0.22	8.63	1.11	2.29
323.1	4.0	4.60	0.22	11.64	1.19	2.68
0.31M p-Nitrodiphenyl ether in Polystyrene						
303.6	267.0	2.78	0.21	31.16	2.53	2.69
309.3	164.7	2.98	0.21	32.22	2.65	2.69
315.1	83.6	3.28	0.21	33.60	2.74	2.60
319.3	49.0	3.51	0.21	35.17	2.82	2.62
322.6	31.2	3.70	0.20	36.49	2.96	2.30
325.6	18.4	3.94	0.20	38.33	-	2.29
329.3	10.1	4.20	0.19	40.41	3.16	2.68
0.36M p-Biphenylyl phenyl ether in Polystyrene						
263.1	13.9	4.06	0.27	2.61	0.52	3.02
272.9	9.55	4.22	0.29	2.62	0.52	3.02
280.5	5.04	4.50	0.28	2.68	0.54	3.00
285.8	4.56	4.54	0.27	2.53	0.54	3.00
295.2	5.22	4.48	0.38	2.45	0.46	3.00
301.4	4.59	4.54	0.38	2.43	0.46	3.01

TABLE VI-6: Structures of Some Asymmetric Diaryl Molecules

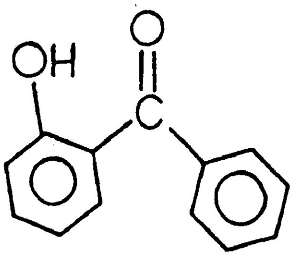
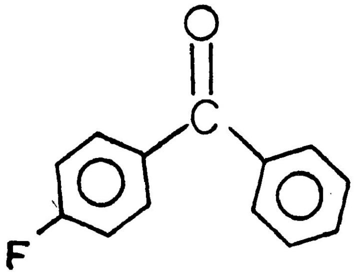
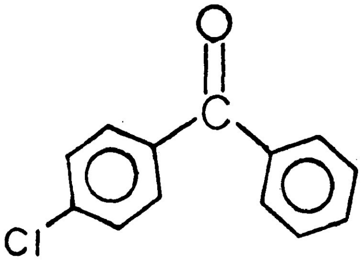
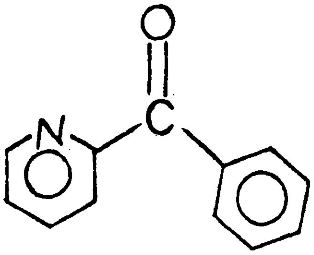
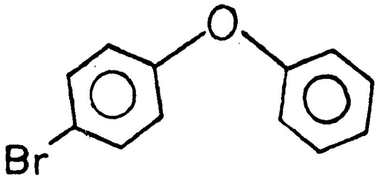
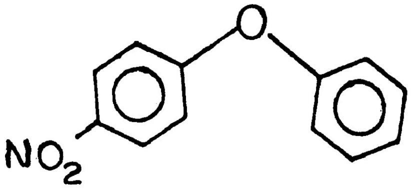
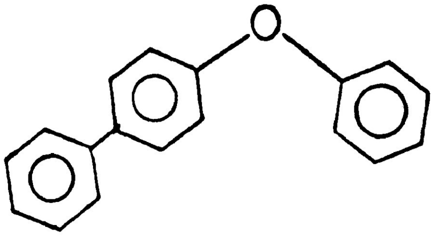
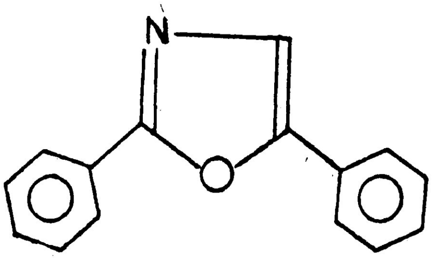
NAME	STRUCTURE
o-Hydroxybenzophenone	
p-Fluorobenzophenone	
p-Chlorobenzophenone	
2-Benzoylpyridine	

TABLE VI:6 continued.....

NAME	STRUCTURE
p-Bromodiphenyl ether	
p-Nitrodiphenyl ether	
4-Biphenylyl phenyl	
2,5-Diphenyl oxazole	

REFERENCES

1. K. D. Nelson and C. P. Smyth, J. Chem. Phys., 69, 1006, (1965).
2. J. E. Anderson and C. P. Smyth, J. Chem. Phys., 42, 473 (1965).
3. W. P. Purcell and C. P. Smyth, J. Amer. Chem. Soc., 83, 1063 (1961).
4. F. Hufnazel, G. Kloges, and P. Koblock, F. Naturforsh, 17a, 96 (1962).
5. D. W. Davidson, Can. J. Chem., 39, 571 (1961).
6. A. Aihure and M. Davies, J. Colloidal Sci., 11, 671 (1956).
7. F. Perrin, J. Phys. Radium, 5, 497 (1934).
8. F. K. Fong, J. Chem. Physics, 40, 132 (1964).
9. D. B. Farmer, Ph.D. Thesis, University of Aston In Brimingham, (1967), Coaxial Line Method.
10. K. H. Abbas Khwaja, A. Mazid, this laboratory, private communication.
11. M. Jackson and J. G. Powels, Trans. Faraday Soc., 42a, 101 (1946).
12. A. McCellan, "Tables of Experimental Dipole Moments", W. H. Freeman and Co., San Francisco and London (1963).
13. J. T. Edward, Chemistry and Industry, 774 (1956).
14. M. Davies, Quart. Rev., 8, 250 (1954).
15. W. Maier, Arch. Sci. (Geneva), 12, 20 (1959).
16. D. M. Roberti, O. F. Kalman and C. P. Smyth, J. Am. Chem. Soc., 82, 3523 (1960).
17. J. Chao, this laboratory, private communication.

CHAPTER VII

DIELECTRIC RELAXATION STUDIES OF SOME NON-RIGID DIARYL MOLECULES

INTRODUCTION

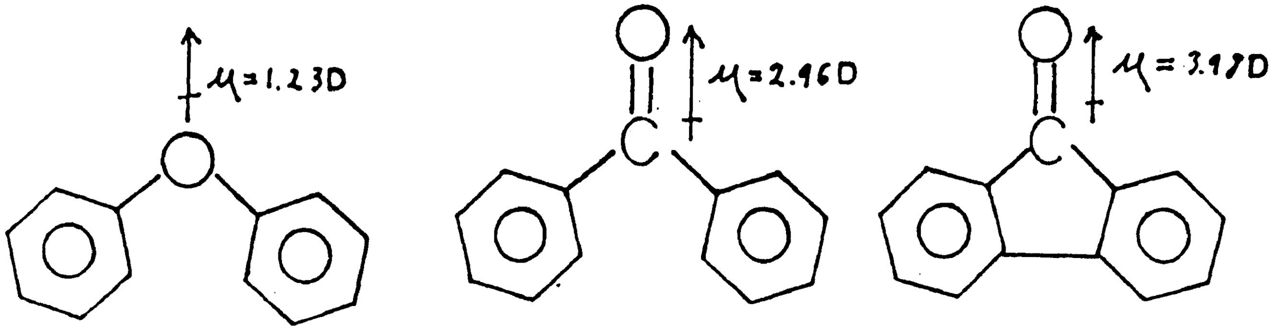
E. Fischer[1] in 1949 discovered that diphenyl ether has an anomalous dielectric relaxation behaviour. He was not able to find a peak of dielectric loss in the expected 5 cm wavelength region. In this region researchers such as Jackson and Powles,[2] as well as Schneider[3] found that benzophenone behavied as a rigid molecule. Benzophenone has similar size, shape, and net dipole direction to those of diphenyl ether.

The molar volume of benzophenone is 170 c.c. as compared to 164 c.c.[4] for diphenyl ether. Both molecules also have a net dipole moment direction which bisects the COC or C(CO)C valency angle (Fig. VII-1). It might therefore be expected that the two molecules would show similar dielectric relaxation behaviour. Dielectric studies have shown that the observed relaxation process of diphenyl ether has a major contribution from a very rapid intramolecular relaxation process, which is different from simple phenoxy group rotation.

Benzophenone, however, has a major contribution to relaxation, from an overall molecular reorientation, as shown by liquid solution studies in the microwave region.[29] A study of the relaxation processes, and their mechanisms for the above molecules and a series of other symmetric diaryl molecules is the subject of this chapter.

The term "symmetric diaryl molecules" as used in this thesis refers to those diaryl molecules in which the bridging species has at least two planes of symmetry, and both the phenyl rings have the same structure.

When Fischer[1] studied diphenyl ether in benzene solution at 296 K he found a relaxation time of 2.8 ps. Under the same conditions benzophenone was found to have a relaxation time of 20.4 ps. Studies of fluorenone[5] have shown that it has a relaxation time of 19.9×10^{-12} s. These seem to indicate that benzophenone has a planar structure. If

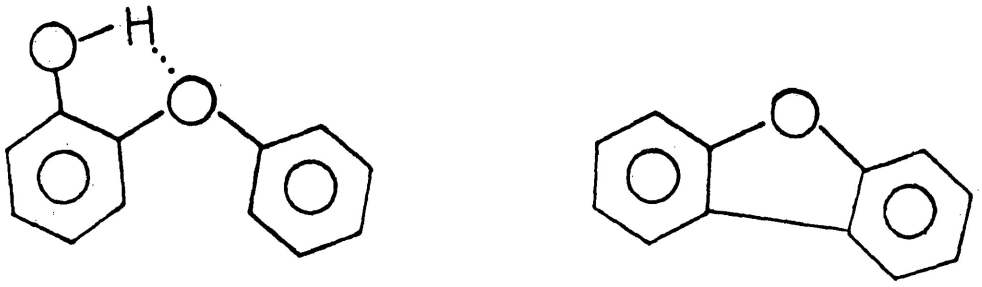


Diphenyl ether Benzophenone Fluorenone

FIGURE VII-1: Dipole Moments and Directions of Some Symmetric Diaryl Molecules.

diphenyl ether had a planar geometry then it would also be expected to have a similar molecular relaxation time to that of benzophenone.

The compound, o-hydroxydiphenyl ether (Fig. VII-2), has been studied by Maier.[6] In this molecule the hydrogen-bond between the hydrogen of the hydroxyl group and the central oxygen atom inhibits rotation of one ring. Measurements of the relaxation time for o-hydroxydiphenyl ether showed no anamalous behaviour. The relaxation time for this molecule was found to be five times that of diphenyl ether and therefore close to the value for benzophenone. Dibenzofuran, in which the two aromatic rings are linked at the ortho positions (Fig. VII-2) fails to show anomalous behaviour.[7] These last two molecules



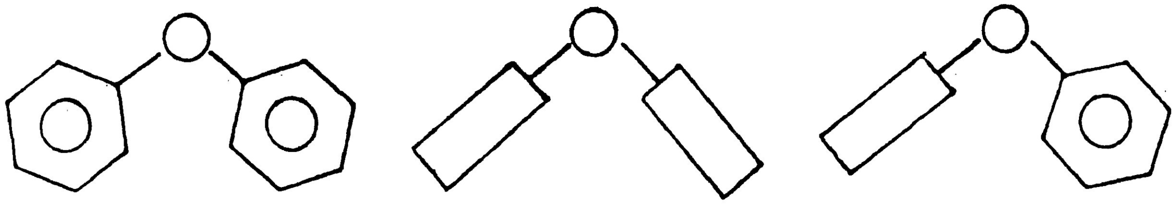
o-Hydroxydiphenyl ether

Dibenzofuran

FIGURE VII-2

give evidence that the anomalous behaviour of the diphenyl ether is associated with internal rotation of both the phenyl rings.

The question as to the geometrical orientation of the two aromatic rings in diphenyl ether type molecules has been contraversial. Smyth and Walls[8] believed that the planes of the two rings are perpendicular to the plane of the oxygen valency angle, which is 120°. Sutton[9] however, stated that the two rings are in the plane of the oxygen valency angle so that a coplanar geometry results. Morino[10,11] made a comprimise, he suggested that the two rings are orthogonal, one is in the plane of the oxygen valency angle and the other perpendicular to it (Fig. VII-3).



Sutton's Model Smyth's model Morino's model

FIGURE VII-3: Possible Geometric Orientations of Diphenyl Ether

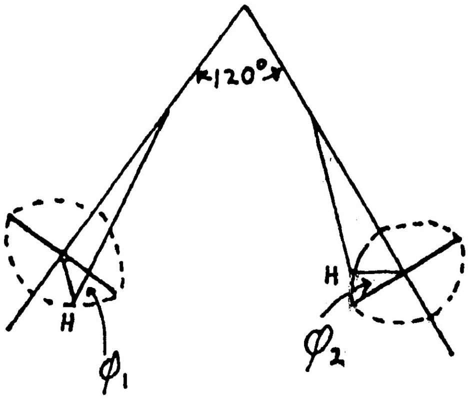


FIGURE VII-4: Angles of Rotation ϕ_1 and ϕ_2 of the two Phenyl Rings Measured from the Coplanar Position

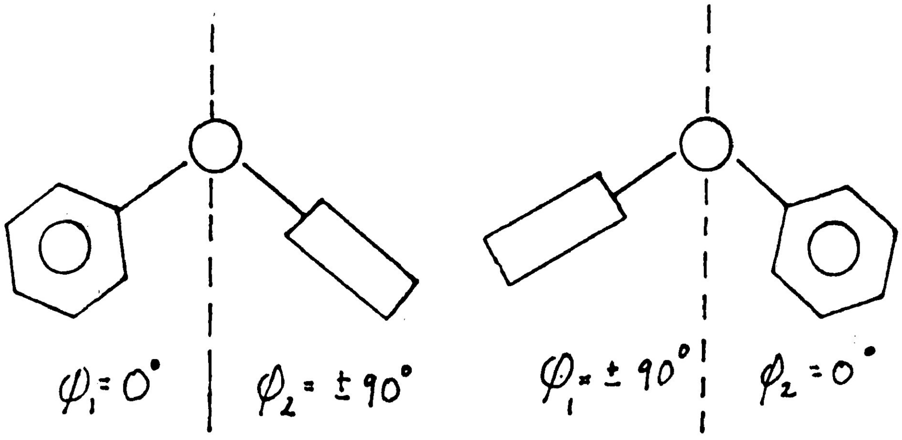


FIGURE VII-5: Orthogonal Structures of Diphenyl Ether

In order to determine the geometrical arrangement of the two rings one has to take into account the conjugation of the unshared electron pairs on the oxygen atom with the aromatic rings, and the steric effect of the protons on both rings. If the rings are coplanar then the resonance energy between the two ortho hydrogens probably does not exceed 41.8 kJ mol^{-1}, but the repulsive energy exceeds 837.2 kJ mol^{-1}.[10] Smyth's model favours less repulsive energy since the two ortho hydrogens are 2.6 Å apart in his model, but there is no stabilization due to conjugation. Morino's model has about half the excess resonance energy of Sutton's model since one ring is conjugated with the oxygen atom. The repulsive energy in this case is a minimum, the ortho H - H distance being 3.2 Å (Fig. VII-3).

Experimental evidence favours Morino's structure for diphenyl ether. Both electron[12] and X-ray[13] diffraction studies of 2,2'-disubstituted ethers, along with proton n.m.r.[14] studies indicate an orthogonal set of rings. Due to this molecular configuration intramolecular rotation can occur with a minimum potential energy barrier if the two twist angles ($\emptyset$) of the two rings vary such that $\emptyset_2$ is kept equal to $180^o - (90^o + \emptyset_1)$, where $\emptyset_1 = 0$ and $\emptyset_2 = 90^o$. The twist angles $\emptyset_1$ and $\emptyset_2$ are the ring angles as measured from a position when the rings are in the same plane (Fig. VII-4) and (Fig. VII-5).

The shortening of the relaxation time of a non-rigid molecule below the expected value for a rigid molecule of similar size and shape can be accomplished by the use of highly viscous solvents. Diphenyl ether, for example, has a relaxation time in benzene of 1/5 to 1/6 that of benzophenone, while in Nujol solution[9] the relaxation time is 1/50 that of benzophenone[2]. The reason for the shorter value of τ for diphenyl ether as compared to a similar molecule such as benzophenone has been attributed to internal rotation of both the phenyl rings.[8] In this hypothesis a fixed volume would be swept out during the rotation. It therefore becomes difficult on the basis of Debye's[33] concept of a rotating sphere in a viscous fluid to explain why the ratio of the rotating volume of diphenyl ether to benzophenone is 2% in Nujol, and 22% in benzene. Some sort of internal rotation is therefore responsible for the rapid relaxation process. Further evidence of an intramolecular relaxation process in diphenyl ether is the fact that pyridine with $\tau = 0.56\times10^{-9}$ s at 293 K in benzene and fluorobenzene with $\tau = 0.84\times10^{-9}$ s at 293 K in benzene, which are similar in shape and size to a phenyl ring, have longer relaxation times than diphenyl ether.

In order to explain the short relaxation times of diphenyl ether and other diaryl ethers several mechanisms have been suggested. These include inversion[1], atomic dipole reversal[15], phenoxy group rotation[7], mesormeric shift of charge[4], and a mechanical double-internal rotation[16]. In-plane inversion has never been observed even in H_2O.

Since in-plane inversion requires a large change in co-ordinates for many carbon atoms and since the force constant for the ether linkage is not low, in-plane inversion is highly improbable.[17] Out-of-plane inversion is simply molecular rotation.

The atomic dipole reversal mechanism was proposed by Fischer[1] who considered that the atomic dipole moment due to the lone-pair electrons on the oxygen atom is modified by resonance with the phenyl rings. As the phenyl rings rotate about their bonds to the oxygen atom, they move into orientations which permit more or less resonance and thus change both the direction and size of the atomic moment. A small rotation of the ring can produce a large orientational effect and might be responsible for the short relaxation time. This mechanism, however, cannot explain the reduced relaxation times of 6.5 and 13.3 ps respectively for diphenyl methane and bibenzyl since these molecules have no lone-pair electrons.[7]

In order to conserve angular momentum the rotation of a phenoxy group with respect to the phenyl ring would require a comparable displacement of each ring, unless one ring were held in plane by external forces. In symmetric diaryl molecules the sum of the external torques acting upon the molecules must equal zero in order to conserve angular momentum, if only the X-Ph (X = O, S, C = O, C = S, etc.) group

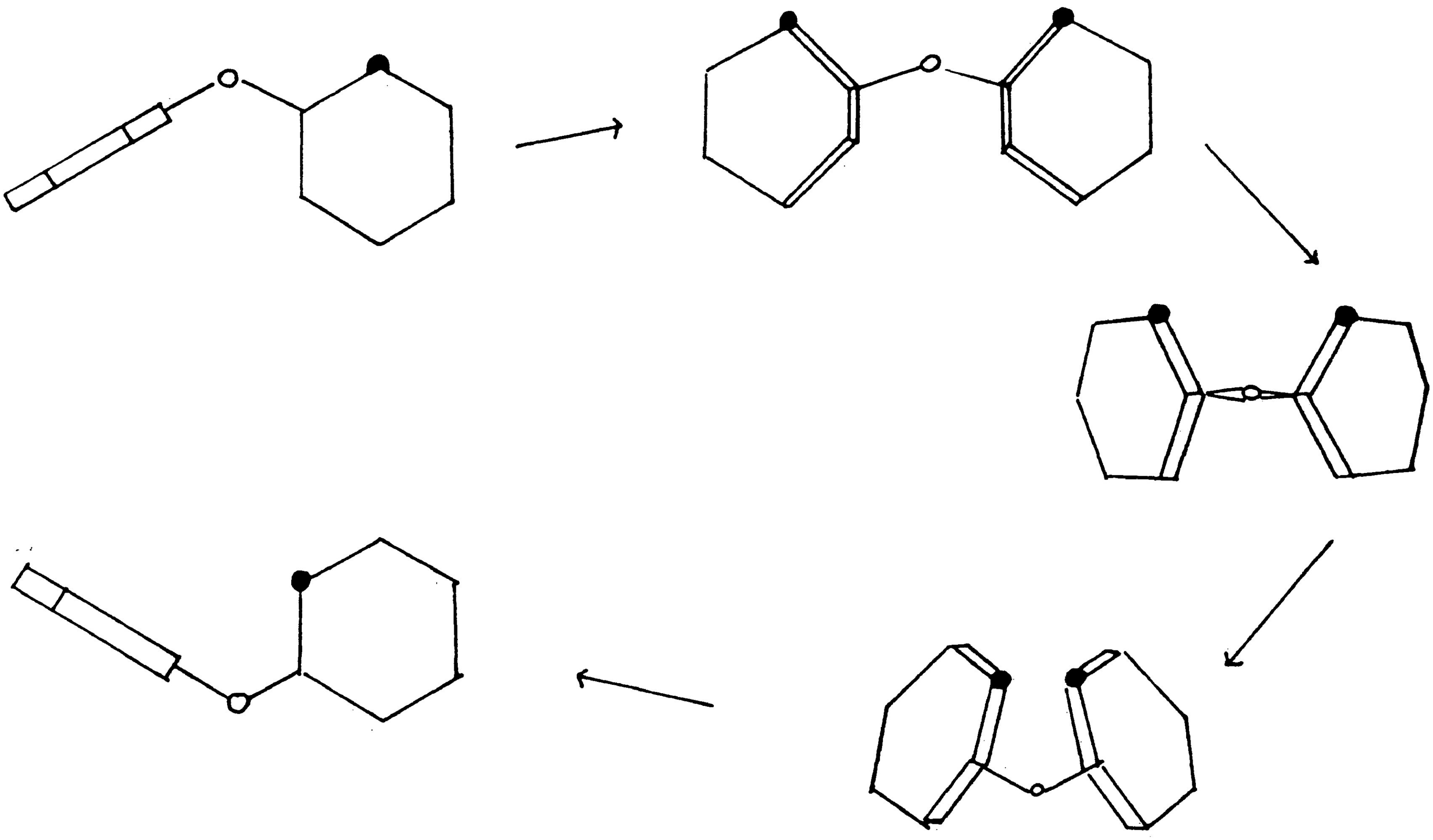


FIGURE VII-6: Dielectric Relaxation by Double-Internal Rotation Resulting from Edgewise Ring Rotation Coupled by Tilting of the other Ring, Ortho Hydrogens are Shown rotates then an external force and consequently a torque must be applied to the other phenyl ring to conserve angular momentum. In these diaryl molecules the centre of mass is at the intersection of the long and short molecular axes. Rotation of only the X-Ph group would cause a shift of the centre of mass. If angular momentum is conserved by allowing both rings to move about a fixed centre of mass then double-internal rotation is developed. This is shown pictorially in Fig. VII-6.

