

SOME STUDIES OF DIELECTRIC RELAXATION

A THESIS SUBMITTED BY:

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## SUMMARY:

A general correlation function is firstly reviewed in line with Kubo's formulation (Chap. 1, (a)), and dielectric relaxation processes together with some fundamental properties are considered with the help of the function (Chap. 1, (b)). The introduction of Hoffmann's site model enables us to calculate a dielectric correlation function. This technique is applied to the dielectric relaxation of some molecules, (Chap. 1 (c)).

Discussion with respect to the calculation of the molecular dipole moment for a molecule which contains two equivalent rotational groups is made (Chap. 2, (a)). The results are applied to two convenient models, i.e., a free rotation model and a model called "free oscillation" which is proposed in this thesis. The latter model is employed for the cases of o-haloanisole and o-halothioanisole, (Chap. 2, (b) and (c)).

Experimental dielectric constant and loss data were analyzed by the Cole-Cole equation as well as Budó's equation (Chap. 3).

Rotation of the methoxy group in dimethoxy compounds was examined by relaxation time and dipole moment. The mean relaxation time for o-dimethoxybenzene is found to be short. (Chap. 4).

The variation of the relaxation time of the methoxy group of anisole is considered theoretically (Chap. 4, (c)).

Mesomeric and double internal rotation mechanisms concerning the anomalously short relaxation time of diphenyl ether are discussed. Correlation function treatments are made based on

the former mechanism. ( Chap. 5).

Rotation around S-S bonds is concluded to be restrictive. (Chap. 6). Relaxation time and dipole moment values of difuryl mercury are explained in terms of the non-linearity of C-Hg-C bond. (Chap. 7).

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(a) *CORRELATION FUNCTION*

Dielectric relaxation can be treated as a problem of time-dependent statistical mechanics. A traditional approach to treat this problem is the Boltzmann's transport equation or Kinetic equation<sup>1</sup>, i.e.:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} \quad (1-1)$$

where  $f$  is the distribution function,  $\mathbf{v}$  the velocity vector,  $\nabla_{\mathbf{r}}$  the position gradient,  $\nabla_{\mathbf{v}}$  the velocity gradient,  $\mathbf{F}$  an external force,  $m$  the mass, and  $\left( \frac{\partial f}{\partial t} \right)_{\text{coll}}$  is the so-called "collision term". The other is a rather elegant correlation function treatment, which was initiated by R. Kubo<sup>2</sup>. In this section we shall review the theory briefly on the basis of purely statistical standpoint.

Let us consider an isolated system, the Hamiltonian of which is represented by  $H$ . If an external field  $F(t)$  is applied to the system, the perturbation energy  $H'$  is

$$H'(t) = -AF(t) \quad (1-2)$$

where  $A$  is a generalized dipole moment operator. Introducing the Poisson bracket, we can express the Liouville equation for "the natural motion" as



$$\begin{aligned} \frac{\partial f(p,q)}{\partial t} &= \left( \frac{\partial f}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial f}{\partial p} \frac{\partial H}{\partial q} \right) \\ &= (H, f) \end{aligned} \quad (1-3)$$

where  $f$  is the distribution function in the phase space, and  $(H, f)$  is the Poisson bracket which is in general

$$(X, Y) = \sum \left( \frac{\partial X}{\partial q} \frac{\partial Y}{\partial p} - \frac{\partial X}{\partial p} \frac{\partial Y}{\partial q} \right) \quad (1-4)$$

We assume that the distribution function is given by  $f^\circ$  at  $t = -\infty$ , that is, at the infinite past and it is in equilibrium, i.e.,  $(H, f^\circ) = 0$ . Since we have confined ourselves to the linear perturbation, the distribution function at time  $t$  may be expressed as

$$f = f^\circ + \Delta f$$

therefore

$$\frac{\partial \Delta f}{\partial t} = (H, \Delta f) - F(t) (A, f^\circ) \quad (1-5)$$

Now we must solve the differential equation above to get  $\Delta f(t)$ . Let us define a linear self-adjoint operator  $L$  as<sup>3</sup>

$$iLg = (H, g) = \frac{\partial g}{\partial t}$$

Here it should be remembered that  $\exp(itL)$  represents the unperturbed or natural motion of the system, and it induces the natural motion of a phase point  $P$  to  $P_t$  over the time  $t$ , i.e.,

$$e^{-itL}P = P_t$$

correspondingly the natural motion of any dynamical quantity

$(p, q) = Q(p)$  is given by

$$Q(t) \equiv Q(P_t) = e^{-itL}Q(P_{t-\tau})$$

which is the solution of the equation of motion

$$\frac{dQ}{dt} = (Q, H) \quad (1-6)$$

Using the conditions  $F(-\infty) = 0$  and  $\Delta f(-\infty) = 0$ ,

we have the solution of Eq. (1-5):

$$f(t) = - \int_{-\infty}^t e^{i(t-t')} L(A, f^0) dt' F(t') \quad (1-7)$$

where  $t'$  is a time parameter;  $-\infty \leq t' \leq t$ .

Once we know  $\Delta f(t)$ , we can obtain ensemble average of an arbitrary quantity  $B(t)$  from

$$\begin{aligned} \langle AB(t) \rangle &= \int B(t) \Delta f(t) d\Gamma \\ &= - \int_{-\infty}^t dt' \int d\Gamma B e^{i(t-t')} L(A, f^0) F(t') \\ &= \int_{-\infty}^t dt' F(t') (A, f^0) B(t-t') d\Gamma \end{aligned} \quad (1-8)$$

It should be noted that  $B(p, q)$  satisfies Eq (1-6). Now we define a new function called "response function"  $\phi_{BA}(t)$  as

$$\begin{aligned} \phi_{BA}(t) &= \int (f^0, A) B(t) d\Gamma \\ &= \int f^0(A, B(t)) d\Gamma \\ &= \langle (A(0), B(t)) \rangle \end{aligned} \quad (1-9)$$