The final mechanism is the mesomeric one in which there is a shift of charge due to the interaction of the π electrons of the phenyl rings with the unshared electron pairs on the oxygen atom as a function of ring twisting with respect to the COC plane. The last two mechanisms mentioned are the most accepted ones.

If the mesomeric shift of charge was the principle mechanism for the rapid relaxation of diphenyl ether there should be a decrease in the relaxation time below the $\sim$20 ps expected for n-butyl phenyl ether as a rigid rotator, even though there is one ring which can interact with the oxygen atom.[17]

As was mentioned earlier, one ring in diphenyl ether is in the plane of the oxygen valency angle and the other ring is perpendicular to that plane. The mesomeric moment arises when the p-orbitals

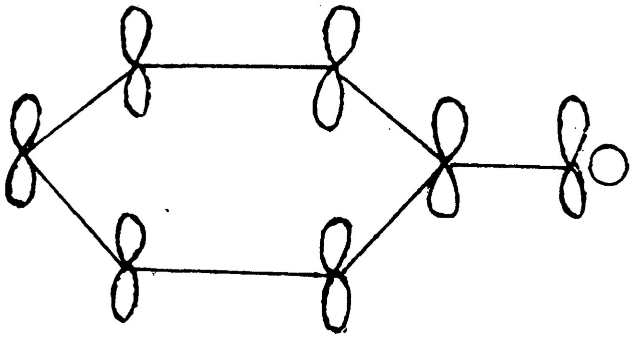


FIGURE VII-7: Conjugation of the π-Electrons in Benzene with the p-Electrons of the Oxygen Atom

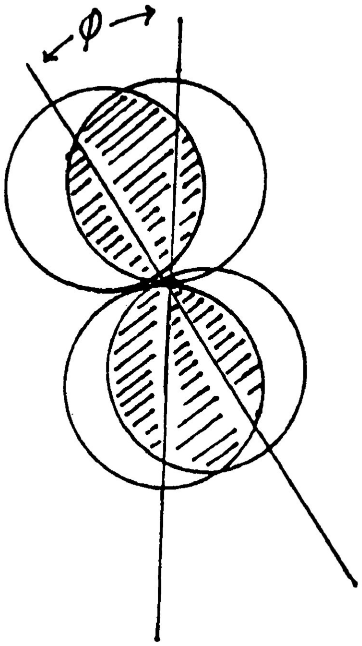


FIGURE VII-8:

The Overlap Between the p-Orbital of Oxygen and the p-Orbital of the Neighbouring Carbon Atom, the Angle Ø being the Angle of Rotation Measured from the Position of maximum Overlap of the ring which is coplanar with the oxygen valency angle have a maximum overlap with the p-orbital of the oxygen atom (Fig. VII-7) and (Fig. VII-8).

As a result of the conjugation of these orbitals electric charge flows from the oxygen atom to the side of the ring. Consequently, the mesomeric moment has its positive end at the oxygen atom and its dipole axis in the direction of the O - C bond. Such a shift of electronic charge is at a minimum when the ring is perpendicular to the COC plane and at a maximum when the ring is in the plane of the COC plane. The part of the moment which is dependent on the angle ($\emptyset$) between the ring plane and the COC plane is given by:

$$M = M_o \cos^2 \emptyset \qquad \text{VII-1}$$

Higasi[4] stated that the mesomeric moment for diphenyl ether is the result of an averaging of all the possible positions of the phenyl groups. He estimated the maximum mesomeric moment in diphenyl ether to be 1.32 D. With a mesomeric moment of this magnitude the mesomeric mechanism could give a significant contribution to the observed relaxation time. The mesomeric theory, however, has received some criticism. Smyth and co-workers[17,18] have concluded that while the mesomeric mechanism may have some effect on shortening the relaxation time, the double-internal rotation mechanism is more common and plays a greater role in the intramolecular relaxation process. One of the criticisms of the mesomeric effect is that in order to account for the short relaxation times of diaryl ethers mesomeric moments far larger than normally expected would have to be assumed. Anderson and Smyth[18] carried out a number of calculations of dipole moments of substituted aromatic ethers assuming a zero mesomeric moment. They concluded that a comparison of calculated and observed dipole moments gives no evidence of the large mesomeric moments necessary to make the mesomeric charge shift an important factor in lowering the relaxation time of diaryl ethers.

Whether the mesomeric or some other intramolecular mechanism gives the larger contribution to the observed relaxation process for diphenyl ether type of molecules may depend on the magnitude, direction, and components of the molecular and mesomeric moments. The mesomeric moment will make an important contribution to the observed relaxation time if the molecular dipole moment is of the same order as the mesomeric moment (Fig. VII-9).

For example, bis-(4-nitrophenyl)ether and bis-(4-bromophenyl)-ether have dipole moments of 2.79 and 0.60 D respectively at 298 K in benzene[41]. The latter molecule will therefore have a significant contribution to intramolecular rotation from the mesomeric mechanism.

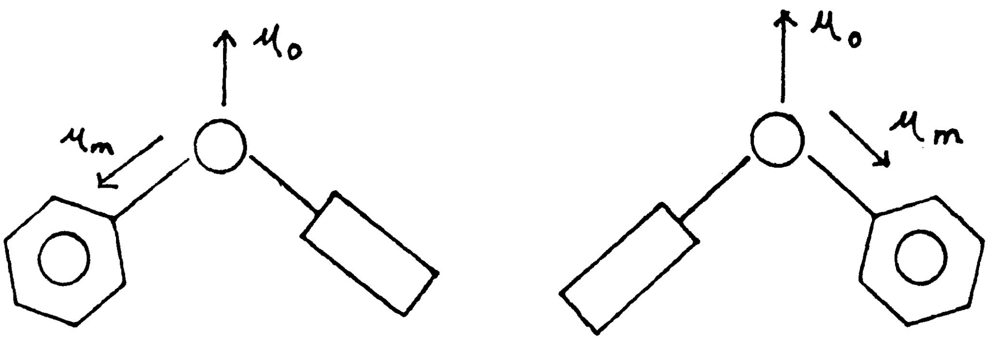


FIGURE VII-9: Change of Mesomeric Moment μ_m of Diphenyl Ether with Internal Rotation, μ_0 Represents the Molecular Dipole Moment

This type of behaviour can also be seen when the τ values for bis-(4-bromophenyl) sulfide and diphenyl sulfide are compared. The former molecule has a shorter τ value^3 of 8.2 ps and a smaller dipole moment of 0.68 D than diphenyl sulfide which has a τ value of 9.2 ps and a dipole moment of 1.55 D. The shorter τ value for bis-(4-bromophenyl) ether could be accounted for by some contribution from the mesomeric mechanism, since although it is a larger molecule its dipole moment is less than half that of diphenyl sulfide thereby leading to a relatively smaller distribution from the molecular relaxation process. When the molecular dipole moment is much larger than the mesomeric moment then the mesomeric moment may not make a big contribution to the observed relaxation time. This can be seen in the case of benzophenone where the dipole moment is 2.93 D at 298 K in benzene[41] and the mesomeric moment is -0.5 D. As a consequence,the molecular relaxation process would predominate and the mean relaxation time would be of the order of that for the relaxation of the rigid molecule.

The importance of the magnitude and direction of the resultant dipole moment with regard to double-internal rotation can be observed in the cases of 4-biphenylyl phenyl ether and 2-methylphenyl phenyl ether. Unlike most of the molecules studied in this chapter these two molecules are asymmetric, yet they have shorter relaxation times (9.4 and 6.6 ps in benzene at 293 K respectively) than similar and smaller sized rigid molecules (e.g. for o-hydroxydiphenyl ether τ = 20 ps in benzene at 293 K). The dipole moment of 4-biphenylyl phenyl ether is 1.10 D in benzene[41] at 298 K. The dipole components of 4-biphenylyl phenyl ether are shown in Fig. VI-7 of Chapter VI. It is obvious from Fig. VI-7 that the resultant dipole moment is not far off the Y axis. The X and Y axis components of the resultant dipole moment are 0.43 and 0.98 D respectively.

In the case of 2-methylphenyl phenyl ether the resultant dipole moment is smaller ($\mu = 1.57$ D at 298 K in benzene[41]) and is parallel to the Y axis. Some diaryl molecules which have dipole moments very near or along the Y axis and whose dipole moment is close in magnitude to that of diphenyl ether (1.23 D) appear to undergo double-internal rotation even though they are asymmetric. This statement is not conclusive since there is the possibility that the observed relaxation times could also be explained by phenoxy group rotation. 2-Benzoyl pyridine, however, is also asymmetric, yet its enthalpy of activation (75.4 kJ mol^{-1}) in polystyrene appears to be too large for double-internal rotation when compared to the ΔH_E values of molecules which show double-internal rotation. Its dipole moment is 2.95 D in benzene[41] at 298 K (See Fig. VI-5, VI-6, in Chapter VI). Unlike 4-biphenylyl phenyl ether and 2-methylphenyl phenyl ether its dipole moment is larger than that of diphenyl ether. Since the molecular wieght (171 g/mole) of 2-benzoyl pyridine is very close to that of diphenyl ether (170 g/mole), and since the direction of the resultant dipole moment is parallel to the Y axis, if the rings are coplanar, it appears that the magnitude of the dipole moment with respect to that of diphenyl ether, as well as the magnitude of the mesomeric moment could be important factors in deciding whether double-internal rotation takes place. In the case of 2-methylphenyl phenyl ether the dipole moment of 1.57 D at 298 K in benzene[41] is along the Y axis (Fig. VII-10). The net dipole moment is therefore not much greater than that of diphenyl ether so that an intramolecular relaxation process similar to that observed in diphenyl ether may occur. However, phenoxy group rotation could also take place.

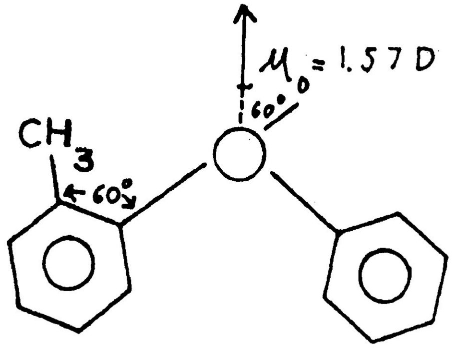


FIGURE VII-10: Dipole Moment μ_0 of 2-Methylphenyl Phenyl Ether

A factor which affects intramolecular rotation in diaryl ethers is the energy barrier for coupled ring rotation about the C_{aryl}—O bonds. For example, if the electron density of the C_{aryl}—O bond is high then rotation would be hindered as in benzophenone.

Fong[16] has stated that the conjugation in benzophenone makes the energy barrier to group rotation so high that it largely inhibits any intramolecular motion such as coupled ring rotations.

The relaxation time[17] of n-butyl ether was found to be 6.5 ps in benzene. The molecular volumes of n-butyl ether and benzophenone are 170.9 and 170.0 c.c. respectively, while the τ value for benzophenone in benzene is 20.1 ps. The difference in relaxation times for n-butyl ether and benzophenone can be attributed to the fact that the aliphatic groups sweep out a lesser volume of solvent than do the phenyl groups. This implies that some internal rotation occurs in n-butyl ether. The small τ value, however, can also be explained by rotation about the C-C single bonds of the alkyl chains. Since there is no chance of a mesomeric moment in alkyl ethers some other mechanism must account for the short relaxation times of alkyl ethers if simultaneous rotation of both alkyl groups occurs about the C-O bonds. Such a mechanism could be that of a mechanical double-internal rotation. This mechanism can also be used to explain the rapid relaxation of diphenyl ether type molecules.

Double-internal rotation involves the simultaneous, coupled rotation of both phenyl groups such that there is a rapid reversal of the molecular dipole moment. The relaxation time for double-internal rotation is much shorter than that for molecular rotation since less volume is swept out during double-internal rotation. Both the molecular and intramolecular relaxation processes can and do occur simultaneously since there is no cause for the molecule to remain rigid while it is rotating as a whole, or for intramolecular rotation to cease.

It was mentioned earlier that simple phenoxy group rotation is not a suitable case for explaining the short relaxation time of diphenyl ether. However, if phenoxy group rotation is coupled with suitable motions of the other ring then a rapid internal relaxation process is possible. Fong[16] has discussed two such coupled internal rotation mechanisms. One is shown in Fig. VII-6 where edgewise rotation of the C_6H_5X groups sweeps out a volume of about 380 $Å^3$, which is only slightly larger than the volume of 365 $Å^3$ swept out by the rotation of a benzene molecule around an axis in the ring plane. Such a C_6H_5X group rotation should not be strictly considered an intramolecular rotation since it involves movement of the centre of mass of the molecule and consequent translational momentum. However, if edgewise rotation of the C_6H_5X group is coupled with tilting of the other phenyl ring as the direction of the X-C bond changes, so that motion of the centre of mass is minimized then the molecule reverses its dipole moment without sweeping out a large volume.

The other type of coupled internal rotation suggested by Fong

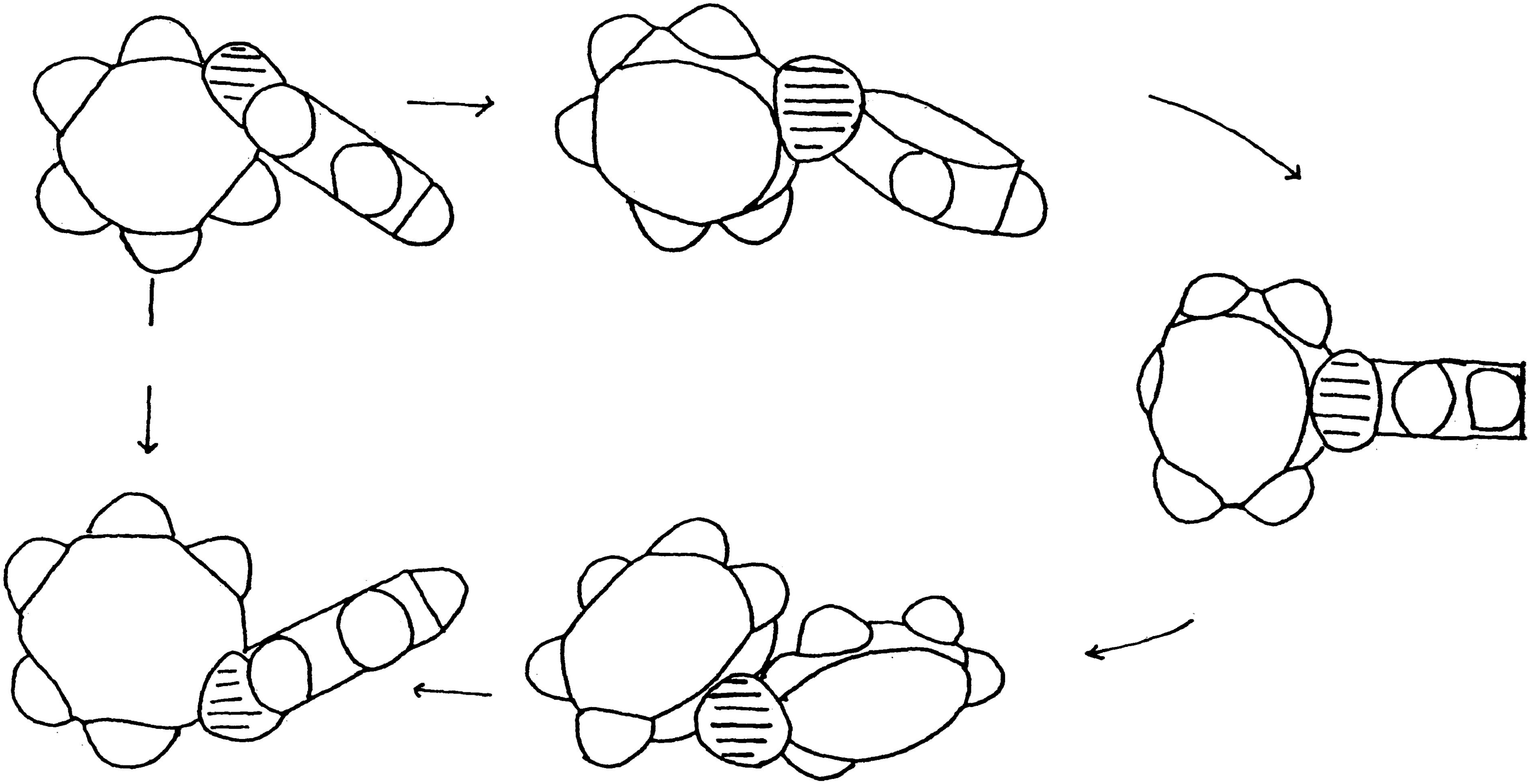


FIGURE VII-11: Molecular Reorientation in Diphenyl Ether by Coupled Ring Rotation about the C-O Bonds is shown in Fig. VII-11. In this type of rotation process there is a 180° change in molecular orientation by rotational motions of the C_6H_5X groups around the C-X bonds through a continuous series of successive configurations as illustrated in Fig. VII-11. The molecular dipole reverses its direction by intramolecular motions which should involve a much shorter relaxation time than rotational orientation of the molecule as a whole. Bonding between the two rings prevents rotation around the C-X bonds, as may also steric repulsion between large substituent groups. Volume swept out by such a rotation can be approximately written as:

$$V = \frac{16}{9} \pi r_b^3 + (\tfrac{1}{2}\pi) r_b r_o^2 \qquad \text{VII-2}$$

where r_b is the radius of the benzene ring, and r_o the radius of the linking oxygen atom. The second term on the right is small compared to the first. As a result, the first term is equal to four-thirds of the volume swept out by a 180° rotation of the benzene molecule, which is $\frac{4}{3} \pi r_b^3$.

Both molecular and double-internal rotation follow different paths between the same initial and final states. In both cases, the final state is the reversal of the molecular dipole moment. Fong[16] indicated that if alternative paths have equal probabilities, then the observed relaxation time (τ_o) is a composite value given by Eqn VII-3.

TABLE VII-1: Literature Values of Observed Relaxation Times (τ_o) of some Symmetric Diaryl Molecules Studied in Solutions at Microwave Frequencies

Compound	Solvent	Temp(°C)	τ_o(ps)	Ref.
Diphenyl ether	Benzene	20	4	29
Benzophenone	Benzene	20	21.2	29
Fluorenone	Benzene	20	19.9	34
Diphenyl methane		30	6.5	7
Dibenzyl ether	Benzene	20	18	18
Bibenzyl		60	13.3	7
Bis(p-bromophenyl) ether	Nujol	20	8.7	25
p,p'-Dibromodiphenyl sulfide	Benzene	20	8.2	29
Bis(p-nitrophenyl) ether	Benzene	20	12.5	17
Bis(diphenylmethyl) ether	Benzene	20	130	17
Bis(p-nitrophenyl) methane	Benzene	20	22.8	25

$$\frac{1}{\tau_o} = \frac{1}{\tau_m} + \frac{1}{\tau_g} \qquad \text{VII-3}$$

where τ_m and τ_g are the molecular and intramolecular relaxation times respectively.

The previous discussion showed how diphenyl ether behaves in alternating electric fields. Many of the characteristics of diphenyl ether's relaxation can be equally applied to other symmetric ethers, sulfides, ketones, and related compounds. Table VII-1 shows a list of some symmetric diaryl molecules which have been studied in solution at microwave frequencies.

Diphenyl ether has served as a model compound for diaryl molecules which have been studied in solution at microwave frequencies as well as in polystyrene matrices.