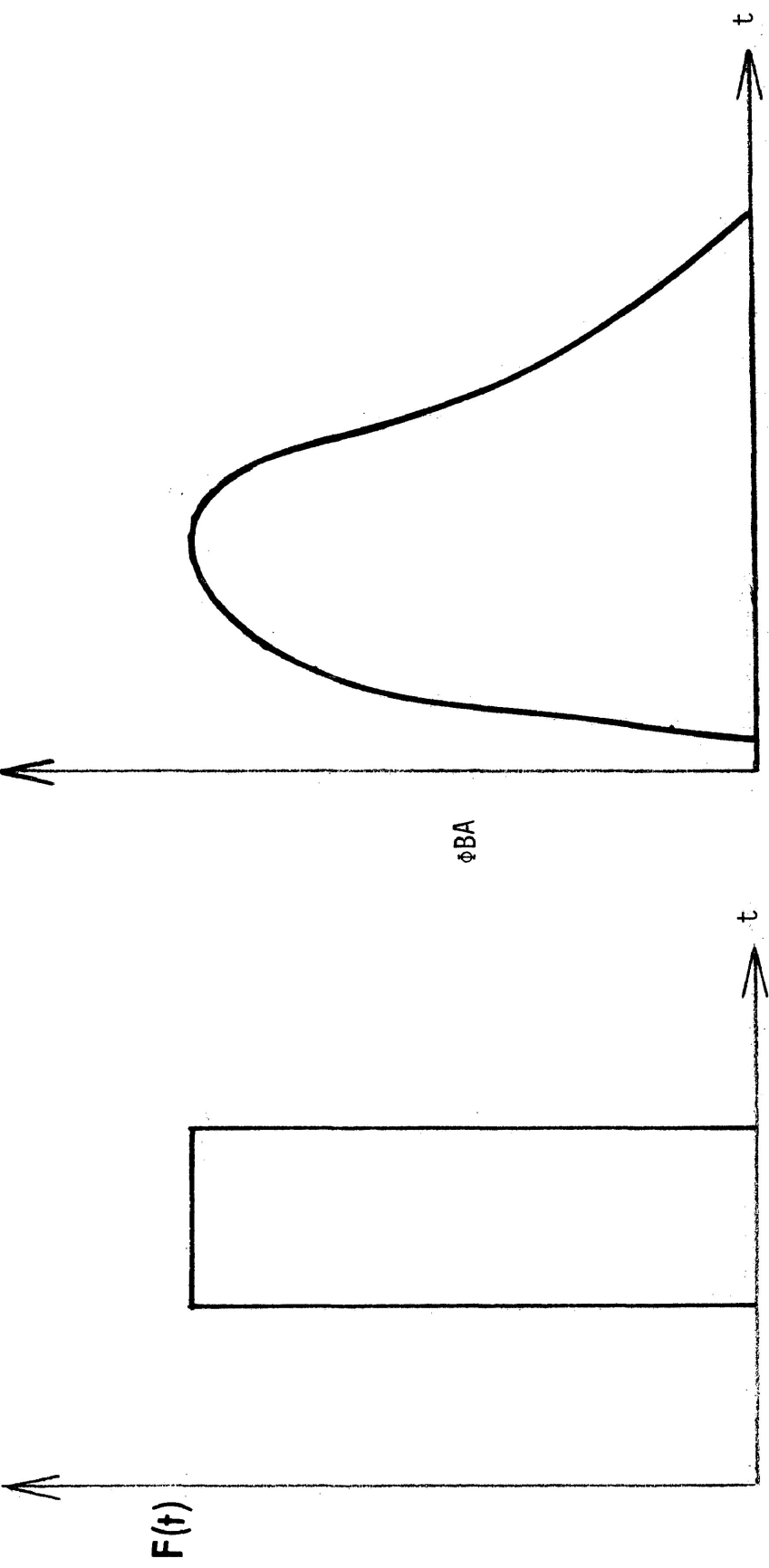


Figure 1-1: External field  $F(t)$  and its correlation function  $\phi_{BA}$

therefore

$$\langle \Delta B(t) \rangle = \int_{-\infty}^t \phi_{BA}(t-t') PF(t') dt' \quad (1-10)$$

when  $f^\circ$  is canonical, i.e.,

$$f^\circ = Ce^{-\beta H}, \quad \beta = \frac{1}{kT}$$

then

$$(f^\circ, A) = \beta \dot{A} f^\circ$$

so that

$$\phi_{BA}(t) = \beta \langle \dot{A}(0) B(t) \rangle = -\beta \langle A(0) \dot{B}(t) \rangle \quad (1-11)$$

Now let us define the general correlation function  $\phi_{BA}$  as

$$\phi_{BA} = \frac{\langle A(0) B(t) \rangle}{\langle A(0) B(0) \rangle} \quad (1-12)$$

therefore  $\dot{\phi}_{BA} \langle A(0) B(0) \rangle = \frac{\dot{\phi}_{BA}}{\beta}$

Eq. (1-9) can be interpreted as follows  $-(A, f^\circ)$  is the change of the distribution function produced by a pulse. The effect of this on the average value of B at a later time is given by the first equation of (1-9). Instead of talking about the change of distribution function, we may also think of the effect of the pulse on the motion of B. In the second equation of (1-9),  $(A, B(t))$  represents such an effect.

(b) DIELECTRIC CORRELATION FUNCTION

General correlation function in the previous section is directly related to the dielectric correlation function formally by replacing B and A by  $\langle \tilde{M}(t) \cdot \tilde{e} \rangle$  (the average number of the macroscopic dipole moments  $\tilde{M}$  along a direction of an applied electric field  $F(t)$ , whose unit vector is denoted by  $\tilde{e}$ ) and the microscopic dipole moment  $\tilde{\mu}$ , respectively. At first, let us define the dielectric correlation function  $\phi$  as

$$\phi(t) = \frac{\langle \tilde{\mu}(0) \cdot \tilde{M}(t) \rangle}{\langle \tilde{\mu}(0) \cdot \tilde{M}(0) \rangle} \quad (1-13)$$

This corresponds to the definition of Eq. (1-12). From Eqs. (1-10), (1-11), (1-12), and (1-13), adding the contribution from the polarizability term to the total polarization  $\langle \tilde{M}(t) \cdot \tilde{e} \rangle$ , we have

$$\langle \tilde{M}(t) \cdot \tilde{e} \rangle = N\alpha F(t) - \frac{N \langle \tilde{\mu}(0) \cdot \tilde{M}(0) \rangle}{3kT} \int_{-\infty}^t \phi(t-t') F(t') dt' \quad (1-14)$$

where the factor 1/3 in the second term on the right hand have been introduced taking into account the above problem three-dimensionally.

The second term in Eq. (1-14) may be regarded as the effect of reorientation of dipoles on the total polarization.