Diphenyl sulfide[5] was studied in the microwave region in liquid solution and was found to have a short relaxation time of 10×10^{-12} s in benzene at 298 K. Comparison of this relaxation time with that of benzophenone (20.4 ps), indicates a double-internal rotation process for diphenyl sulfide. Symmetric 4,4' derivatives of Ph_2X such as bis(4-bromophenyl) ether, bis(4-nitrophenyl) ether, and bis(4-bromophenyl)[19] sulfide have short relaxation times, such as 12.5×10^{-12} s for p,p'-nitrophenyl ether. This value is too small for a molecular relaxation process and so is indicative of an internal rotation process.

From Table VII-1 it is noticeable that bis(4-nitrophenyl) ether has a relaxation time of 12.5 ps in benzene at 293 K, yet its dipole moment (2.22 D in benzene at 298 K[41]) is significantly larger than that of diphenyl ether ($\mu = 1.23$ D in benzene at 298 K[41]).

The X and Y mesomeric moment components and the resultant (μ_o) dipole moments for diphenyl ether type molecules are shown in Fig. VII-12.

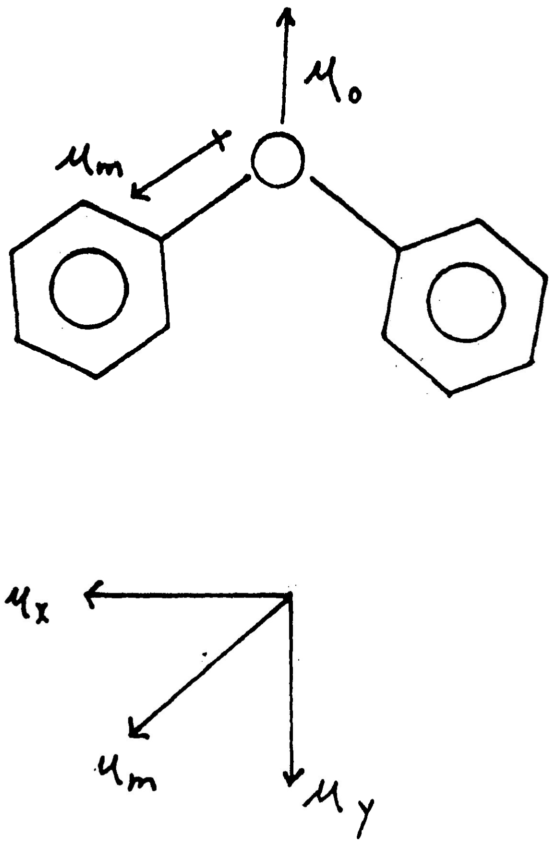


FIGURE VII-12: Dipole Moment (μ_o) and Mesomeric Moment (μ_m) Components of Diphenyl Ether Type Molecules

C_1 and C_2 are related to the dipole moment components by the following equations:

$$C_1 + C_2 = 1 \qquad \text{VII-4}$$

$$C_1 = \frac{\mu_y^2}{\mu_x^2+\mu_y^2}, \qquad C_2 = \frac{\mu_x^2}{\mu_x^2+\mu_y^2} \qquad \text{VII-5}$$

C_2 is the weight factor for the relaxation processes involving the μ_x component. C_2 can also be expressed as:

$$C_2 = \frac{1}{1 + (\frac{\mu_x}{\mu_y})^2} = \frac{1}{1 + (\frac{2\mu_{C-O} - 1}{\mu_m})^2 \cot^2 \theta} \qquad \text{VII-6}$$

where μ_{C-O} is the C-O bond moment.

If the $\mu_{\text{mesomeric}}$ (μ_m) is taken as 0.95 and $\theta = 60^\circ$ then C_2 will be 0.75 and so internal rotation will dominate. It can be seen from Eqn. VII-6 that when $\mu_{C-O} \sim \mu_m$ and μ_{C-O} has the same direction as the mesomeric moment then Eqn. VII-6 becomes:

$$C_2 = \frac{1}{1 + \cot^2\Theta} \qquad \text{VII-7}$$

It is also evident from Eqn. VII-6 that as μ_m reaches 1 so does C_2.

In the case of p,p'-disubstituted molecules such as para-halogen substituted molecules,

$$\mu_{c\text{-}hal} - \mu_{C\text{-}O} = \mu'_{CO} \qquad \text{VII-8}$$

and $\mu_{c\text{-}hal}$ and μ_m have the same direction. The smaller the μ'_{CO} the bigger the C_2. μ'_{CO} values for the para-substituted halogen and nitro groups are as follows:

$$\mu'_{CO} = \mu_{hal} - \mu_{C\text{-}O} = 1.5 - \mu_{C\text{-}O} \sim 0.5$$

$$\mu'_{CO} = \mu_{NO_2} - \mu_{C\text{-}O} = 3.95 - \mu_{C\text{-}O} \sim 3$$

If μ_{CO} for the nitro compound is taken as 3 D then C_2 becomes:

$$\frac{1}{1 + (\frac{2 \times 3}{\mu_m} - 1)^2 - 34}$$

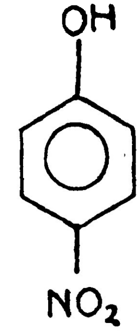
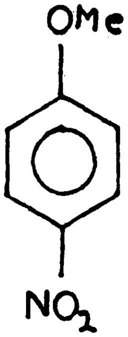
μ'_{CO} will be the same as μ_m when μ_m is about 3 D, but such a μ_m for p,p'-dinitrodiphenyl ether appears to be too large yet τ_o = 12.5 ps at 293 K in benzene and the dipole moment is 2.2 D at 293 K in benzene.[17]

If for p,p'-dinitrodiphenyl ether μ_m is taken as 1.5 D and μ'_{CO} as 3 D then substitution of these values into Eqn. VII-6 yields a C_2 value of $\sim$0.25. This C_2 value can be compared with that of 1,3,5-trinitrobenzene which has a C_2 value of 0.30, the τ_o value is 6.1 ps. The C_1 value is 0.70 and τ_m is 35 ps. This data can be compared to that for p,p'-dinitrodiphenyl ether if for this molecule τ_m $\sim$23, τ_g $\sim$7 ps, μ_m = 1.5 D and C_2 $\sim$0.25, then τ_o will be 12.5 ps. The questions remains whether a μ_m of 1.5 is reasonable for p,p'-dinitrodiphenyl ether.

The above question can be answered in part by examining the mutual conjugation in para-nitroanisole and para-nitrophenol (see Table VII-2).

The extra mesomeric moment in the above molecules is $\sim$0.32 to 0.46 D. However, enhanced conjugation in ethers will be greater. Since diphenyl ether has a mesomeric moment, μ_m^2 $\sim$1 D, then a μ_m of 1.5 D would seem reasonable for p,p'-dinitrodiphenyl ether.

TABLE VII-2: Observed and Calculated Dipole Moments of p-Nitrophenol and p-Nitroanisole

MOLECULE	μ_{obs}(D)	μ_{calc}(D)	$\mu_{obs}-\mu_{calc}$(D)
	5.04	4.58	0.46
	4.82	4.58	0.32

Besides aromatic ethers and sulfides there is some evidence that a double-internal rotation type mechanism may take place in some symmetric dialkyl ethers and sulfides. Dasgupta *et al.*[20] studied diethyl, dihexyl, didodecyl ethers and didodecyl sulfide (see Table VII-3). Ethyl ether was found to have a relaxation time of 1.3 ps in heptane solution at 298 K with a very small distribution parameter

TABLE VII-3: Relaxation Times and Distribution Functions of some Dialkyl Ethers in Heptane Solution[20]

TEMP	τ_o (ps)	α	τ_m (ps)	τ_g (ps)
		Ethyl Ether		
6	1.9	0.03		
25	1.3	0.06		
		Dihexyl Ether		
12	18.6	0.14	42.5	8.0
30	14.8	0.11	30.7	7.1
50	5.9	0.01	-	-
		Didodecyl Ether		
12	42.4	0.35	204	9.3
30	28.6	0.25	119	7.7
50	10.6	0.12	41	6.2
		Didodecyl Sulfide		
20	45.1	0.35	213	11.9
35	29.2	0.26	122	10.3
50	13.3	0.13	47.7	8.5

(α) of 0.06. Dielectric relaxation may occur in diethyl ether by both overall molecular and intramolecular rotation, but the difference in the relaxation times is not sufficient to permit analysis into τ_m and τ_g. The increase in τ_o from diethyl to dihexyl ether (τ_o = 14.8 ps at 303 K) is much greater than the almost threefold increase in molecular volume. The observed relaxation time (28.6 ps at 303 K) for didodecyl ether is also about twice the magnitude of τ_o (14.8 ps at 303 K) for dihexyl ether. However, τ_m, the molecular relaxation time is four to five times larger than that of dihexyl ether. The relaxation times of didodecyl sulfide correspond well with those of didodecyl ether, but are slightly larger (see Table VII-3) because of the increased size and polarizability of the sulfur atom as compared to an oxygen atom.

From Table VII-3 it can be seen that the intramolecular relaxation time (τ_g) is **shorter** and less temperature dependent than the molecular relaxation time for symmetric dialkyl ethers and sulfides. The small τ_g values can arise from twisting or rotation about the C-C single bonds or from rotation of the alkyl chain at or near the central oxygen or sulfur atom. This latter type of relaxation may be similar to double-internal rotation if there is coupled rotation of both chains about the central bridging atom.

Johari *et al.*[21] examined n-butyl ether in heptane at 298 K and found a τ value of 3.4 ps which is smaller than that for methoxy group rotation in n-dodecylmethyl ether.[20,22] Srivastava[23] also measured n-butyl ether as a pure liquid and obtained a relaxation time of 5 ps. It may be difficult to distinguish whether the intramolecular process is segmental rotation or double-internal rotation, since the volume swept out in each case is small, consequently for both cases there would be very small τ_g values.

Other molecules such as diphenyl methanes,[5] dibenzyl ether,[18] and diaryl ketones have also been investigated for rapid internal rotation processes.

EXPERIMENTAL

A number of symmetric molecules have been studied in order to gain further information concerning the intramolecular relaxation processes in the following types of molecules. These include diphenyl ether, diphenyl sulfide, benzophenone, di-4-pyridyl sulfide, diallyl sulfide, di-t-butyl sulfide, di-n-butyl ether, p,p'-dibromodiphenyl ether, dibenzyl ether, p,p'-diamino-diphenyl ether, di-2-pyridyl ketone, p,p'-dimethoxythiobenzophenone, and p,p'-dibromodiphenyl methane.

All of these molecules have been examined in polystyrene matrices, except for benzophenone, p,p'-dibromodiphenyl ether, p,p'-dibromodiphenyl methane, p,p'-diaminodiphenyl ether and diphenyl ether which were also studied as compressed solid discs. All the samples were appropriately dried and stored prior to use. Since diphenyl ether appeared to be hygroscopic it was dried for 24 hours in a desiccator over calcium chloride. The preparation of the polystyrene and compressed solid discs was as outlined in Chapter III.

All the compounds studied were purchased from either the Aldrich Chemical Co. or the K & K Laboratory except for di-p-tolyl sulfide and di-4-pyridyl sulfide which were synthesized (see Chapter IV). The polystyrene matrices and compressed solids were stored in a desiccator over calcium chloride.

Measurements were made in the frequency range 10^2 - 10^5 Hz with a General Radio 1615A capacitance bridge. In the frequency range 0.022 - 22 MHz measurements were made with a Hewlett-Packard HP4342A Q-meter.

The methods utilized for the evaluation of relaxation and activation parameters are as described in Chapter III.

The experimental values of τ, $\log_{10}f_m$, β, ε''_{max}, ε_∞, and μ

at various temperatures are listed in Table VII-11. Table VII-8 lists the relaxation and activation parameters for the molecules studied in this chapter. A sample plot of dielectric loss ($\varepsilon'' = \varepsilon''_{obs} - \varepsilon''_{polystyrene}$) versus $\log_{10}$ frequency for di-2-pyridyl ketone is shown in Fig. VII-20. Fig. VII-21 shows a plot of log $T\tau$ versus 1/T for di-2-pyridyl ketone. The structures of the molecules discussed in this chapter are given in Table VII-12.

DISCUSSION

Several symmetric diaryl molecules, most of which were ethers, sulfides and ketones were studied in polystyrene matrices and in some cases also in a compressed solid form. It was mentioned in the introduction to this chapter that most of the research on diaryl molecules was with ethers, particularly diphenyl ether. Because of the anomalously short relaxation time of diphenyl ether many investigations have been carried out on molecules of the type $(C_6H_5)_2X$ where X = 0, S, C = 0, CH_2, C = S. Since a controversy existed over the nature and mechanism of the rapid intramolecular process of diphenyl ether it seemed reasonable to study these systems and other symmetric diaryl molecules in a different medium. The medium chosen was atactic polystyrene,which had been studied initially by Davies and Edwards.[24] They had shown that in some cases molecular and intramolecular relaxation processes could be separated and studied individualy.

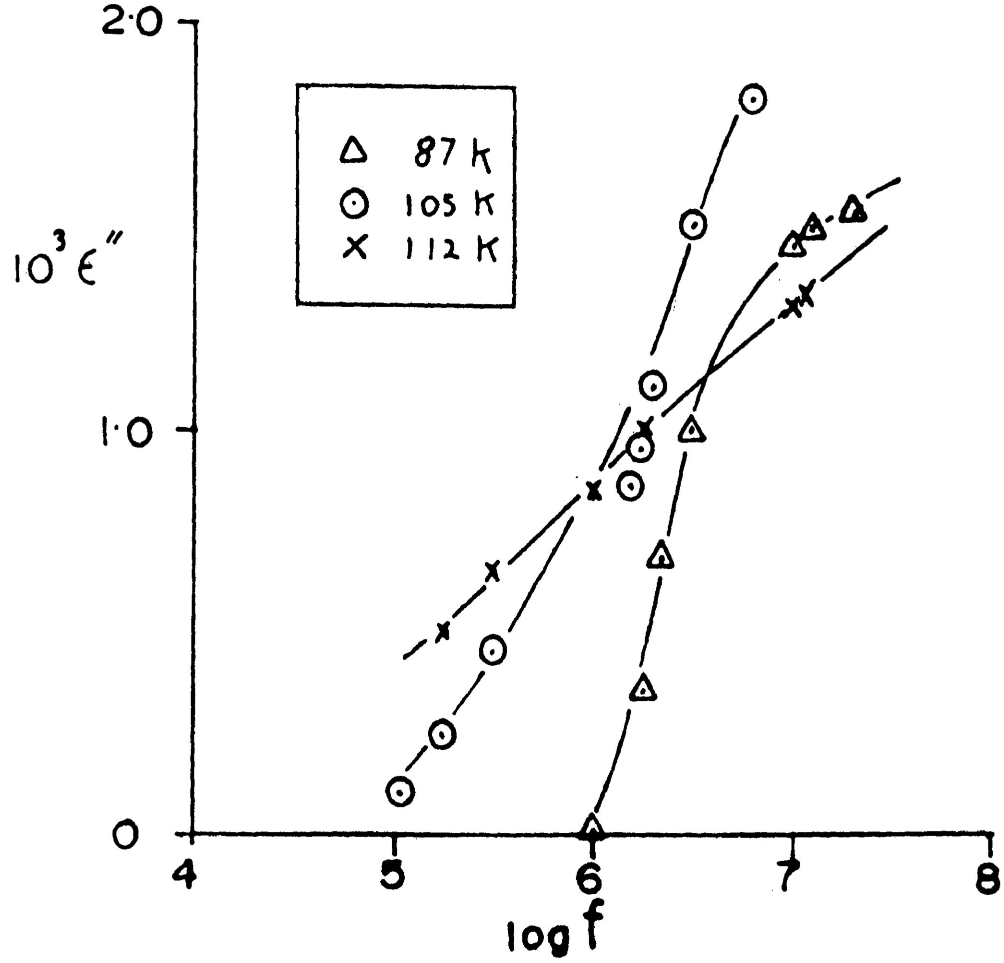


FIGURE VII-13: Dielectric Absorption of Diphenyl Ether as a Compressed Solid in the Range 10^4 - 10^8 Hz.

Studies of the polystyrene matrices and compressed solids have shown that a low energy internal relaxation process exists in many symmetric diaryl ethers, sulfides, and related compounds.

Since diphenyl ether had received much attention in the past in liquid solution studies it seemed a logical compound to examine first. Diphenyl ether was studied as a pure compressed solid disc and in a polystyrene matrix.

Because of the crystalline structure of a compressed solid it is normally not possible to observe molecular rotation. A few exceptions, however, are spherical molecules such as t-butyl chloride and camphor[24] which can relax within their own volume without displacing much of the surrounding medium. It should therefore be possible in a compressed solid to isolate and observe a loss curve for an internal relaxation process such as double-internal rotation. Such an experiment was performed with a 2.76 mm thick disc of diphenyl ether. The study was performed with a Hewlett-Packard Q-meter at the lowest temperature achievable, which was 87.1 K. At this temperature and at 105, and 112.1 K loss curves (Fig. VII-13) were obtained at the high frequency end of the 0.022 to 22 MHz frequency range. The loss and frequency data were put into the computer which extrapolated the curves to find the frequency maxima. The computer extrapolation also gave ΔG_E, τ, and β values for

TABLE VII-4: DIELECTRIC RELAXATION PARAMETERS FROM COMPUTER EXTRAPOLATION OF LOSS CURVES FOR SOME SYMMETRIC DIARYL MOLECULES

STRUCTURAL FORMULA		T(K)	$\log_{10} f_m$	β	ΔG_E (kJ mol^{-1})	τ(s)	μ_{lit}(D)	$10^3 \varepsilon''$
Diphenyl	(i)	87.1	7.38	0.80	6.8	6.6×10^{-9}	1.23	1.58
ether	(ii)	105	7.22	0.65	8.7	9.7×10^{-9}		2.02
c.s.	(iii)	112.1	7.19	0.40	9.4	10.4×10^{-9}		1.36
p,p'Dibromodi-	(i)	88.4	8.20	1.00	5.5	9.9×10^{-10}	0.6	2.46
phenyl ether	(ii)	93.9	9.60	0.35	3.4	4.0×10^{-11}		1.52
p.s.	(iii)	99.8	7.35	0.48	7.9	7.1×10^{-9}		0.58
p,p'-Dibromodi-	(i)	89.3	8.90	0.63	6.0	1.8×10^{-9}	0.6	1.18
phenyl ether	(ii)	99.5	7.40	0.91	7.8	6.3×10^{-9}		1.04
c.s.	(iii)	109.4	7.66	1.00	8.2	3.5×10^{-9}		1.20
p,p'-Diaminodi-	(i)	88.9	7.60	0.76	6.5	3.8×10^{-9}	2.69	1.07
phenyl ether	(ii)	93	2.62	0.34	5.1	8.8×10^{-10}		3.14
c.s.	(iii)	106.7	8.33	0.44	6.6	7.5×10^{-10}		8.33
Di-4-pyridyl	(i)	119.2 (p.s.)	8.17	0.54	7.8	1.1×10^{-9}	—	4,69
sulfide	(ii)	88.4 (c.s.)	8.23	0.72	5.5	9.4×10^{-10}		1.36
p.s. and c.s.								

NOTE: p.s. stands for studies in a polystyrene matrix
c.s. stands for studies as compressed crystalline solids

TABLE VII-5: Comparison of $\Delta G_{E(obs)}$ and $\Delta G_{E(calc)}$ values from computer extrapolations of part of the full loss curves for a series of diaryl molecules

T(K)	$freq_{max}$ calc (c.p.s.)	$freq_{max}$ obs (c.p.s.)	ΔG_{calc} (kJ mol^{-1})	ΔG_{obs} (kJ mol^{-1})
	Dibenzothiophene in Polystyrene			
219	13,594	22,700	34.2	34.2
226.2	7,857	11,544	34.5	34.2
230.6	9,992	6,399	32.9	34.2
	Dibenzothiophene sulfone in Polystyrene			
221.3	12,828	6,880	31.1	34.7
230.8	5,847	7,224	34.3	34.7
	o-Hydroxybenzophenone in Polystyrene			
279.1	12,458	12,649	42.1	42.0
284.3	53,801	19,603	39.4	41.8
289	68,190	29,536	39.6	41.6
	2,5-Diphenyl-1,3,4-oxadiazole in Polystyrene			
277.7	13,351	10,129	41.7	42.3
292.1	16,834	22,679	37.8	42.7
	1,2-Diphenylcyclopropenone in polystyrene			
277.7	3,733	3,936	44.6	44.5
293.6	31,466	22,530	42.1	42.9
303.4		47,733	35.3	42.5

TABLE VII-5: continued.....

T(K)	$freq_{max}$ calc (c.p.s.)	$freq_{max}$ obs (c.p.s.)	ΔG_{calc} (kJ mol^{-1})	ΔG_{obs} (kJ mol^{-1})
		Diphenyl sulfide in Polystyrene		
89	1.75×10^5	1.61×10^5	10.6	10.7
94.1	6.05×10^5	4.72×10^5	10.3	10.5
96.7	1.95×10^6	8.27×10^5	9.7	10.4
98.9	1.64×10^6	1.08×10^6	10.0	10.4
		Di-p-tolyl sulfide in Polystyrene		
97.5	4.60×10^5	3.8×10^5	10.9	11.3
101.2	3.33×10^6	8.4×10^5	9.7	10.9
103.2	6.62×10^6	5.97×10^6	9.3	9.4

the loss curves (see Table VII-4). In order to check the validity of the extropolation procedure a number of molecules were analyzed by taking parts of their absorption curves and extrapolating them. The dielectric parameters obtained were compared with those from analysis of the full absorption curves. The data obtained is shown in Table VII-5.

In order to test whether the dielectric loss curves observed for the compressed solid samples are not a phenomenon due to these types of samples at near liquid nitrogen temperatures,or due to the instrumentation, a compressed solid disc of a rigid molecule was studied under similar conditions.

The molecule chosen was dibenzothiophene sulfone since it is similar in size to the molecules studied. At 93.4 K the dielectric loss for dibenzothiophene sulfone was zero thereby giving no absorption curve at the high frequency end of the Q-meter frequency range. This indicates that the loss curves for the non-rigid symmetric diaryl molecules studied as compressed solids on the Q-meter are possibly due to a rapid intramolecular relaxation process, such as double-internal rotation.

Some molecules such as bis(4-bromophenyl) ether and di-4-pyridyl sulfide were also studied in polystyrene matrices at near

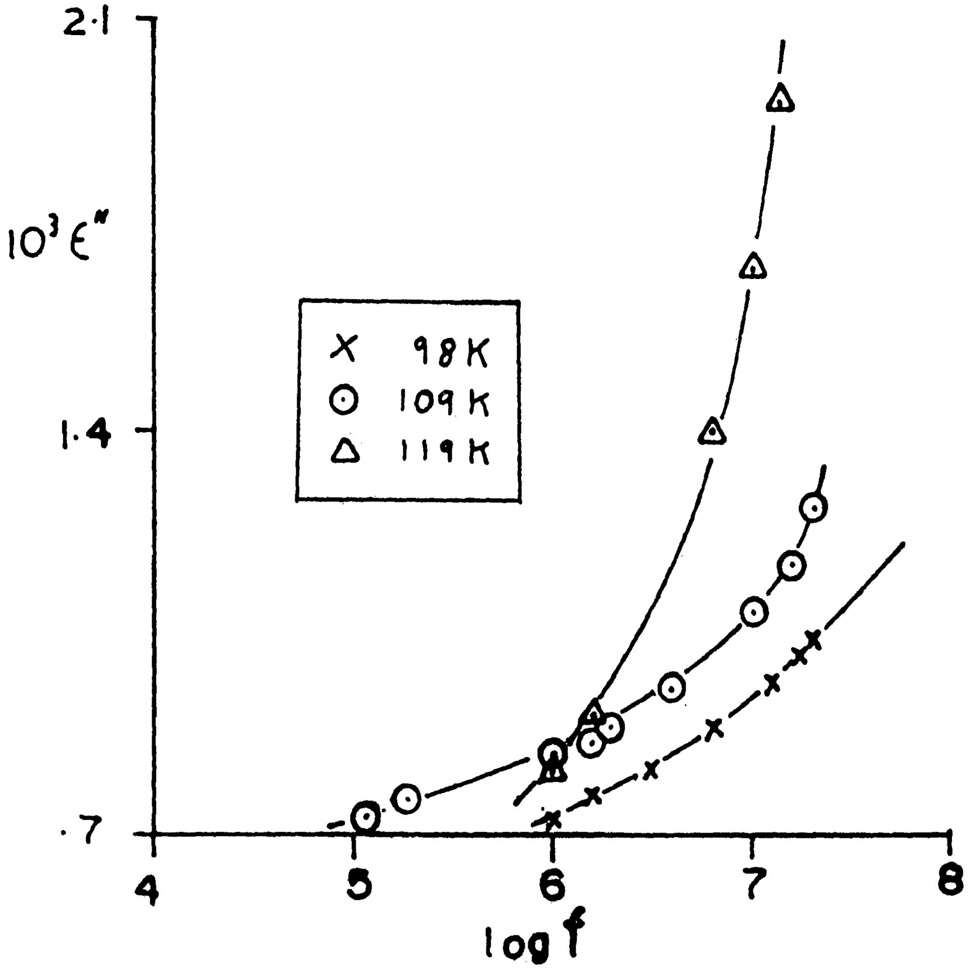


FIGURE VII-14: Dielectric Absorption of 0.572M di-4-Pyridyl Sulfide in Polystyrene in the Range 10^4 - 10^8 Hz

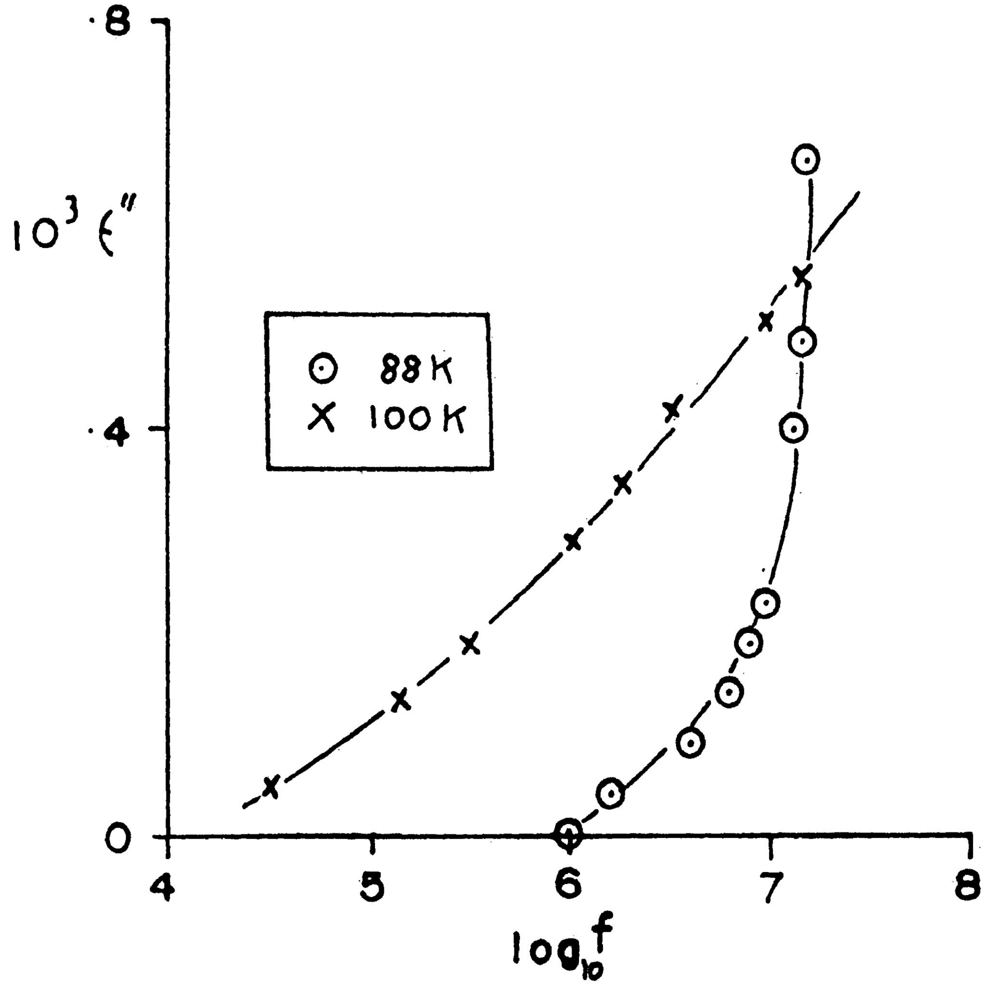
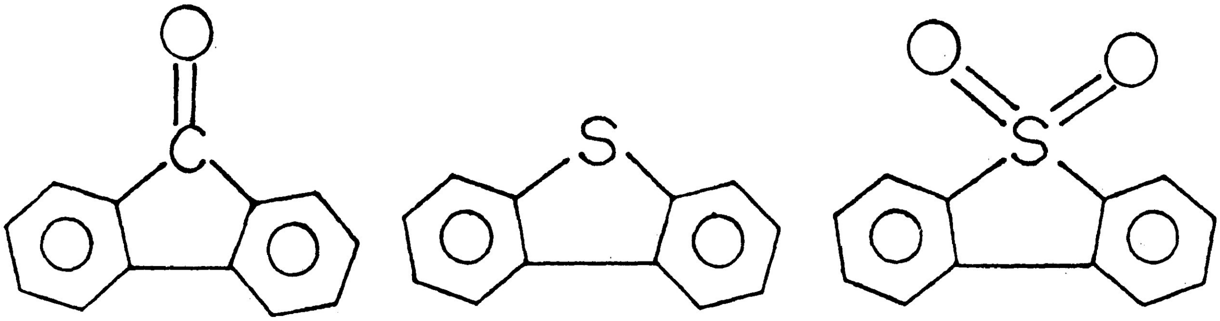


FIGURE VII-15: Dielectric Absorption of 0.510M p,p'-Dibromodiphenyl Ether in Polystrene in the Range 10^4 - 10^8 Hz liquid nitrogen temperature on the Q-meter. As with the compressed solid samples loss curves were observed at the high frequency end (see Fig. VII-14 and Fig. VII-15). In order to test whether these observations were not due to experimental error, or instrumentation phenomena a rigid molecule (o-hydroxybenzophenone) was studied in a polystyrene matrix at near liquid nitrogen temperature (97.9 K) on the Q-meter. The dielectric loss of this sample did not show any peaks or loss curves at high frequencies, instead very low loss was observed with an average $10^3\varepsilon''$ of 0.23. This low loss may be due to polystyrene.

From the study of diphenyl ether as a compressed solid the ΔG_E value at 87.1 K was found to be 6.8 kJ mol^{-1}, which is enough to indicate an internal relaxation process, as does also the τ value of 6.6×10^{-9} s. Similarly, the low temperatures at which absorption curves were observed, and the frequency maximum ($\log f_m = 7.38$), support the idea of a low energy intramolecular relaxation process. Whether the relaxation process is intramolecular can be discerned by comparing the above parameters with rigid molecules which are of similar size and shape to diphenyl ether. Studies of diphenyl ether in polystyrene have shown a set of molecular peaks, these will be discussed later.

In early studies of diaryl compounds workers[4] considered benzophenone to be a good comparison molecule with diphenyl ether. They assumed that benzophenone is planar as well as diphenyl ether. If diphenyl ether is planar then molecular relaxation should have similar relaxation parameters to fluorenone[24], dibenzothiophene, and dibenzothiophene sulfone in polystyrene matrices. All three



Fluorenone Dibenzothiophene Dibenzothiophene Sulfone

FIGURE VII-16

compounds have a C-C bridge connecting the two aromatic rings at the ortho positions, thereby making the rings coplanar (Fig. VII-16).

The three rigid molecules have absorption peaks at nearly similar temperature ranges, (173 - 230.6 K) which are considerably higher than that for diphenyl ether. Also the frequency range (200 - 100,000 Hz) of absorption peaks is less than that of diphenyl ether. The ΔG_E value of diphenyl ether at 87.1 K is 6.8 kJ mol^{-1} while for dibenzothiophene at 150 K it is 35.2 kJ mol^{-1}. These facts as well as the relaxation time of 6.6×10^{-9} s at 87.1 K indicate that diphenyl ether undergoes a very low energy rapid intramolecular relaxation process.

As was mentioned in the introduction to this chapter diphenyl ether most likely does not have a planar geometry, but one in which both rings are orthogonal.[35,36,37,38] In this case diphenyl ether can be compared to o-hydroxydiphenyl ether (Fig. VII-2) in terms of size and shape. In this molecule the ring with the hydroxyl group is prevented from free rotation by a hydrogen bond to the central oxygen atom. Maier[6] measured the relaxation time of this molecule in benzene and found no anomalous behaviour. The relaxation time was five times that of diphenyl ether (τ = 2.8 ps in benzene at 298 K).

Another molecule with which diphenyl ether can be compared is o-hydroxybenzophenone in which a hydrogen-bond keeps one ring in the $\rangle C = O$ plane and the other perpendicular to it. The ΔG_E value for this molecule at 150 K is 49.5 kJ mol^{-1}. Consequently, if diphenyl ether has two orthogonal rings the observed process is not over-all molecular rotation. Diphenyl ether has a β of 0.8 at 87.1 K, which indicates a narrow distribution of relaxation times. A distribution of relaxation times may be due in part to diphenyl ether molecules temporarily locked in a rigid position in which molecular rotation occurs independently of the coupled ring rotation process.[16]

From the discussion in the previous sections it appears that the relaxation process which gives the largest contribution to the observed relaxation time of diphenyl ether is a double-internal rotation type motion, with contribution from a mesomeric mechanism. Evidence that there are other relaxation processes for diphenyl ether in a polystyrene matrix is a set of absorption peaks in the temperature range 212.9 - 250 K.

Diphenyl ether as a compressed solid was found to show a set of dielectric loss curves (Fig. VII-13) which rise at the high frequencies on the Q-meter, at near liquid nitrogen temperatures. From computer extrapolation and analysis of the loss curves dielectric parameters (Table VII-4) were obtained which suggest a very rapid relaxation process. The ΔG_E values (6.8, 8.7, and 9.4 kJ mol^{-1}) at

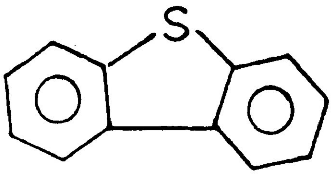
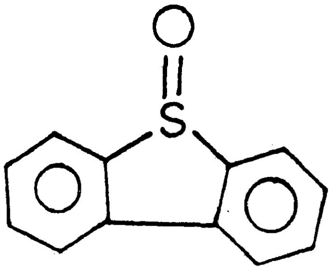
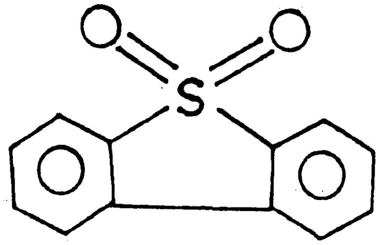
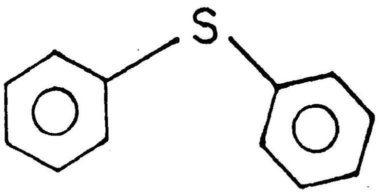
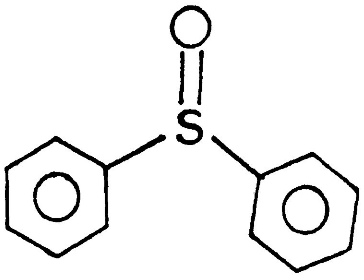
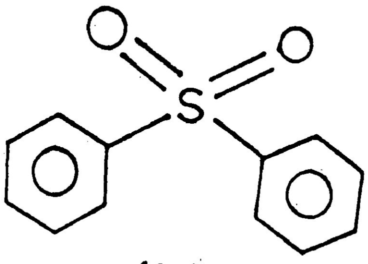
87.1, 105, and 112.1 K respectively are suggestive of a low energy rotational barrier when compared to the ΔG_E values of other non-rigid symmetric ethers and sulfides (Table VII-4) and to the ΔG_E values of rigid similarly sized and shaped molecules such as o-hydroxybenzophenone (ΔG_E, 49.5 kJ mol^{-1} at 150 K). Another set of dielectric absorption maxima for diphenyl ether was observed in the frequency range 200 to 100,000 Hz at temperatures of 213 to 235 K. Computer analysis of this set of loss curves gave ΔH_E as 74.7 kJ mol^{-1} and ΔS_E as 180.3 J K^{-1} mol^{-1}.

The magnitude of the ΔS_E value for diphenyl ether seems much too big for an intramolecular or a molecular relaxation process. It does, however, suggest that the molecule may be undergoing co-operative motion with the polymer chains. This is borne out by a comparison of the observed ΔS_E value with that calculated from Eqn. VII-9. This equation was developed for co-operative motion of solute molecules in polymer matrices:

$$\Delta S_E = 2.5\ \Delta H_E - 73 \qquad \text{VII-9}$$

The calculated ΔS_E value is 160 J K^{-1} mol^{-1} which compares well with the observed ΔS_E value (180 J K^{-1} mol^{-1}). The relatively high β values (0.42 to 0.55) are suggestive of a major contribution to the observed relaxation from one type of rotation process. A comparison of the $\Delta G_{E(200\ K)}$ value for diphenyl ether ($\Delta G_E = 38.6$ kJ mol^{-1}) with those for rigid, similarly shaped and sized molecules, such as o-hydroxybenzophenone ($\Delta H_E = 58.2$ kJ mol^{-1}, $\Delta G_{E(200\ K)} = 46.6$ mol^{-1}, $\Delta S_E = 57.6$ J K^{-1} mol^{-1}) in polystyrene, implies that the predominant relaxation process observed for diphenyl ether may not be molecular rotation. Another molecule which is of similar size and shape to diphenyl ether and has loss maxima in a similar frequency range (0.2 - 100 KHz) and temperature range (205 - 240 K) is diphenyl sulfone in a polystyrene matrix. Table VII-6 clearly shows that molecules

TABLE VII-6: Enthalpies of Activation (ΔH_E) for some Symmetric Diaryl Molecules in Polystyrene

			
ΔH_E (kJ mol^{-1})	38.5	38.9	39.7
			
ΔH_E (kJ mol^{-1})	13.6	59.9	62.0

such as diphenyl sulfone and diphenyl sulfoxide which are similar in size and shape to each other have ΔH_E values of about 60 kJ mol^{-1}. Diphenyl ether, however, which is of similar size and shape has a significantly bigger ΔH_E value (74.7 kJ mol^{-1}). The ΔS_E values (60 and 121 kJ mol^{-1}) for diphenyl sulfoxide and diphenyl sulfone, respectively,are smaller than that for diphenyl ether (ΔS_E = 180 J K^{-1} mol^{-1}).

On the basis of the above experimental evidence it appears that diphenyl ether also exhibits a set of dielectric loss maxima which do not arise from overall molecular rotation,but from co-operative motion with the polymer chains. Co-operative motion of a solute with the polymer chains is usually observed near or above the glass-transition temperature of the polymer. However, the dielectric loss maxima for diphenyl ether were observed in the temperature range 212.9 - 235.3 K, while the glass-transition temperature for **atactic** polystyrene is about 330 K.

2-Benzoyl pyridine (Chapter VI) as in the case of diphenyl ether also shows dielectric loss maxima below the glass transition temperature of the polymer. 2-Benzoyl pyridine in a polystyrene matrix, in the frequency range 0.2 to 100 KHz from 249.1 to 294.5 K shows a dielectric relaxation process whose enthalpy of activation is 75.4 kJ mol^{-1}. The ΔH_E value compares well with that of diphenyl ether (ΔH_E = 74.7 kJ mol^{-1}). The ΔS_E value of 127 kJ mol^{-1} for 2-benzoyl pyridine is relatively large and positive as is that of diphenyl ether (ΔS_E = 180 J K^{-1} mol^{-1}). At 150 K the free energies of activation for diphenyl ether and 2-benzoyl pyridine are 47.6 and 56.4 kJ mol^{-1} respectively. The above experimental data suggest that diphenyl ehter may be undergoing a co-operative rotation process as does 2-benzoyl pyridine (see Chapter VI), which is of similar size and shape.

Besides diphenyl ether other symmetric diaryl ethers have been studied in a polystyrene matrix, and as compressed solids. These include p,p'-dibromodiphenyl ether, p,p'-diaminodiphenyl ether, and dibenzyl ether

Since diphenyl ether and many of its symmetrical 4,4'-disubstituted derivatives have resultant dipole moments lying on the line bisecting the COC valency angle along the short molecular Y axis, it seems reasonable to study 4,4'-substituted diaryl molecules. Notable exceptions are the amino and methoxy groups in which group moments are not along the Ph-O bond. A 0.514 molar polystyrene sample of p,p'-dibromodiphenyl ether was measured in the frequency range from 200 Hz to 30 MHz, and the temperature range from 93 to 320 K. In the log frequency maximum range from 2.47 to 4.46 and temperature range from 204.6 to 232.6 a set of dielectric absorption peaks was found. The enthalpy of activation for the molecule was found to be approximately 63 kJ mol^{-1} which when compared with similarly sized and shaped molecules such as diphenyl sulfone, diphenyl sulfoxide, and o-hydroxybenzophenone is what would be expected. The last three compounds mentioned which are slightly smaller than p,p'-dibromodiphenyl ether have ΔH_E values of 61.9, 59.9, and 58.2 kJ mol^{-1} respectively. The temperature range (205 - 233 K) at which p,p'-dibromodiphenyl ether exhibits loss maxima is similar to that for diphenyl sulfone (205 - 240K). Also, the ΔS_E values are similar (129 and 121 J K^{-1} mol^{-1}) for p,p'-dibromodiphenyl ether and diphenyl sulfone respectively. It therefore appears, in light of these parameters, that p,p'-dibromodiphenyl ether exhibits an overall molecular rotation process in the above specified temperature range.

p,p'-Dibromodiphenyl ether was also studied in a polystyrene matrix in the frequency range 0.022 MHz to 30 MHz at 88.4 K. Absorption curves were found at the high frequency end of the Q-meter frequency range (Fig. VII-15). The curve at 88.4 K was extrapolated by computer to give a $\log_{10}$ frequency maximum of 8.2. A β value of 1.00 was found which indicates one relaxation process. Since this compound was found to have a set of peaks for a molecular relaxation process, from 204.6 to 232.6 K in a polystyrene matrix it appears that it also has an intramolecular relaxation process at 88.4 K. The ΔG_E value of 5.5 kJ mol^{-1} at 88.4 K further indicates a low energy process similar to the double internal rotation of diphenyl ether as also does the τ value of 9.9×10^{-10} s.