From the definition of polarization,  $\langle \underline{M} \cdot \underline{e} \rangle$  has a relation;

$$\frac{\epsilon^* - 1}{4\pi} V = \frac{\langle \underline{M} \cdot \underline{e} \rangle}{F_0 \exp(i\omega t)} \quad (1-15)$$

where  $\epsilon^*$  is the complex dielectric constant,  $V$  the volume of the system,  $\omega$  the frequency of the applied field,  $F_0$  the amplitude of the field  $F(t)$ , and  $i = \sqrt{-1}$ . Neglecting the internal field factor, we have;

$$\begin{aligned} \frac{\epsilon^* - 1}{4\pi} V &= N\alpha - \frac{N \langle \underline{\mu}(0) \cdot \underline{M}(0) \rangle}{3kT} \int_{-\infty}^t \dot{\phi}(t-t') dt' e^{-i\omega t'} \\ &= N\alpha + \frac{N \langle \underline{\mu}(0) \cdot \underline{M}(0) \rangle}{3kT} L(-\dot{\phi}(t)) \end{aligned} \quad (1-16)$$

where  $L$  represents the Laplace transform, whose definition is

$$\int_0^{\infty} f(t) e^{-i\omega t} dt = L(f(t))$$

Now it is assumed that the first term on the right hand in Eq(1-16) remains unaffected even if the frequency  $\omega$  goes to infinity, therefore

$$\frac{\epsilon_{\infty} - 1}{4\pi} V = N\alpha \quad (1-17)$$

On the other hand, when  $\omega$  goes to zero, it is assumed that

$$\frac{\epsilon_0 - 1}{4\pi} V = N\alpha + \frac{N \langle \underline{\mu}(0) \cdot \underline{M}(0) \rangle}{3kT} \quad (1-18)$$

Hence from Eqs. (1-16), (1-17) and (1-18), it follows that

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = L(-\dot{\phi}(t)) = - \int_0^\infty \dot{\phi}(t) e^{-i\omega t} dt \quad (1-19)$$

It should be noted Eq. (1-19) is the same as Cole's result<sup>4</sup>. Cole took account of Hamiltonian explicitly by approximating the assembly of dipoles as that of harmonic oscillators. However, the present derivation does not depend on such an approximation. The assumptions employed here are (i) neglect of internal field, (ii) all molecules have isotropic polarizability (otherwise we must consider tensor expression for polarizability), and (iii) a microscopic dipolar molecule is surrounded by macroscopic dipolar molecules, which eventually act as "background" for the microscopic molecule.

We shall examine some important consequences from Eq. (1-19). Mathematically Eq. (1-19) can be rewritten as

$$\begin{aligned} \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} &= - \int_0^\infty \dot{\phi}(t) e^{-i\omega t} dt \\ &= - \left( \phi(t) e^{-i\omega t} \Big|_0^\infty + i\omega \int_0^\infty \phi(t) e^{-i\omega t} dt \right) \\ &= 1 - i\omega \int_0^\infty \phi(t) e^{-i\omega t} dt \\ &= 1 - i\omega L(\phi(t)) \end{aligned} \quad (1-20)$$

since  $\phi(0) \equiv 1$

therefore

$$\frac{1}{i\omega} \left( 1 - \frac{\epsilon^*(\omega) - \epsilon_0}{\epsilon_0 - \epsilon_\infty} \right) = L(\phi(t)) \quad (1-21)$$

or

$$\phi(t) = L^{-1} \left\{ \frac{1}{i\omega} \left( 1 - \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} \right) \right\} \quad (1-22)$$

where  $L^{-1}$  stands for the inverse Laplace transform.

The representations of Eqs. (1-21), and (1-22) would be more straight forward than that of Eq. (1-19) because the former equations do not contain <sup>a</sup>time derivative of <sup>the</sup> correlation function, i.e.,  $\dot{\phi}(t)$ , whereas the latter equation does.

Let us consider a simple example to obtain <sup>a</sup>correlation function from <sup>the</sup> Debye equation using Eq. (1-22). According to Debye, an expression for dielectric dispersion was given by

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau}$$

where  $\tau$  is the dielectric relaxation time.