Purcell and Smyth[25] also found an anomalously short relaxation time of 8.7×10^{-12} s at 293 K in Nujol for p,p'-dibromodyphenyl ether. The experimentally observed relaxation time (9.8×10^{-10} s) in a polystyrene matrix is shorter than that of diphenyl ether as a compressed solid (6.6×10^{-9} s) at nearly the same temperatures (87.1 K and 88.4 K) as is also the ΔG_E value of 5.52 kJ mol^{-1} for the dibromo compound as compared to 6.8 kJ mol^{-1} for diphenyl ether, These experimental results can be possibly explained by the fact that p,p'-dibromodiphenyl ether in a polystyrene matrix has a different environment and interaction with the solvent than in the compressed solid. It may also be that the differences in τ and ΔG_E values for p,p'-dibromodiphenyl ether and diphenyl ether may be so small that they are due to the inaccuracies of the estimation technique.

p,p'-Dibromodiphenyl ether was also studied as a compressed solid on the Q-meter at 89.3, 99.5, and 109.4 K. A series of complete loss peaks was not observed, but curves at the high frequency end were found (Fig. VII-17). Computer extrapolation of the curve at 89.3 K gave a ΔG_E value of 6.0 kJ mol^{-1}, a τ value of 1.8×10^{-9} s, and a β value of 0.63 (see Table VII-4). Again as with the polystyrene matrix sample a relatively large β value was observed, thereby indicating a narrow distribution of relaxation processes with a large contribution from one process, such as double-internal

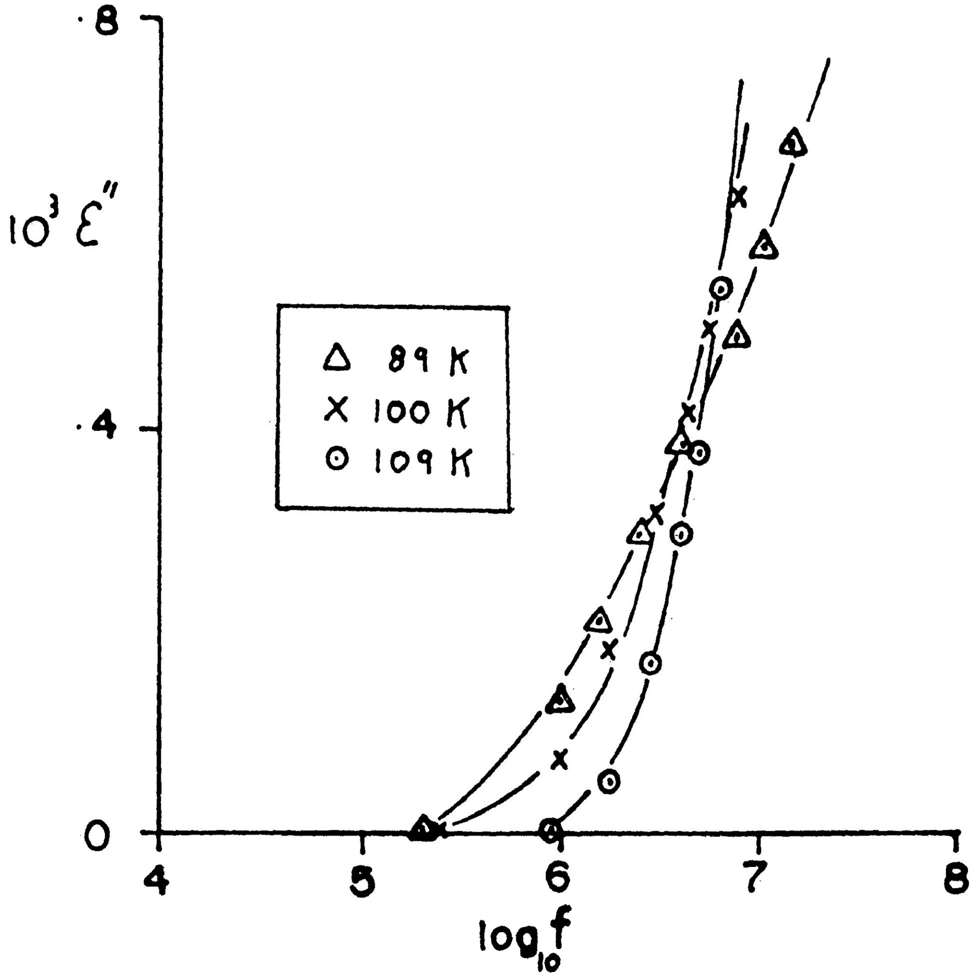


FIGURE VII-17: Dielectric Absorption of p,p'-Dibromodiphenyl Ether as a Compressed Solid in the Range 10^4 - 10^8 Hz rotation. Also the ΔG_E and τ values follow the same pattern as the polystyrene matrix sample since both values are less than those of diphenyl ether.

A number of reasons may account for the smaller τ and ΔG_E values for the p,p'-substituted ether as compared to those for diphenyl ether. One explanation is that the bromine atoms in the para positions can withdraw charge from the ring and the $O\text{-}C_{aryl}$ bond. Consequently the $O\text{-}C_{aryl}$ bond electron density will be less than in diphenyl ether, thereby resulting in a smaller energy barrier to rotation about the $O\text{-}C_{aryl}$ bonds. Another factor which may cause the lower energy barrier is the bond angle of 123°[26] as compared with that of 120° for diphenyl ether[27]. As a result the two aromatic rings are farther apart so that there is less steric hinderance to internal rotation.

A further trait of the p,p'-dibromodiphenyl ether molecule which may cause the low energy barrier to internal rotation is the small dipole moment of 0.60 D at 293 K in benzene[41] as compared to 1.55 D at 298 K in benzene for diphenyl ether. Such a dipole moment indicates that some mesomeric shift of charge from the oxygen atom into the ring is likely to occur. The mesomeric mechanism therefore could contribute to the shortening of the relaxation time and the low ΔG_E values for p,p'-dibromodiphenyl ether. Diphenyl ether with a higher molecular dipole moment would have a smaller contribution from the mesomeric mechanism and therefore a longer τ value. Sutton and Hampson[9] obtained a mesomeric interaction moment of 0.3 D over the 1.32 D value which Higasi[28] determined for diphenyl ether. The mesomeric moment estimated by Higasi is a maximum one for diphenyl ether. That of Sutton is the mesomeric moment for a diphenyl ether molecule which has a coplanar structure.

The implications of the observations for p,p'-dibromodiphenyl ether in a polystyrene matrix and as a compressed solid are as follows. Firstly, it appears from the loss curves for p,p'-dibromodiphenyl ether and other symmetric diaryl ethers in the temperature range 82 - 100 K that double-internal rotation occurs. A second observation is that it seems from the low temperature work that molecular and intramolecular rotation processes can be separated. This is understandable if the double-internal rotation gives loss maxima at frequencies greater than 10^7 Hz, since in benzene and in Nujol they occur in the microwave range, and the τ values seem independent of the solvent viscosity. Another reason why the two relaxation processes can be separated is that in compressed solids of many compounds the molecules are not able to rotate. However, intramolecular rotations can still occur.

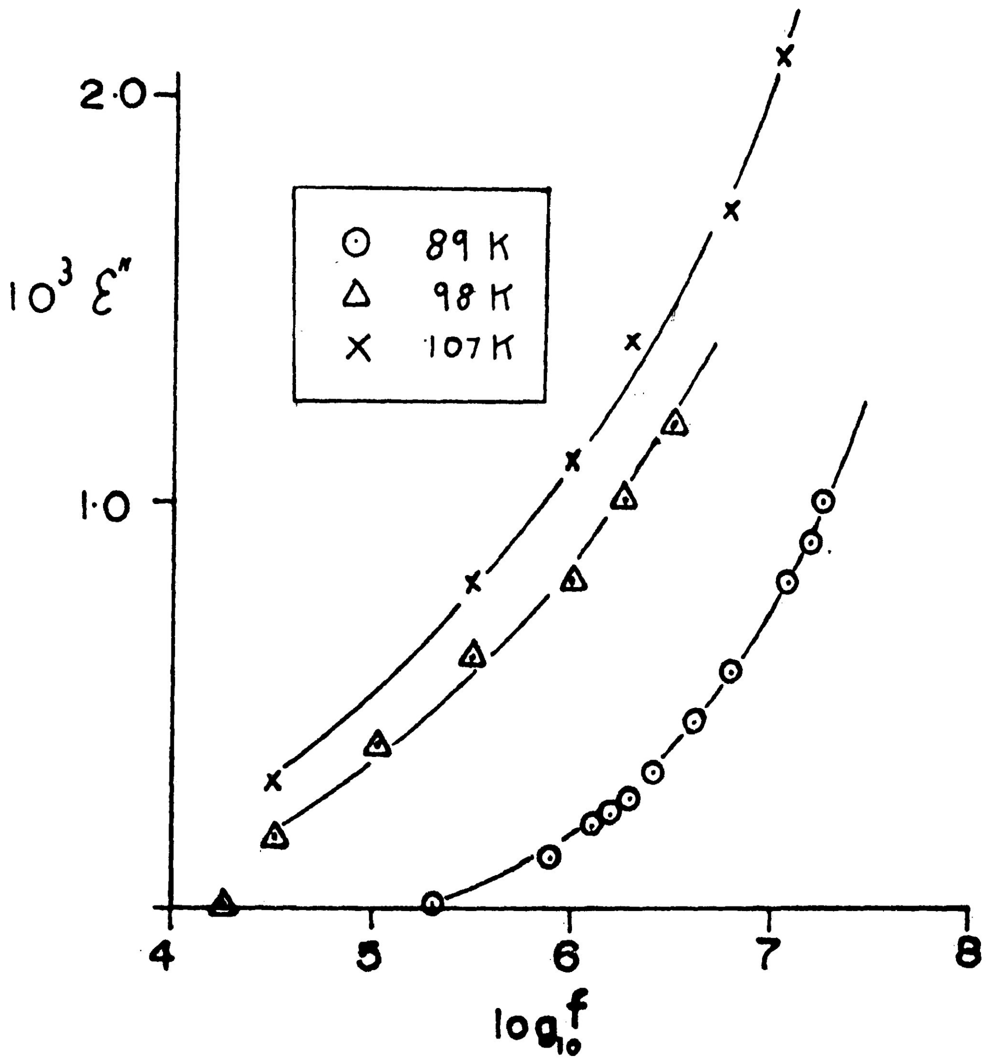


FIGURE VII-18: Dielectric Absorption of p,p'-Diaminodiphenyl Ether as a Compressed Solid in the Range 10^4 - 10^8 Hz

A similar behaviour to that of p,p'-dibromodiphenyl ether and diphenyl ether was observed for p,p'-dibromodiphenyl sulfide[29] and diphenyl sulfide in solution studies at microwave frequencies. p,p'-Dibromodiphenyl sulfide has a τ value of 8.2×10^{-12} s in benzene at 293 K and a dipole moment of 0.68 D at 298 K in benzene[41], while diphenyl sulfide has a τ value of 9.2×10^{-12} s and a dipole moment of 1.55 D at 298 K in benzene.[41] Although p,p'-dibromodiphenyl sulfide is the larger molecule its dipole moment is less than that of diphenyl sulfide, thereby giving a smaller contribution to the molecular relaxation process. Diphenyl sulfide and diphenyl ether with their higher dipole moments have smaller contributions from a mesomeric mechanism and, therefore, have longer relaxation times. It therefore seems probable that both the double-internal rotation and mesomeric mechanisms contribute to the relaxation processes of these molecules.

p,p'-diaminodiphenyl ether was studied in polystyrene and as a compressed solid. In polystyrene form no absorption peaks were found from 80 to 273 K in the frequency range 200 to 100,000 Hz. In the compressed solid form loss curves (Fig. VII-18) were found at 88.9, 97.5, and 106.7 K at the high frequencies on the Q-meter and as with the other ethers a computer extrapolation was performed on the absorption curves. The dielectric parameters are similar to those of diphenyl ether and p,p'-dibromodiphenyl ether, thereby indicating an internal relaxation process. It can be seen from Table VII-4 that the absorption temperature and log f_m (7.63) are near those of diphenyl ether. It can also be seen that the relaxation time of 3.7 x 10^{-9} s is shorter than that of diphenyl ether (6.6 x 10^{-9} s) in polystyrene.

The possibility exists that the observed relaxation process may be nitrogen inversion or amino group rotation. In p,p'-diaminodiphenyl ether the inversion barrier for each nitrogen atom of the two amino groups can be compared to that for the nitrogen atom in aniline. Microwave studies[39] of aniline give inversion barriers as 6.7 kJ mol^{-1}, which is close to the ΔG_E values of 6.5 kJ mol^{-1} for p,p'-diaminodiphenyl ether. The rotational energy barrier for the amino group in aniline has been estimated as 33.6 kJ mol^{-1}. This value is considerably larger than the energy barrier for the relaxation process observed in p,p'-diaminodiphenyl ether.

The discrepancy between diphenyl ether values and those of p,p'-diaminodiphenyl ether may be due to experimental error or the 2 K difference in temperatures at which the two molecules were measured. Amino groups exert a +M effect thereby increasing the electron density of the C-O bonds and very likely increasing the

ΔG_E value. The beta value of 0.76 at 88.9 K is indicative of a narrow disturbution of relaxation times as is also the case with diphenyl ether. Since p,p'-diaminodiphenyl ether has a dipole moment of 2.69 D in benzene at 298 K[41] the contribution from molecular rotation is increased over that of the other two ethers. If the amino groups withdraw charge from the rings and the C-O bonds then the shorter τ value (3.7×10^{-9} s) and ΔG_E value (6.5 kJ mol^{-1}) could be explained. However, in this molecule it is more likely that the p-aminophenoxy groups push charge into the other ring thereby increasing the electron density. The τ and ΔG_E values for p,p'-diaminodiphenyl ether appear to be too small for nitrogen inversion or amino group rotation. Therefore it appears that the most probable relaxation process which gives the greatest contribution to the dielectric relaxation of p,p'-diaminodiphenyl ether in compressed solid form is double-internal rotation.

A study of dibenzyl ether in a polystyrene matrix showed the molecule to exhibit an anomalous relaxation behaviour. A set of peaks was found from 107.5 to 122 K in the $\log_{10}f_m$ range of 3.82 - 4.84. This molecule has a dipole moment of 1.39 D at 298 K in benzene,[41] which is close to the 1.23 D value of diphenyl ether. Since the aromatic rings in dibenzyl ether are separated from the oxygen atom by methylene groups it appears that a mesomeric shift of charge from the oxygen atom to the aromatic rings is not possible.

The ΔH_E value was calculated to be 5.9 kJ mol^{-1} which is much too low to be accounted for by molecular rotation. The relaxation process which occurs is therefore either segmental rotation of the $-CH_2-O-CH_2-$ groups or some form of double-internal rotation. Segmental rotation can occur either about the $C_{\text{aryl}}\text{—}C_{\text{methylene}}$ or $C_{\text{methylene}}\text{—}O$ bonds. If rotation of the benzyl groups about the oxygen atom is coupled then a double-internal rotation type of relaxation process may occur. Dibenzyl ether may have a number of possible conformations (Fig. VII-19). Conformer I is the most favoured since steric inter-

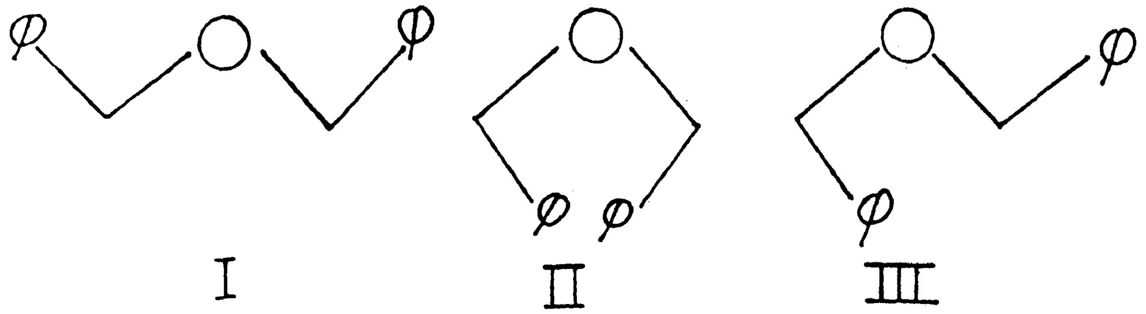


FIGURE VII-19:

Possible Conformations of Dibenzyl Ether actions are less than in the other two conformers shown. It is also symmetric and therefore as with other symmetric non-rigid diaryl molecules has the possibility of exhibiting double-internal rotation. Conformer II is also symmetric but steric factors do not favour this conformation. Conformer III is asymmetric and has slightly greater steric interactions than conformer I.

Robertj *et al.*[7] found liquid dibenzyl ether to have a reduced relaxation time, such that it indicated contribution from internal rotation. Anderson and Smyth[18] carried out experiments in benzene solution and found that dibenzyl ether has a relaxation time close to that of fluorenone, thereby indicating that molecular reorientation is the predominant process. This is in agreement with the normal relaxation time (22×10^{-12} s) found for dibenzyl sulfide in benzene. The polystyrene matrix studies give a ΔH_E value of 5.9 kJ mol^{-1} and a negative ΔS_E value of -92.6 J K^{-1} mol^{-1}, which support the idea of an internal relaxation process as does also the short relaxation time of 2.6×10^{-6} s at 150 K.

Another ether which was studied was n-buty ether in a polystyrene matrix. An approximately 10% by weight matrix sample showed no absorption peaks from 83.0 to 322.9 K. As was mentioned in the introduction section Johari *et al.*[21], studied n-Bu ether as did Srivastava [23]. These studies gave relaxation times which ranged from 3.4 ps to 6.3 ps and seemed to indicate some internal relaxation process such as double-internal rotation. Such observations might advance the theory that a mesomeric moment is not necessary for double-internal rotation to occur, since there is no chance of mesomerism in dialkyl ethers. However, the observed τ value may also be due to internal-rotation about the C-C single bonds.

Another category of compounds which would be expected to exhibit double-internal rotation are symmetric sulfides such as diphenyl sulfide, since sulfur is situated below oxygen in group VI of the periodic table. Since sulfur (van der Waals radius = 1.9 Å) is larger than oxygen (van der Waals radius = 1.4 Å) and the CSC angle is 109° as compared to 120° for the COC angle there should be more steric hinderance in diphenyl sulfide than in diphenyl ether. The implications of these factors are shown in matrix studies of diphenyl sulfides.

Diphenyl sulfide was found to have a set of dielectric loss peaks from 87 to 103 K at a $\log_{10}f_m$ range of 5.37 to 8.06. The ΔH_E value was found to be 13.6 kJ mol^{-1} (Table VII-6) as compared to dibenzothiophene with ΔH_E of 38.5 kJ. Dibenzothiophene is rigid because of the linking of the two aromatic rings. Diphenyl sulfide can also be compared with o-hydroxybenzophenone which is about the same size as diphenyl sulfide and has the two aromatic rings orthogonal. In this case the ΔH_E value in a polystyrene matrix was found to be 58.2 kJ mol^{-1}. These facts indicate that diphenyl sulfide undergoes intramolecular rotation such as double-internal rotation. In Chapter V it was established that the ΔH_E (39 kJ mol^{-1}) is almost independent of the extension of the molecular size by adding an oxygen atom in the series, dibenzothiophene, dibenzothiophene sulfoxide, dibenzothiophene sulfone (Table VII-6). The same behaviour, however, was not observed in the series, diphenyl sulfide, diphenyl sulfoxide, diphenyl sulfone (Table VII-6).

Whereas the ΔH_E values ($\sim$60 kJ mol^{-1}) for diphenyl sulfoxide and diphenyl sulfone are almost independent of the addition of an oxygen atom the ΔH_E value of diphenyl sulfide is much too small for solely molecular relaxation. It is therefore likely that diphenyl sulfide undergoes an intramolecular relaxation process such as rapid coupled ring rotations.