Thus

$$\frac{1}{i\omega} \left( 1 - \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} \right) = \frac{\tau}{1 + i\omega\tau}$$



From Eq. (1-22)

$$\begin{aligned}\phi(t) &= L^{-1} \left\{ \frac{1}{i\omega - (-\frac{1}{\tau})} \right\} \\ &= e^{-\frac{t}{\tau}}\end{aligned}$$

This is a well-known correlation function for <sup>the</sup> Debye equation. It will be seen that Eq. (1-22) can be used to obtain <sup>a</sup> correlation function from an empirical equation or an equation derived without reference to the correlation function treatment to examine its physical meaning.

Separating both sides of Eq. (1-20) into the real and imaginary parts, we have other representations below;

$$\frac{\epsilon'(\omega) - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = 1 - \omega \int_0^{\infty} \phi(t) \sin \omega t \, dt \quad (1-23)$$

$$\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_{\infty}} = \omega \int_0^{\infty} \phi(t) \cos \omega t \, dt$$

where  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  are dielectric constant and loss, respectively.

Let us now turn back to Eq. (1-19) and define

$$\phi(t) \equiv -\dot{\Phi}(t)$$

It will be seen that  $\phi(t)$  corresponds to <sup>the</sup> "decay function" defined by Frölich<sup>5</sup>.

From Eq. (1-19),

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = L(\phi(t)) = \int_0^\infty \phi(t) e^{-i\omega t} dt$$

Separation into the real and imaginary parts leads to

$$\frac{\epsilon'(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \phi(t) \cos \omega t dt \quad (1-24)$$

$$\frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \phi(t) \sin \omega t dt \quad (1-25)$$

It should be pointed out that Eqs. (1-24) and (1-25) can be regarded as Fourier transforms for the odd and even functions of  $\omega$  respectively. Therefore,  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  require evenness and oddness, respectively, with respect to  $\omega$ , which is a quite general requirement for the generalized susceptibility<sup>6</sup>. In addition, Eqs. (1-24), and (1-25) are identical with those derived by Frölich<sup>5</sup>.

From Eqs. (1-24) and (1-25),

$$\phi(t) = \frac{2}{\pi} \int_0^\infty \frac{\epsilon'(\eta) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} \cos \eta t d\eta \quad (1-26)$$

$$= \frac{2}{\pi} \int_0^\infty \frac{\epsilon''(\eta)}{\epsilon_0 - \epsilon_\infty} \sin \eta t d\eta \quad (1-27)$$

where  $\eta$  is an integral parameter.

Substitutions of Eqs. (1-26) and (1-27), respectively, in Eqs. (1-24) and (1-25) give the widely known Kramers-Kronig equations;

$$\epsilon'(\omega) - \epsilon_\infty = \frac{2}{\pi} \int_0^\infty \epsilon''(\eta) \frac{\eta}{\eta^2 - \omega^2} d\eta \quad (1-28)$$

$$\epsilon''(\omega) = \frac{2}{\pi} \int_0^\infty \left\{ \epsilon'(\eta) - \epsilon_\infty \right\} \frac{\omega}{\omega^2 - \eta^2} d\eta \quad (1-29)$$

Therefore it is seen that in order to satisfy Eqs. (1-28), and (1-29),  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  should be even and odd functions of  $\omega$ , respectively, because <sup>the</sup> Kramers-Kronig equations require the conditions.

Setting  $\omega=0$  in Eq. (1-28), we have

$$\begin{aligned} \epsilon_0 - \epsilon_\infty &= \frac{2}{\pi} \int_0^\infty \epsilon''(\eta) \frac{d\eta}{\eta} \\ &= \frac{2}{\pi} \int_0^\infty \epsilon''(\eta) d(\log \eta) \end{aligned} \quad (1-30)$$

From this expression,  $(\epsilon_0 - \epsilon_\infty)$  can be calculated by measuring only  $\epsilon''(\omega)$  with the whole frequency range.

From the above discussion, it is seen that  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  are not independent from each other.

(c) APPLICATION OF DIELECTRIC CORRELATION FUNCTION

(i) Hindered Internal Rotation Characterized by Two Equipotential Wells.

The molecular model employed here consists of <sup>the</sup> dipole moment of <sup>a</sup> rotational group  $\mu_g$  and that of <sup>a</sup> molecule  $\mu_m$  as shown in Figures 1 and 2. With the help of Hoffman's site model<sup>7</sup> the rate equations for populations  $P_A$  and  $P_{A'}$  of the two sites can be expressed in terms of <sup>the</sup> transition probability  $k$ :

$$\frac{dP_A}{dt} = -kP_A + kP_{A'} \quad (1-30)$$

$$\frac{dP_{A'}}{dt} = kP_A - kP_{A'}$$

These equations must satisfy the following secular determinant:

$$\begin{vmatrix} D + k & -k \\ -k & D + k \end{vmatrix} = 0$$

where  $D$  is a differential operator, which is  $d/dt$ . The solutions of the secular equation are:

$$D = 0 \text{ and } -2k.$$

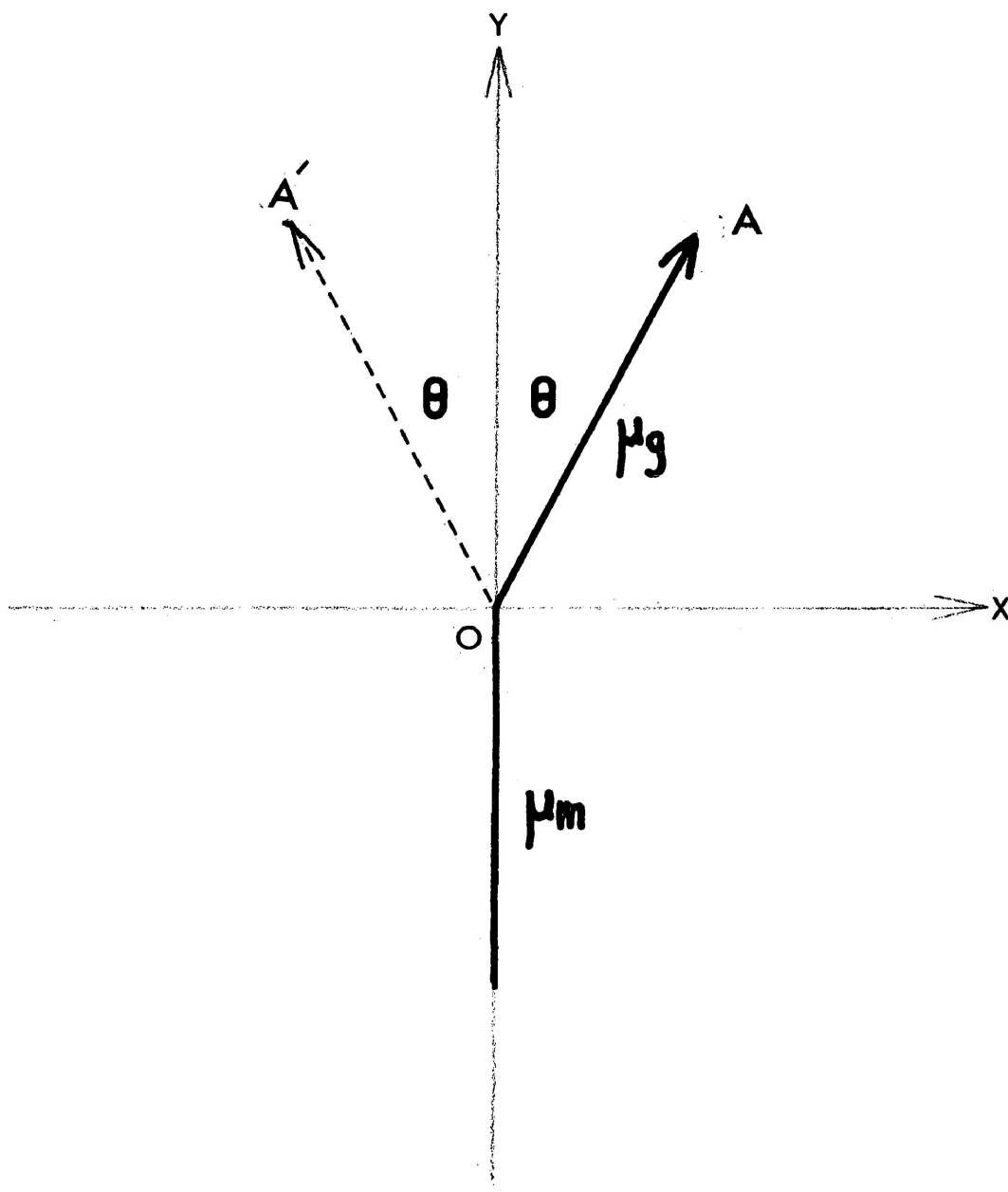


Figure 1-2: Dipole moment coordinates for a single rotator.