Diphenyl sulfide was also studied by Di Carlo and Smyth[5] who found $\tau = 10 \times 10^{-12}$ s in benzene solution at 293 K. Such a relaxation time is too short to be interpreted as to be completely due to overall molecular rotation. This type of behaviour can also be seen in polystyrene matrix studies. Diphenyl sulfide in polystyrene was found to have a τ value of 1.6×10^{-11} s at 200 K. Dibenzothiophene and o-hydroxybenzophenone have τ values of 2.0×10^{-4} s and

3.7×10^{-1} s at 200 K, respectively. ΔG_E values further substantiate the possibility of an internal rotation process, for example, $\Delta G_E = 3.6$ kJ mol^{-1} for diphenyl sulfide at 300 K, while $\Delta G_E = 31.9$ kJ mol^{-1} for dibenzothiophene and $\Delta G_E = 40.8$ kJ mol^{-1} for o-hydroxybenzophenone in polystyrene matrices at 300 K. These small values for diphenyl sulfide can possibly be accounted for in part by a contribution from a mesomeric mechanism since diphenyl sulfide has a small dipole moment of 1.55 D. Because of the higher dipole moment over that of diphenyl ether, diphenyl sulfide should have a smaller contribution from the mesomeric mechanism and so would have a larger τ value. This is what is observed, since for diphenyl sulfide $\tau_{100\ K} = 1.14 \times 10^{-7}$ s while for diphenyl ether $\tau_{87.1\ K} = 6.62 \times 10^{-9}$ s. It therefore appears from the parameters discussed that diphenyl sulfide undergoes a double-internal rotation process.

In order to further study diaryl sulfides di-4-pyridyl sulfide was synthesized (see Chapter IV) and studied in a polystyrene matrix. No sets of absorption peaks were found in the temperatrure range 80.9 - 309 K at frequencies from 200 - 100,000 Hz. The sample was examined on the Q-meter and a set of curves was found at frequencies from 10^5 to 10^8 Hz at 98.3, 110, and 119.2 K (Fig. VII-14). This behaviour as in the case of the ethers is indicative of a low energy intramolecular relaxation process. In this case one would expect a slightly lower energy barrier since the nitrogen atoms at the 4 positions may withdraw charge from the ring and the C-S bonds.

In a polystyrene matrix di-4-pyridyl sulfide was found to have a ΔG_E value of 7.8 kJ mol^{-1} at 119.2 K. The ΔG_E value was determined by computer analysis of the extrapolated loss curve (Fig. VII-14). This value compares well with the ΔG_E values of other symmetric diaryl ethers and sulfides (Table VII-4) which show dielectric loss curves in a similar temperature and frequency range. For example, p,p'-dibromodiphenyl ether in a polystyrene matrix has a ΔG_E value of 7.9 kJ mol^{-1} at 99.8 K. The relaxation times of di-4-pyridyl sulfide (1.1×10^{-9} s at 119.2 K) and p,p'-dibromodiphenyl ether (7.1×10^{-9} s at 99.8 K) are of the same order of magnitude.

The ΔG_E value (7.8 kJ mol^{-1}) at 119.2 K for di-4-pyridyl sulfide in a polystyrene matrix compares well with the ΔG_E value (8.6 kJ mol^{-1}) at 100 K for diphenyl sulfide in polystyrene and the ΔG_E value (8.2 kJ mol^{-1}) at 100 K for di-p-tolyl sulfide in polystyrene. The β value for di-4-pyridyl sulfide at 119.2 K is 0.54. Other symmetric diaryl ethers and sulfides also have large β values in similar temperature and frequency ranges (Table VII-4). For example, p,p'-dibromodiphenyl ether in polystyrene at 99.8 K has a β value of 0.48, and di-p-tolyl sulfide in polystyrene in the temperature range 92.3 - 106.4 K has a β range of 0.27 - 0.67. These large β values suggest that di-4-pyridyl sulfide and other symmetric diaryl ethers and sulfides have a major contribution to the observed relaxation from one process. The ΔG_E and τ values (Table VII-4) for these molecules are suggestive of a rapid intramolecular relaxation process, such as coupled ring rotations.

Di-4-pyridyl sulfide was also studied as a compressed solid at the same temperature and frequency range as the polystyrene matrix sample. For example, at 88.4 K a partial absorption curve was observed which rises at the high frequencies (1 - 20 MHz) on the Q-meter. Computer analysis of the extrapolated curve gave the ΔG_E value of di-4-pyridyl sulfide as 5.5 kJ mol^{-1}.

Symmetric diaryl ethers which were studied as compressed solids, (Table VII-4) also have low ΔG_E values similar to those for di-4-pyridyl sulfide. For example, diphenyl ether, p,p'-dibromodiphenyl ether and p,p'-diaminodiphenyl ether have ΔG_E values of 6.8 kJ mol^{-1} at 87.1 K, 6.0 kJ mol^{-1} at 89.3 K, and 6.5 kJ mol^{-1} at 88.9 K, respectively. These ΔG_E values are too low to be due to overall molecular rotation as in diphenyl sulfone, (ΔG_E = 43.8 kJ mol^{-1} at 150 K) and o-hydroxybenzophenone (ΔG_E = 49.5 kJ mol^{-1} at 150 K). These latter two molecules are of similar size and shape to the above mentioned ethers and sulfides.

Di-4-pyridyl sulfide appears from the above experimental data to undergo a rapid intramolecular relaxation process, such as coupled ring rotations,as does diphenyl ether. The very short relaxation time of 9.4×10^{-10} s at 88.4 K is also suggestive of the above relaxation process. The relaxation time also compares well with that of p,p'-diaminodiphenyl ether as a compressed solid ($\tau = 8.8 \times 10^{-10}$ s at 93 K). Diphenyl sulfone and o-hydroxybenzophenone which are of similar size and shape to the above symmetric ethers and sulfides have relaxation times of 1.1×10^{0} s at 150 K and 64×10^{4} s at 150 K respectively. These relaxation times can be attributed to overall molecular rotation.

The β value at 88.4 K for di-4-pyridyl sulfide as a compressed solid is relatively high (0.72) as is also the β value (0.54 at 119.2 K) for the polystyrene matrix. The β value for diphenyl ether as a compressed solid ranges 0.40 - 0.80 in the temperature range 87.1 - 112.1 K. For p,p'-dibromodiphenyl ether as a compressed solid the β value range is 0.63 - 1.00 in the temperature range 89.3 - 109.4 K. In polystyrene p,p'-dibromodiphenyl ether has a β value range of 0.48 - 1.00 in the temperature range 88.4 - 99.8 K. p,p'-Diaminodiphenyl ether as a compressed solid has a β value range of 0.44 - 0.76 in the temperature range 88.9 - 106.7 K. Di-p-tolyl sulfide in polystyrene has β values ranging from 0.27 - 0.67 in the temperature range 92.5 - 106.4 K. Di-p-tolyl sulfide in polystyrene has a β value range of 0.27 - 0.67 in the temperature range 92.5 - 106.4 K.

Di-4-pyridyl sulfide and the above mentioned ethers and sulfides have large β values in similar temperature and frequency ranges. These β values suggest a large contribution to the observed relaxation by one type of rotation process. It is shown in this chapter that the rotation process which occurs in the symmetric diaryl ethers and sulfides studied in polystyrene and as compressed solids is rapid low energy coupled ring rotation. Di-4-pyridyl sulfide appears from the experimental results to undergo such a relaxation process.

Di-p-tolyl sulfide which was also synthesized (see Chapter IV) would also be expected to have a different energy barrier for double-internal rotation. In this case the two methyl groups at the para positions would direct a small fraction of charge into the aromatic rings and may, to a small extent, stiffen the C-S bond and possibly increase the energy barrier for double-internal rotation slightly. Di-p-tolyl was studied in polystyrene throughout the frequency range 200 Hz - 20 MHz at temperatures from 92.5 - 320 K. Absorption maxima were observed in the $\log_{10}f_m$ range 5.20 - 6.45 at temperatures from 92.5 - 106.4 K. No absorption maxima were observed in other frequency and temperature ranges.

In the case of di-p-tolyl sulfoxide and di-p-tolyl sulfone the ΔH_E values (68 kJ mol^{-1} and 71 kJ mol^{-1}, respectively) are almost independent of the increase in molecular size by the addition of an oxygen atom (Table VII-7). In comparison with these molecules di-p-tolyl sulfide has a ΔH_E value of 16.2 kJ mol^{-1}, which is much too low to be accounted for solely by molecular rotation. It is, therefore, more likely that it undergoes a rapid coupled ring rotation process as in diphenyl sulfide.

TABLE VII-7: Enthalpies (ΔH_E), Entropies (ΔS_E), and Free Energies (ΔG_E) of Activation of some Symmetric Ditolyl Molecules in Polystyrene

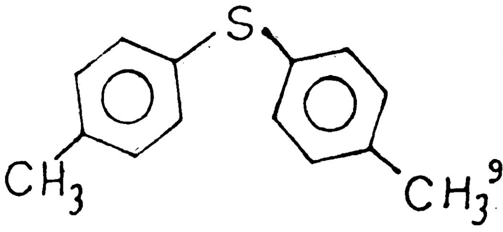
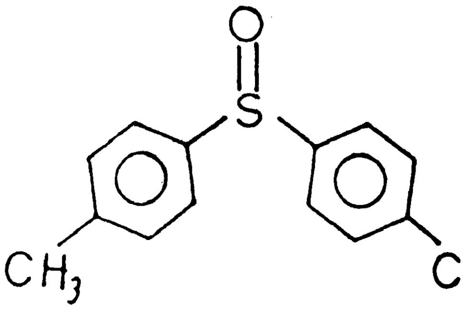
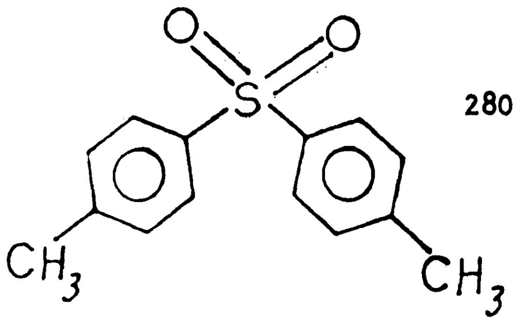
	ΔT (K)	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})	ΔG_E (kJ mol^{-1}) at 150 K
	93-106	16	53	8
	294-324	68	49	61
	280-300	71	84	54

TABLE VII-8: DIELECTRIC RELAXATION AND ACTIVATION PARAMETERS FOR SOME DIARYL MOLECULES IN POLYSTYRENE

Molecule	$\Delta T(K)$	$\tau(s)$			$\Delta G_E (kJ\ mol^{-1})$			ΔH_E $(kJ\ mol^{-1})$	ΔS_E $(J\ K^{-1}\ mol^{-1})$
		150 K	200 K	300 K	150 K	200 K	300 K		
Diphenyl sulfide	89-103	3.3×10^{-10}	1.6×10^{-11}	7.0×10^{-13}	8.6	7.0	3.7	13.6 ±1.9	33 ±20
Di-p-tolyl sulfide	93-106	2.3×10^{-10}	6.8×10^{-12}	1.8×10^{-13}	8.2	5.6	2.5	16.2 ±2.6	53 ±26
p,p'-Dibromo-diphenyl ether	205-233	4.3×10^{2}	1.1×10^{-3}	2.6×10^{-9}	43.5	37.0	24.2	62.7 ±7.7	129 ±35
Dibenzyl ether	108-122	2.6×10^{-6}	5.9×10^{-7}	1.2×10^{-7}	19.8	24.5	33.7	5.9 ±1.3	- 93 ±9.9
Benzophenone	139-164	4.9×10^{-5}	5.0×10^{-7}	4.6×10^{-9}	23.5	24.2	25.6	21.4 ±0.8	- 4 ±5
Di-2-pyridyl ketone	168-221	1.7×10^{-3}	5.3×10^{-3}	1.4×10^{-8}	28.0	28.1	28.4	27.5 ±1.9	- 3 ±10
Diallyl sulfide	108-129	5.3×10^{-7}	1.7×10^{-8}	4.6×10^{-10}	17.9	18.5	19.8	15.9 ±4.3	- 13 ±36
Di-t-butyl sulfide	80-100	4.9×10^{-7}	1.7×10^{-7}	5.4×10^{-8}	17.8	22.4	31.7	3.8 ±0.9	- 93 ±11

Table VII-8 lists the relaxation and Eyring parameters from the computer analysis of the dielectric absorption peaks for di-p-tolyl sulfide in polystyrene. The ΔH_E value (16.2 kJ mol^{-1}) for di-p-tolyl sulfide is marginally greater than the ΔH_E value (13.6 kJ mol^{-1}) for diphenyl sulfide. This observation is to be expected because of the electron-donating properties of the methyl group. This would tend to cause an increase in the electron density of the C-S bonds over that for diphenyl sulfide. The energy barrier for a coupled ring rotation process would consequently be greater for di-p-tolyl sulfide than for diphenyl sulfide.

The free energy of activation (ΔG_E) for di-p-tolyl sulfide has a value of 8.2 kJ mol^{-1} at a temperature of 100 K. This ΔG_E value compares well with the ΔG_E value (8.6 kJ mol^{-1}) for diphenyl sulfide at 100 K. Other symmetric diaryl molecules which exhibit rapid coupled ring rotations also have similar ΔG_E values (Table VII-4) at temperatures near 100 K. For example, p,p'-dibromodiphenyl ether in polystyrene has a ΔG_E value of 7.9 kJ mol^{-1} at 99.8 K (Table VII-4).

The ΔS_E value (53 J K^{-1} mol^{-1}) for di-p-tolyl sulfide is relatively high and positive as is also the ΔS_E value (33 J K^{-1} mol^{-1}) for diphenyl sulfide. The relaxation time (6.8×10^{-12} s) for di-p-tolyl sulfide at 200 K is very short as it is also for other symmetric diaryl ethers and sulfides under similar experimental conditions. For example, diphenyl sulfide in polystyrene has a relaxation time of 1.6 x 10^{-11} s at 200 K.

The distribution parameter (β) for di-p-tolyl sulfide in polystyrene ranges from 0.27 - 0.67 in the temperature range of 92.5 - 106.4 K (Table VII-8). Other symmetric diaryl ethers and sulfides which exhibit dielectric absorption in similar temperature and frequency ranges as di-p-tolyl sulfide also have large β values (Table VII-4 and Table VII-8). For example, p,p'-dibromodiphenyl ether in polystyrene in the temperature range 88.4 - 99.8 K and $\log_{10}f_m$ range 7.35 - 8.20 has a β value range of 0.48 - 1.00.

The relatively large β values are suggestive of a major contribution to the observed relaxation by one process. In the case of di-p-tolyl sulfide and other symmetric diaryl ethers and sulfides the predominant observed relaxation process is coupled ring rotations.

The above experimental data seem to suggest that di-p-tolyl sulfide undergoes a very rapid intramolecular relaxation process such as double-internal rotation.

It was stated earlier that aliphatic ethers such as n-butyl ether exhibit a low-energy intramolecular relaxation process. As a result some aliphatic sulfides were studied to see if there is any similar behaviour. The two compounds studied were di-allyl sulfide and di-t-butyl sulfide in polystyrene matrices.

Di-allyl sulfide was studied from 107.6 K to 129.9 K in the $\log_{10}f_m$ range 1.35-4.55. Analysis of the set of absorption peaks gave ΔH_E as 15.9 kJ mol^{-1}. Courtauld models of this molecule show that the volume sweep out in molecular reorientation about the short and long molecular axes is about the same as that for dibenzothiophene. Since dibenzothiophene has a ΔH_E value of 38.5 kJ mol^{-1} it appears that di-allyl sulfide undergoes some intramolecular relaxation process. Although double-internal rotation might occur as suggested by the fact that the ΔH_E values for di-allyl sulfide and diphenyl sulfide are reasonably close, 15.9 and 13.6 kJ mol^{-1}, respectively, segmental rotation may also occur. In support of the later process are the ΔG_E values, which are 6.9 kJ mol^{-1} for diphenyl sulfide and 18.5 kJ mol^{-1} for di-allyl sulfide, both at 200 K. Another parameter which is in favour of segmental rotation is the τ value, for diallyl sulfide at 300 K it is 4.6×10^{-10} s, while for diphenyl sulfide it is 6.9×10^{-13} s at 300 K. Courtauld molels also show that there is steric hinderance for double-internal rotation, but segmental rotation around C-C bonds can occur.

Di-t-butyl sulfide is a nearly spherical molecule with two bulky tertiary butyl groups. This can be seen with the help of Courtauld models.

Whether molecular or segmental rotation or both occur is difficult to judge since the volume swept out during molecular rotation would be small as it would also be segmental rotation or even double-internal rotation. While the ΔH_E value is 3.8 kJ mol^{-1} which suggests internal rotation the ΔG_E value at 300 K is 31.7 kJ mol^{-1} as compared to ΔG_E = 31.9 for dibenzothiophene at 300 K. Also, the $\tau_{300\ K}$ = 5.4 x 10^{-8} s for di-t-butyl sulfide, while $\tau_{300\ K}$ = 5.8 x 10^{-8} s for dibenzothiophene.

Di-t-butyl sulfide has a ΔS_E value of -93 J K^{-1} mol^{-1}, which seems too big for intramolecular motion. A ΔS_E value was calculated from the equation $\Delta S_E = 2\Delta H - 60$, which was developed for molecular rotation of molecules in polystyrene matrices. The calculated ΔS_E value (-54 J K^{-1} mol^{-1}) is in not too unreasonable a correspondence with the observed ΔS_E value (-93 J K^{-1} mol^{-1}) since the error in ΔS_E may be great. The experimental data for di-t-butyl sulfide seems to favour a molecular relaxation process for the molecule.

Since certain diaryl ethers and sulfides undergo rapid intramolecular relaxation it seemed reasonable to investigate other diaryl systems, such as ketones. The simplest symmetric diaryl ketone is benzophenone. Originally it was thought by researchers that benzophenone is a rigid molecule which relaxes predominantly by molecular reorientation. Later studies[30], however, showed benzophenone to have a 6% contribution to internal rotation in liquid solution.

The observed relaxation time (20.4 ps) for benzophenone in a non-interacting solvent is of the correct order for molecular relaxation, but a non-zero distribution parameter (0.09 to 0.19) suggests, but does not establish there may be more than one relaxation process. The existence of a mesomeric moment could explain part of the non-zero distribution parameters. Because of the large fixed dipole moment (2.93 D) the mesomeric contribution should be small. The reason is that the weight of a relaxation process depends on the square of the associated dipole moment component. The dipole moment components for the intramolecular and molecular processes are μ_1 and μ_2, respectively. If μ_{max} is the maximum mesomeric moment and m_o the molecular dipole moment then,[10]

$$\mu_1 = 0.866\ \mu_{max} \qquad \text{VII-10}$$

$$\mu_2 = m_o - \tfrac{1}{2}\mu_{max} \qquad \text{VII-11}$$

putting $m_o = 3$ D and $\mu_{max} = 0.6$ D, then,

$\mu_1 = 0.52$ D and $\mu_2 = 2.7$ D

and $$\frac{C_1}{C_2} = \left(\frac{\mu_1}{\mu_2}\right)^2 = 0.04 \qquad \text{VII-12}$$

Consequently, even with a mesomeric moment of almost 0.6 D the overall molecular relaxation process should predominate.

Fong[16] considered that the conjugation in benzophenone makes the energy barrier to group rotation so high that it inhibits double-internal rotation. Since the mesomeric moment of benzophenone is not very different from that of acetophenone[31] then the resonance effects in both systems might be similar, so that benzophenone is not necessarily rigid. This was the case when benzophenone was studied in a polystyrene matrix.

A set of absorption peaks was observed from 138.5 - 163.5 K in the $\log_{10}f_m$ range 2.87 - 4.16. The $\Delta H_E = 21.4$ kJ mol^{-1} value is too low to be due to molecular relaxation. This can be proven by comparing the ΔH_E value with those of similarly shaped and sized molecules. Benzophenone is of similar size and shape to diphenyl sulfoxide and diphenyl sulfone. Yet the ΔH_E values ($\sim$60 kJ mol^{-1}) for both Ph_2 SO and Ph_2 SO_2 are appreciably different from that of benzophenone ($\Delta H_E = 21.4$ kJ mol^{-1}). Since Ph_2 SO and Ph_2 SO_2 are known to undergo predominantly molecular relaxation, it seems reasonable to conclude that the ΔH_E value for benzophenone is much too low to be accounted for by molecular rotation. It is more probable that it undergoes an intramolecular relaxation process such as double-internal rotation. If the rings are orthogonal then a ΔH_E value of 58.1 kJ mol^{-1} should be found as in o-hydroxybenzophenone, where one ring is held coplanar with the carbonyl group while the other ring is perpendicular to it. The ΔH_E value is too large to originate from H-bond breaking. For example, o-hydroxyacetophenone has a H-bond rupture enthalpy of about 30 kJ mol^{-1}.[32]

Benzophenone was also studied from 83 - 293 K in compressed solid form in the frequency range 200 to 100,000 Hz,but no set of loss peaks was found. In a polystyrene matrix, however, the β values of 0.09 to 0.19 indicate a wide range of relaxation processes for benzophenone. The negative ΔS_E value of -13.8 J K^{-1} mol^{-1}, and the ΔG_E value of 24.2 kJ mol^{-1} at 200 K as compared to 46.6 kJ mol^{-1} for o-hydroxybenzophenone at 200 K suggest an intramolecular relaxation process. The τ values are further evidence of a double-internal rotation motion for benzophenone. o-Hydroxybenzophenone has $\tau = 4.55 \times 10^{-9}$ s at 300 K.

Another symmetric ketone which was studied was di-2-pyridyl ketone in polystyrene. A set of loss peaks was observed from 168.1

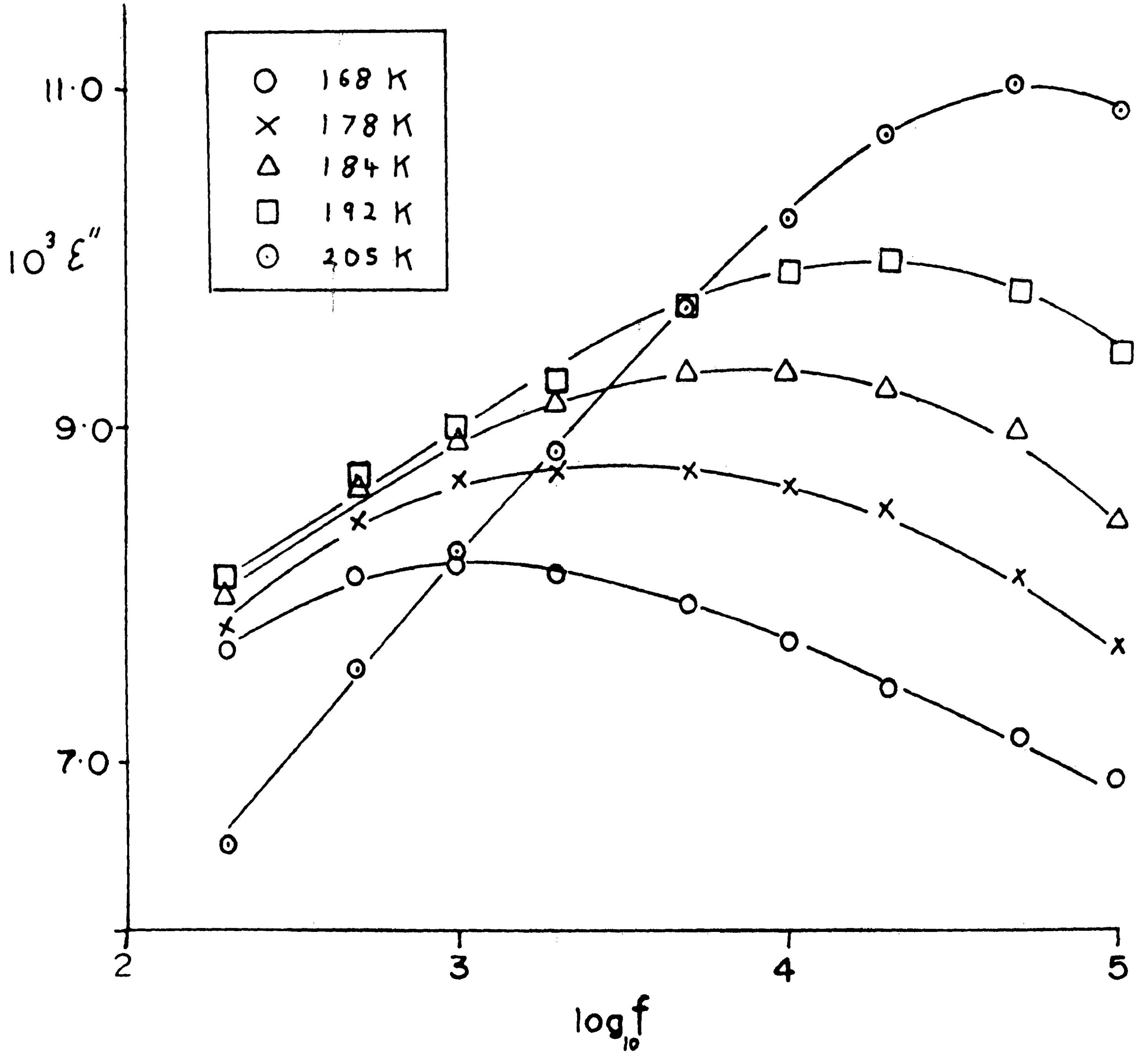


FIGURE VII-20: Dielectric Loss of 0.420M di-2-Pyridyl Ketone in Polystyrene from 10^2 - 10^5 Hz

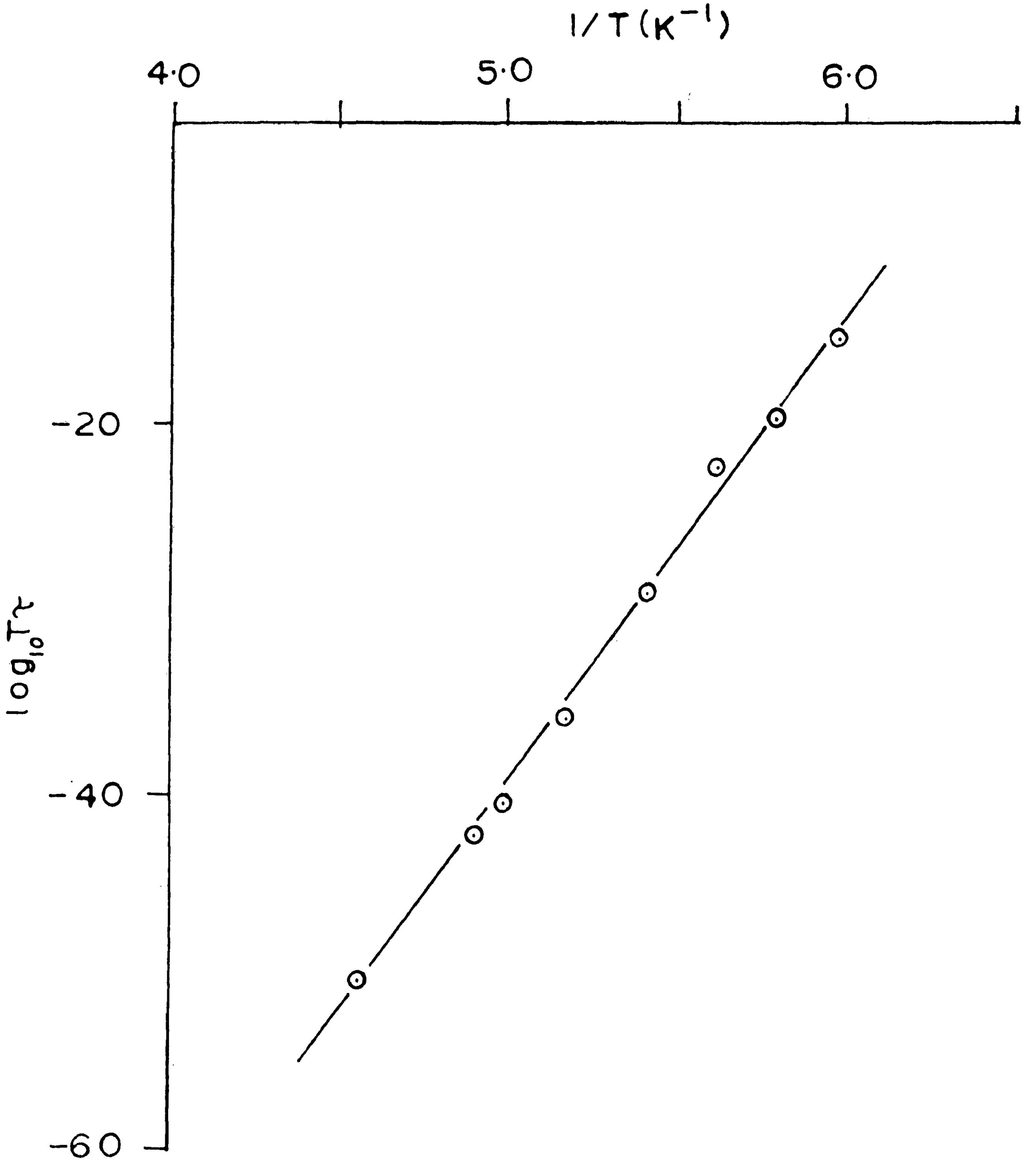


FIGURE VII-21: Eyring Plot for 0.420M di-2-Pyridyl Ketone in Polystyrene to 220.9 K in the frequency range 0.2 - 100 KHz (see Fig. VII-20). Di-2-pyridyl ketone as with benzophenone is similar in size to diphenyl sulfoxide and diphenyl sulfone. Since the ΔH_E value (27.5 kJ mol^{-1}) for di-2-pyridyl ketone is considerably less than that of diphenyl sulfoxide (60 kJ mol^{-1}) and diphenyl sulfone (62 kJ mol^{-1}) which are known to undergo overall molecular rotation, it follows that di-2-pyridyl ketone may undergo an intramolecular relaxation process such as double-internal rotation. This molecule should have greater steric hinderance than benzophenone because of the two nitrogen lone-electron pairs at the ortho positions of the two rings. As a result one would expect a larger energy for internal rotation over that for benzophenone. This is what is observed, ΔH_E being 27.5 kJ mol^{-1} as calculated from an Eyring plot of log $T\tau$ versus $\frac{1}{T}$ (Fig. VII-21). This ΔH_E is larger than that of benzophenone,as is also the ΔG_E value of 28.4 kJ mol^{-1} at 300 K, while that for benzophenone is 25.6 kJ mol^{-1}. The relaxation time is also longer, 1.4×10^{-8} s at 300 K as compared to 4.5×10^{-9} s at 300 K for benzophenone. Since both benzophenone and di-2-pyridyl ketone have net diple moments of 2.96 and 2.91 D (in benzene at 298 K)[41] there should be a significant contribution to the overall relaxation process from molecular rotation. This is substantiated in part by the low β values (< 0.3) in each case (see Table VII-8). Absorption peaks due to molecular rotation were not observed for the above molecules in a polystyrene matrix.

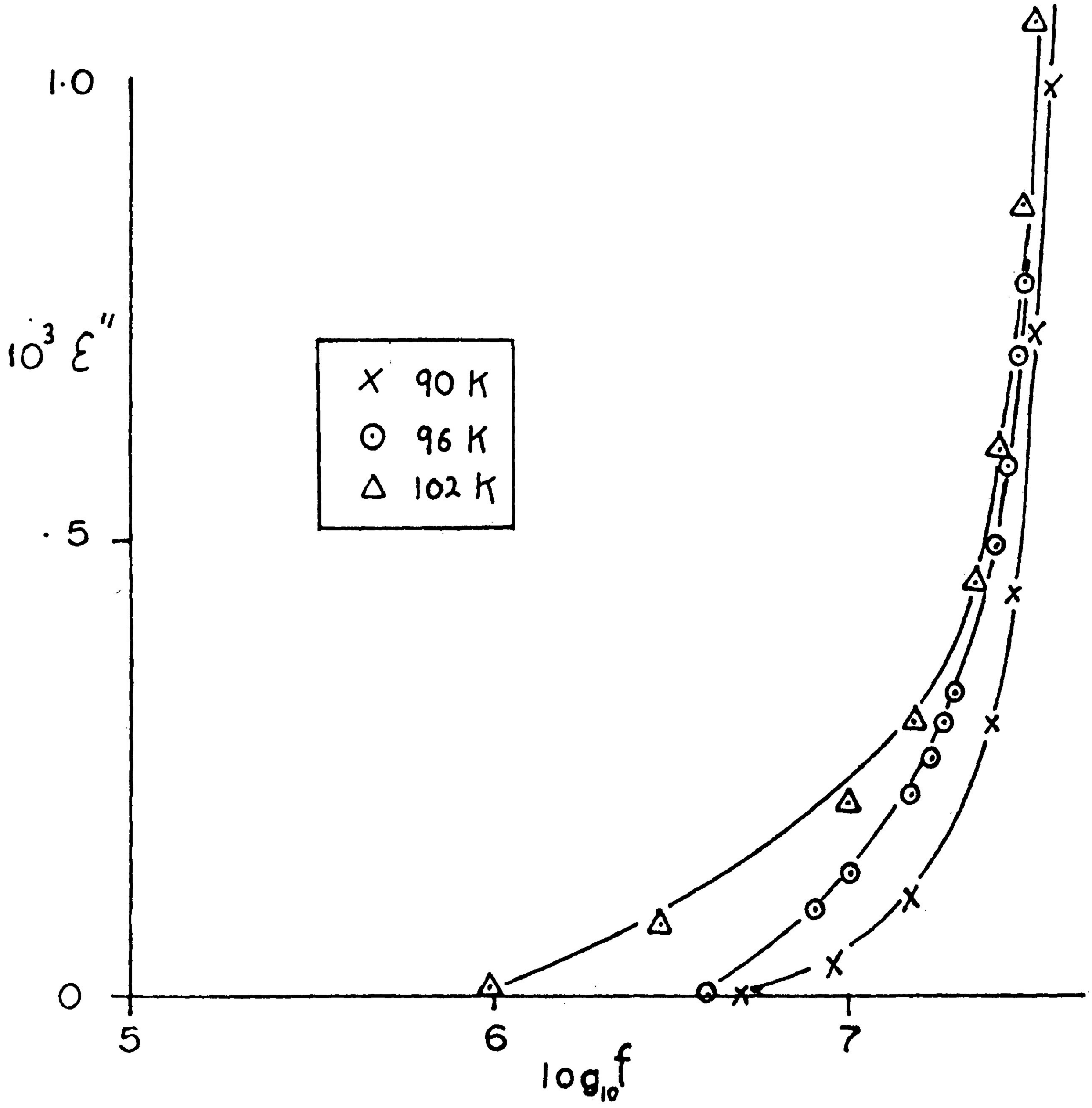


FIGURE VII-22: Dielectric Absorption of p,p'-Dibromodiphenyl Methane as a Compressed Solid in the Range 10^5 - 10^8 Hz

Another compound which was studied in a polystyrene matrix was p,p'-dimethoxythiobenzophenone. In this case a set of double-absorption peaks was observed above room temperature (276.4 - 307.4 K), in the frequency range 2 x 10^2 to 10^5 Hz. Since these peaks could not be resolved it was not possible to obtain a computer analysis for dielectric relaxation parameters. It is difficult to state whether the absorption peaks are due to coupled ring rotations, molecular rotation, co-operative motion with the polymer chains or methoxy group rotation. Since the absorption peaks were observed above room temperature it is unlikely that they could be due to methoxy group rotation. The reason is that in aromatic molecules with methoxy groups the energy barrier for the group rotation is relatively small, and Mazid *et al.*[42] have shown the ΔH_E to be $\sim$10 kJ mol^{-1} in aromatic -O-Me cases where no mutual conjugation is present.

Another molecule which was studied in a polystyrene matrix, as well as a compressed solid was p,p'-dibromodiphenyl methane. No absorption peaks were observed for a polystyrene matrix, but absorption curves were found in the frequency range greater than 20 MHz at 89.8, 95.5, and 101.5 K (Fig. VII-22). Since the absorption curves rise very steeply at the highest frequencies measured it was not possible to obtain a computer extrapolation. Since the loss curves occur at the high frequency end of the Q-meter it appears that this molecule behaves as do the ethers. As a result it could possibly also undergo double-internal rotation.

Diphenyl methane was studied by DiCarlo and Smyth[5] in pure liquid form and was found to have a short relaxation time of 3.9 x 10^{-12} s. Measurements were made at 1.25 and 3.22 cm but the low polarity of diphenyl methane made the experimental data too approximate for a detailed analysis. Smyth could not observe a process whose motion was primarily molecular rotation. He therefore postulated that the observed relaxation time was for a relaxation process whose main contribution was from double-internal rotation. Since the dielectric loss which Smyth observed was at high frequencies it is possible that the absorption could be the tail-end of a broad band absorption from the far-infrared region. This is possible since most molecules possess broad band absorption and experimental evidence was not clear as to the origin of the dielectric absorption noted by Di Carlo and Smyth. These researchers stated that a considerable amount of the relaxation occurs by molecular rotation because of the small fixed dipole moment, but a considerable portion must also occur by an intramolecular process. There are no unshared electron pairs on the central carbon atom so that charge cannot be shifted into the rings by mesomerism. Hyperconjugation can give a very small

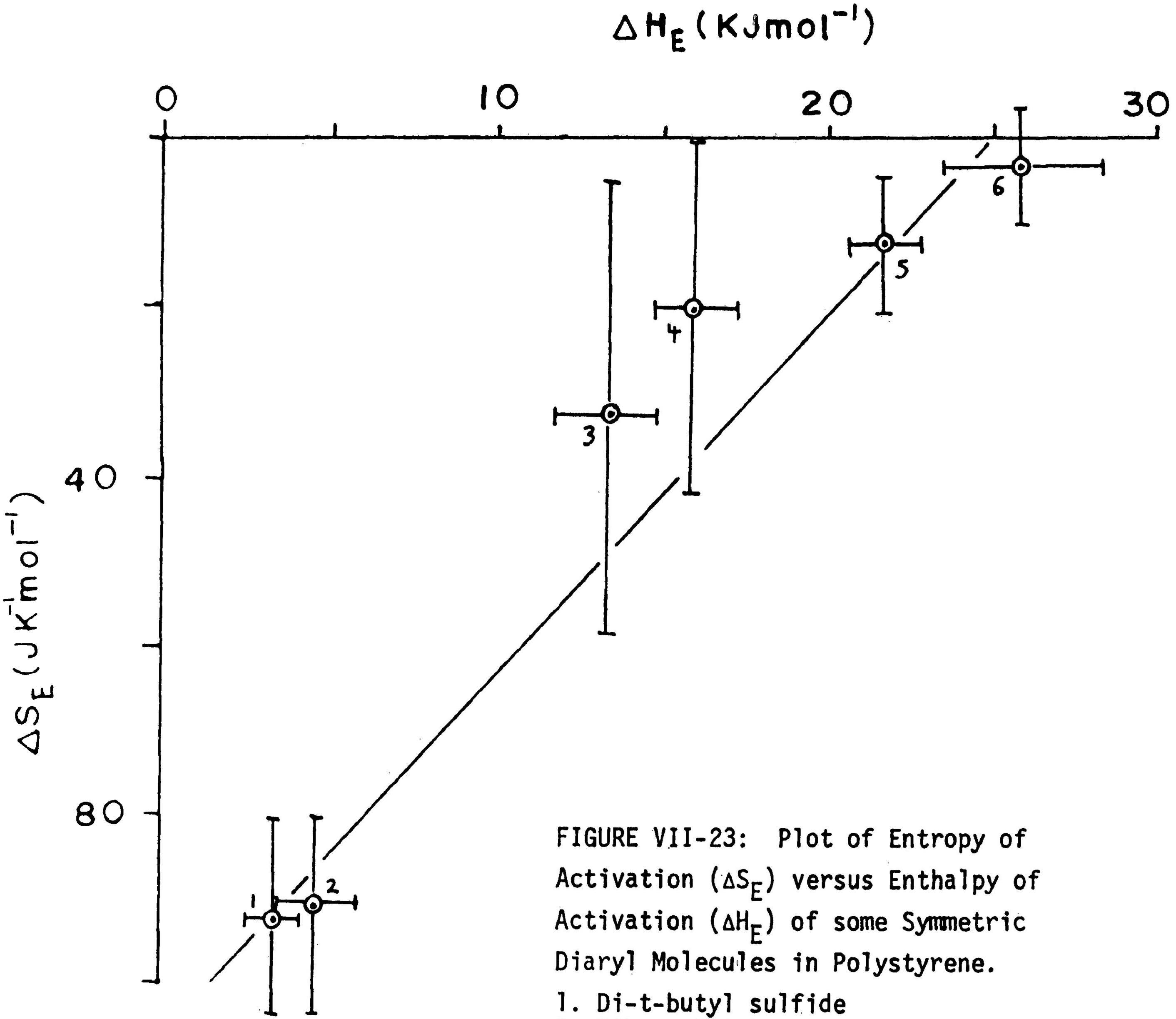


FIGURE VII-23: Plot of Entropy of Activation (ΔS_E) versus Enthalpy of Activation (ΔH_E) of some Symmetric Diaryl Molecules in Polystyrene.

1. Di-t-butyl sulfide
2. Dibenzyl Ether
3. Diphenyl Sulfide
4. Diallyl Sulfide
5. Benzophenone
6. Di-2-pyridyl Ketone

shift of electric charge into the rings. It would therefore be expected that p,p'-dibromodiphenyl methane would behave similarly to diphenyl methane.

A number of workers such as Davies and Swain[40], and Tay and Walker[43] have observed a linear correlation between the entropy of activation, ΔS_E, and the enthalpy of activation, ΔH_E, for a series of molecules molecularly dispersed in polystyrene. For a more detailed discussion of this behaviour see Chapter VI.

A plot, Fig. VII-23, was made of ΔS_E versus ΔH_E for a series of symmetric diaryl molecules which appear to undergo double-internal rotation and whose ΔH_E and ΔS_E values were available. From the slope and intercept of the line an equation (Eqn. VII -13) was derived relating ΔS_E to ΔH_E .

$$\Delta S_E = 4.1\ \Delta H_E - 110 \qquad \text{VII-13}$$

The entropy of activation values calculated from Eqn. VII-13 are compared to the experimentally observed entropies of activation in Table VII-9.

TABLE VII-9: Comparison of Calculated and Observed Entropies of Activation for some Molecules showing Rapid Internal Rotation

Molecule	ΔH_E (kJ mol^{-1})	$\Delta S_{E(calc)}$ Eqn. VII-13 (J K^{-1} mol^{-1})	$\Delta S_{E(obs)}$ (J K^{-1} mol^{-1})
Diphenyl sulfide	13.6 ±1.9	-52	-33 ±20
Di-p-tolyl sulfide	16.1 ±2.6	-44	-53 ±26
Diallyl sulfide	15.9 ±4.3	-45	-14 ±36
Di-t-butyl sulfide	3.8 ±1	-94	-93 ±11
Dibenzyl ether	5.9 ±1.3	-86	-93 ±10
Benzophenone	21.4 ±0.8	-22	-14 ± 5
Di-2-pyridyl ketone	27.5 ±1.9	- 3	- 3 ±10.3

CONCLUSION

From the discussion section of this chapter it was evident that diphenyl ether is not the sole molecule which exhibits a rapid relaxation process arising from an internal rotation mechanism. It was shown that other substituted symmetric ethers, sulfides, and ketones also behave similarly to diphenyl ether. It appears from the research that the largest contribution to the observed relaxation process is from the simultaneous coupled ring rotations, termed double-internal rotation. The exact mechanism and its nature have been the subject of controversy. Some workers have favoured a mesomeric effect and others a coupled mechanical motion of both aromatic rings which conserves angular momentum, or a combination of both where the weight of the process varies in different molecules according to the relative weight of the mesomeric moment and the molecular dipole moment.

One piece of evidence in favour of the mesomeric mechanism is that all the anomalously low relaxation times were for symmetric molecules which possess two aromatic rings with or without substituents at both the para positions. In these symmetric molecules when the magnitude of the molecular dipole moment and that of the mesomeric moment are nearly equal then a significant contribution from the mesomeric effect can take place. Usually this occurs in symmetric diphenyl ether type molecule which have a net dipole moment less than about 1.5 D. However, some asymmetric diaryl ethers such as 4-biphenylyl phenyl ether and o-methylphenyl phenyl ether also appear to undergo an anomalously rapid intramolecular relaxation process (τ_o = 9.4 and 6.6 ps respectively). In these two cases the relaxation process may well be phenoxy group rotation. In these cases the dipole moment (μ = 1.10 D for 4-biphenylyl phenyl ether in benzene at 298 K and μ = 1.57 D for o-methylphenyl phenyl ether in benzene at 298 K)[41] is on or very near the Y molecular axis, and its magnitude is close to that of diphenyl ether (μ = 1.23 D in benzene at 298 K)[41].

When the molecular dipole moment is significantly larger than the mesomeric moment in diphenyl ether type molecules then the major contribution to the observed relaxation process is probably not from the mesomeric mechanism. When there is no mesomeric moment as in dialkyl ethers and sulfides then rapid internal relaxation can take place by two possible processes.

One is segmental rotation about the C-C single bonds and the other may possibly be by a mechanical double-internal rotation. Whether double-internal rotation gives any contribution to the dielectric relaxation of dialkyl ethers and sulfides has not been clearly established. The two aliphatic sulfides (di-allyl and di-t-butyl sulfide) did not give any clear evidence of whether the predominant relaxation process was segmental or double-internal rotation.

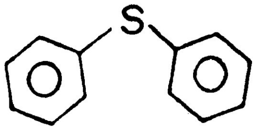
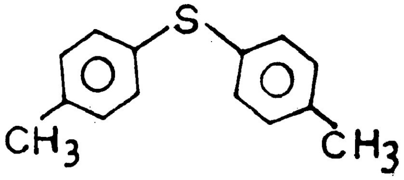
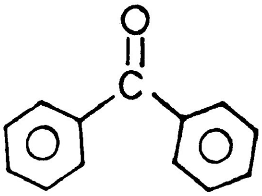
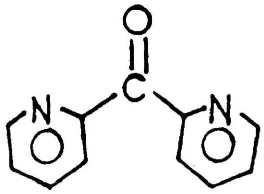
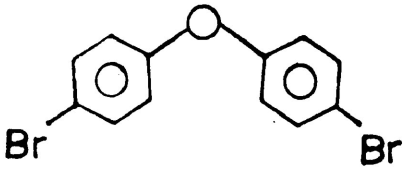
Since most low carbon number symmetric aliphatic ethers and sulfides are highly volatile it is difficult to trap them in polystyrene matrix. Other higher carbon number symmetric aliphatic ethers and sulfides are not commercially available.

Further evidence of a mesomeric effect is that as the dipole moment is decreased below that (1.23 D) for diphenyl ether the relaxation time decreases, as does also the ΔG_E value. This is seen for p,p'-dibromodiphenyl ether where $\tau = 1.8 \times 10^{-9}$ s and $\Delta G_E = 6.0$ kJ mol^{-1} at 89.3 K, while for diphenyl ether $\tau = 6.6 \times 10^{-9}$ s and $\Delta G_E = 6.8$ kJ mol^{-1} at 87.1 K. The dipole moment of p,p'-dibromodiphenyl ether is 0.60 D. Since bromine has the ability to withdraw charge the p-substituted bromo ether will have a larger mesomeric moment leading to more rapid ring rotations.

For p,p'-Diaminodiphenyl **ether** as a compressed solid at 88.9 K the τ value is 3.75×10^{-9} s,which is longer than that of p,p'-dibromodiphenyl ether (9.9×10^{-10} s) at neraly the same temperatures (88.4 K) as is also the ΔG_E value of 6.5 kJ mol^{-1}, as compared to a ΔG_E value of 5.5 kJ mol^{-1} for p,p'-dibromodiphenyl ether. The electronic factors in these cases seem to override the effect of group sizes in determining energy barriers for double-internal rotation. This appears to be the case since a bromine atom is larger (covalent radius - 1.14 Å) than an amino group (covalent radius = 0.70 Å).

The importance of steric effects on double-internal rotation becomes obvious when diphenyl ether, diphenyl sulfide and benzophenone are compared. Since diphenyl ether has a valency angle of 120°

TABLE VII-10: Activation Parameters for some Symmetric Diaryl Molecules in Polystyrene

	ΔT (K)	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})	ΔG_E (kJ mol^{-1}) 150 K
	89-103	14	33	9
	93-106	16	53	8
	139-164	21	-14	24
	168-221	28	- 3	28
	205-233	63	129	44

whereas diphenyl sulfide has one of 109° it is obvious that there will be more steric hinderance in diphenyl sulfide, particulary between the ortho hydrogens of the two rings. Thus diphenyl sulfide has a larger energy barrier (13.6 kJ mol^{-1}) than diphenyl ether for double-internal rotation. Because of diphenyl sulfide's higher dipole moment (1.55 D) as compared to 1.25 D for diphenyl ether it may have a larger contribution from the molecular relaxation process. As a compressed solid diphenyl ether has a β value of 0.80 at 87.1 K which indicates one predominant process, such as double-internal rotation. Benzophenone, however, has β values of 0.09 to 0.19, thereby indicating a wider distribution of relaxation processes with a contribution from molecular reorientation, as reflected in the large dipole moment of 2.96 D.

In benzophenone there is more conjugation between the carbonyl groups and the aromatic rings, consequently, there is a greater electron density in the (OC)-C_{aryl} bond, thereby leading to a larger ΔH_E value of 21.4 kJ mol^{-1} for double-internal rotation.

The data given in this chapter provide evidence that a very fast intramolecular relaxation process occurs in some symmetric diaryl molecules such as ethers, sulfides, and ketones. The energy barrier is determined by steric, geometric, and electronic factors. This is evident from Table VII-10, where ΔT, ΔH_E, ΔS_E, and $\Delta G_{E(150\ K)}$

values are compared for some molecules which exhibit double-internal rotation in a polystyrene matrix. p,p'-Dibromodiphenyl ether which exhibits overall molecular rotation is also listed for comparison purposes. It is evident from Table VII-10 that the increased conjugation in going from the sulfides to the ketones is reflected in the larger ΔH_E and ΔG_E values. The two mechanisms which appear to explain the anomalous behaviour observed in diaryl molecules are mesomerism and a mechanical double-internal rotation. It appears from the results of the research that the intramolecular relaxation process is dependent on both mechanisms. The contribution which each mechanism makes to the observed relaxation process depends on the square of the dipole moment components associated with each mechanism.

Further research on polystyrene matrices and compressed crystalline discs is needed in order to provide an even clearer picture of the behaviour of symmetric diaryl molecules.

TABLE VII-11: Fuoss-Kirkwood Analysis Parameters of Several Symmetric Non-rigid Diaryl Molecules in Polystyrene Matrices at a Variety of Temperatures

T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	μ(D)	ε_∞
0.42M Benzophenone in Polystyrene						
138.5	215.2	2.87	0.19	3.57	0.59	2.14
142.9	116.3	3.14	0.16	4.04	0.68	2.22
146.6	56.1	3.32	0.18	4.31	0.66	2.27
149.9	50.9	3.49	0.18	4.35	0.68	2.25
153.2	44.6	3.67	0.09	4.60	0.98	2.26
155.7	26.6	3.78	0.19	4.73	0.70	2.29
160.0	14.2	4.05	0.17	5.06	0.76	2.30
163.6	10.9	4.16	0.17	5.21	0.79	2.31
0.51M p,p'-Dibromodiphenyl Ether in Polystyrene						
204.6	541.0	2.47	0.62	1.98	0.27	2.18
215.9	503.7	3.50	0.28	3.03	0.51	2.17
223.1	204.4	3.89	0.29	5.06	0.66	2.11
226.5	117.7	4.13	0.29	4.01	0.59	2.11
232.6	5.5	4.46	0.27	4.82	0.68	2.10
0.56M Dibenzyl Ether in Polystyrene						
107.5	23.9	3.82	0.34	2.09	0.27	1.98
121.5	11.2	4.15	0.40	2.43	0.28	2.00
132.1	5.3	4.48	0.27	2.38	0.36	2.02
139.4	3.2	4.70	0.29	2.35	0.34	2.03
147.4	2.6	4.79	0.35	2.27	0.32	2.05
151.0	-	-	-	-	-	2.07
158.8	2.3	4.84	0.40	1.96	0.28	2.09
0.85M Diphenyl Sulfide in Polystyrene						
89.0	1.0	5.21	0.28	1.59	0.18	2.27
91.6	0.7	5.38	0.28	1.59	0.23	2.27
94.1	0.3	5.67	0.26	1.64	0.19	2.27
96.7	0.2	5.92	0.23	1.68	0.21	2.27
98.9	0.1	6.03	0.26	1.85	0.21	2.27

TABLE VII-11: continued...

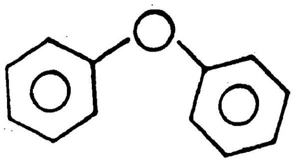
T(K)	$10^6\tau(s)$	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	μ(D)	ε_∞
0.42M Di-2-pyridyl Ketone in Polystyrene						
168.1	174.7	2.96	0.13	8.2	1.12	2.32
172.7	88.0	3.26	0.14	8.5	1.13	2.32
177.7	46.5	3.53	0.16	8.8	1.09	2.33
183.5	21.3	3.87	0.17	9.5	1.09	2.39
191.8	9.6	4.22	0.18	10.0	1.12	2.39
200.2	4.8	4.52	0.19	10.7	1.14	2.40
204.5	3.5	4.65	0.21	11.1	1.15	2.41
213.1	2.6	4.78	0.23	11.2	1.11	2.42
220.9	1.2	5.11	0.23	11.6	1.16	2.42
0.52M Diallyl Sulfide in Polystyrene						
107.6	70.3	1.35	0.10	2.93	0.65	1.60
111.7	61.8	3.41	0.23	2.92	0.45	1.61
116.1	24.9	3.80	0.27	2.84	0.42	1.56
120.7	10.5	4.18	0.29	3.03	0.43	1.56
126.0	8.6	4.27	0.38	3.34	-	-
129.2	4.4	4.56	0.40	3.25	0.39	1.56
0.66M Di-tertiary Butyl Sulfide in Polystyrene						
80.0	10.1	4.20	0.34	2.09	0.27	1.98
81.8	11.1	4.15	0.40	2.43	0.28	2.00
82.7	11.8	4.13	0.27	2.38	0.36	2.02
86.0	8.9	4.25	0.29	2.35	0.34	2.03
89.8	5.5	4.46	0.35	2.27	0.32	2.05
93.8	5.5	4.46	-	-	-	-
100.0	3.4	4.67	0.40	1.96	0.28	2.09
0.362M Di-p-tolyl Sulfide in Polystyrene						
92.5	2.34	4.83	0.58	0.81	0.15	2.06
97.5	0.30	5.78	0.47	1.07	0.19	2.06
99.4	0.40	5.58	0.61	1.00	0.16	2.06
101.2	0.20	5.92	0.47	1.14	0.20	2.06
103.1	0.03	6.78	0.63	0.28	0.15	2.06
106.4	0.01	7.80	0.27	0.88	0.24	2.06

TABLE VII-11: continued...

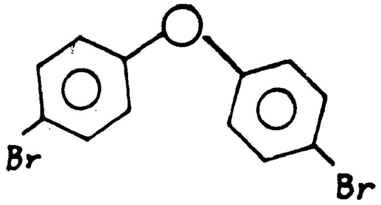
T(K)	$10^6\tau$(s)	$\log f_{max}$	β	$10^3\varepsilon''_{max}$	μ(D)	ε_∞
		0.646M Diphenyl Ether in Polystyrene				
212.9	168.4	2.98	0.41	1.10	0.23	2.05
219.8	48.7	3.51	0.56	1.21	0.21	2.05
224.4	19.5	3.91	0.55	1.23	0.22	2.05
229.8	7.6	4.32	0.51	1.28	0.23	2.06
233.6	25.2	3.80	0.57	1.04	0.18	2.06
235.3	2.8	4.76	0.52	1.50	0.25	2.06
238.7	13.2	4.08	0.55	1.05	0.20	2.06

TABLE VII-12: Structure of some Symmetric Diaryl Molecules

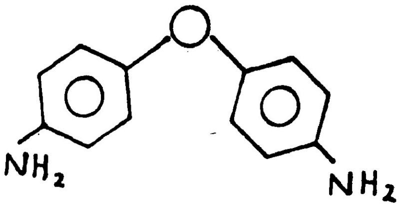
Diphenyl ether



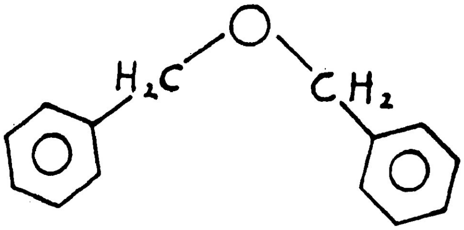
p,p'-Dibromodiphenyl ether



p,p'-Diaminodiphenyl ether



Dibenzyl ether



Diphenyl sulfide

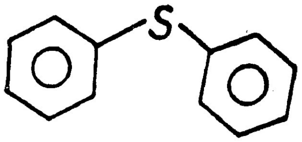


TABLE VII-12 continued...

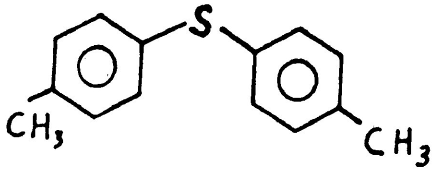
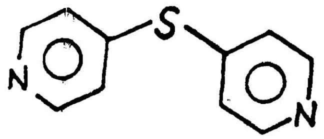
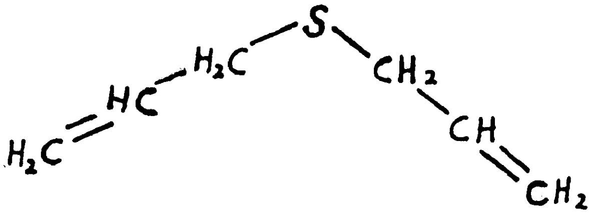
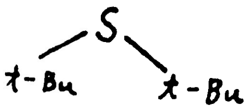
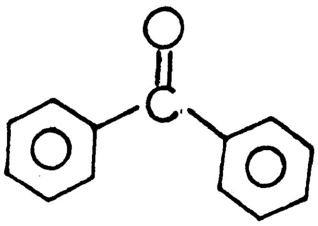
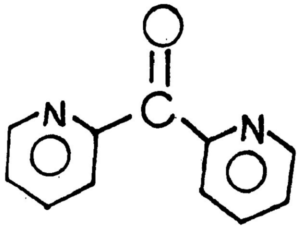
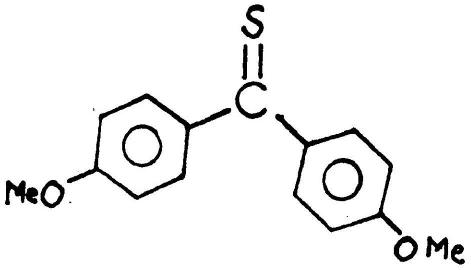
Di-p-tolyl sulfide	
Di-4-pyridyl sulfide	
Diallyl sulfide	
Di-t-butyl sulfide	 t-Bu = tertiary butyl
Benzophenone	

TABLE VII-12 continued....

Di-2-pyridyl ketone	
p,p'-Dimethoxythiobenzophenone	

REFERENCES

1. E. Fischer, Z. Electrochem., 53, 16 (1949).

2. W. Jackson and J. G. Powles, Trans. Faraday Soc., 42A, 101 (1946).

3. J. Schneider, J. Chem. Phys., 32, 665 (1960).

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

5. E. N. Di Carlo and C. P. Smyth, J. Am. Chem. Soc., 84, 3638 (1962).

6. W. Maier, Arch. sci. (Geneva), 12, 20 (1959).

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

8. C. P. Smyth and W. S. Walls, J. Am. Chem. Soc., 54, 3230 (1932).

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

10. K. Higasi, Dielectric Relaxation and Molecular Structure, (Research Institute of Applied Electricity, Hokkaido University, Japan, 1961).

11. Ibid., p. 106.

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

13. K. Higasi, Dielectric Relaxation and Molecular Structure, (Research Institute of Applied Electricity, Hokkaido University, Japan, 1961), p. 86.

14. H. Shisnizu, S. Fujiwara and Y. Morino, J. Chem., Phys. (1962).

References continued...

15. F. Dieringer, Z. Physik, 145, 184 (1956).

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

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

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

19. D. B. Farmer and S. Walker, Trans. Faraday Soc., 63, 966 (1967).

20. S. Dasgupta, K. N. Abd El Nour and C. P. Smyth, J. Chem. Phys., 50, 4810 (1969).

21. G. P. Johari, J. Crossley, and C. P. Smyth, J. Am. Chem. Soc., 91, 5197 (1969).

22. G. B. Rathman, A. J. Curtis, P. Z. McGeer and C. P. Smyth, J. Chem. Phys., 25, 413 (1956).

23. K. K. Srivastava, J. Phys. Chem., 74, 152 (1970).

24. M. Davies and A. Edwards, Trans. Faraday Soc., 63, 2163 (1967).

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

26. Interatomic distances, 1958, The Chem. Soc., London.

27. E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods", Academic Press, Inc., N. Y. (1955).

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

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

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

References continued....

31. L. E. Sutton, Proc. Roy. Soc., A, 133, 668 (1931).

32. M. A. Mazid, Private Communication, this laboratory.

33. P. Debye, Trans. Faraday Soc., 30, 679 (1934).

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

35. M. Horak, N. Josefi, Collect. Czeck. Chem. Comm., 39(11), 3209 (1974).

36. S. Trovato, E. Zuccarello, G. Favina, Gazz. Chim. Ital., 103(6-7), 709 (1973).

37. V. Galosso *et al.*, Tet., 27(24), 6151 (1971).

38. G. Garrigou-Lagrangle, M. Hurak, R. K. Khonna, E. K. Lippincott, Cobet. Czeck. Chem. Comm., 35(11), 3231 (1970).

39. T. B. Grindley, A. R. Katritzky, R. D. Tompson, J. Chem. Soc. Perkin II, 3, 1202 (1973).

40. M. Davies and J. Swain, Trans. Faraday Soc., 67, 1637 (1971).

41. A. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman and Co., San Francisco and London (1963).

42. M. A. Mazid, J. P. Shukla, and J. Warren, (In Press).

43. S. P. Tay and S. Walker, J. Chem. Phys., 63, 1634 (1975).