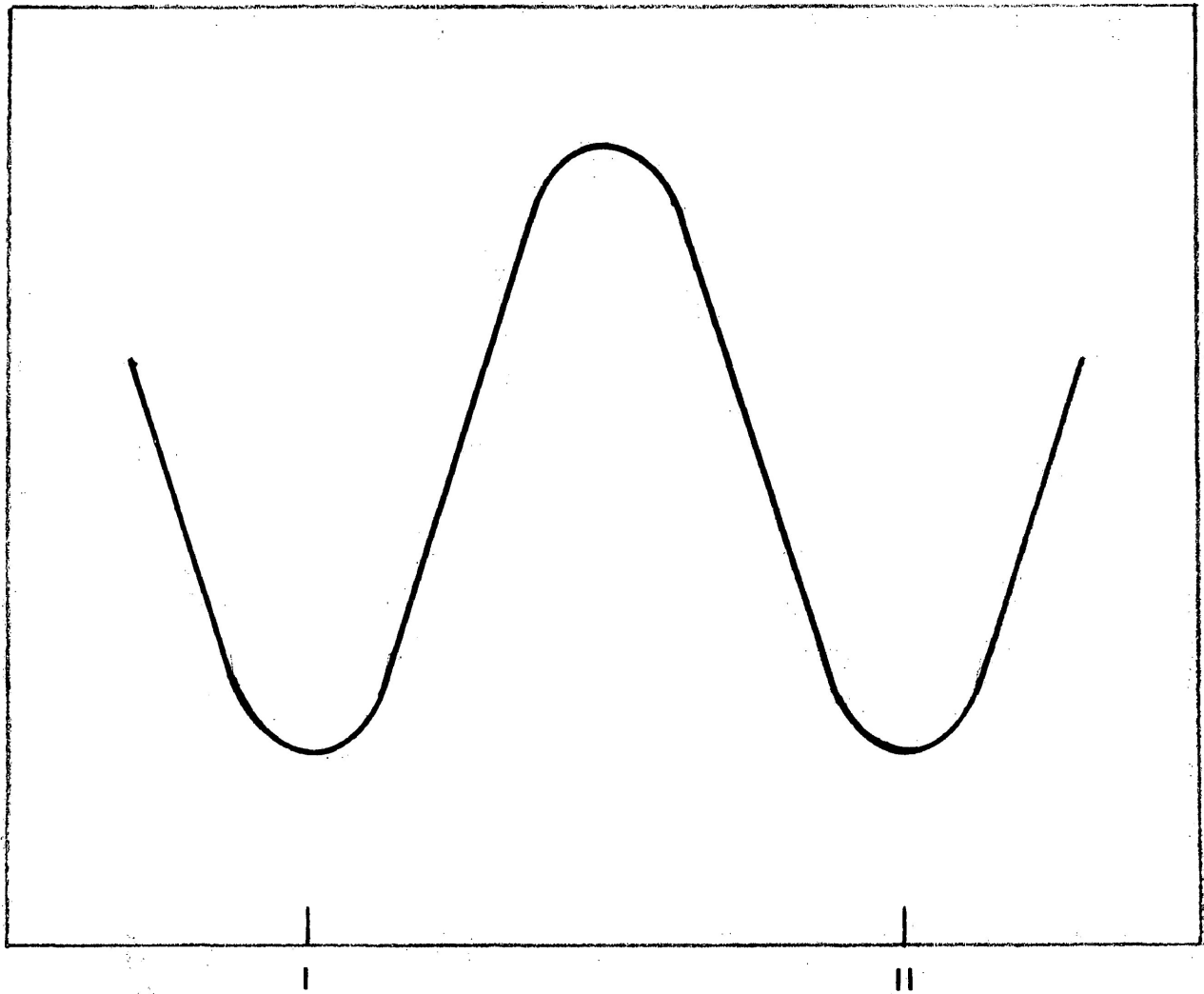


Figure 1-3: Potential energy curve versus rotational angle for a single group rotator

Therefore the occupational probabilities for states 1 and 2 are given by

$$P_A = a_{11} + a_{12} \exp(-2kt) \quad (1-31)$$

$$P_{A'} = a_{21} + a_{22} \exp(-2kt)$$

where  $a_{ij}$  is <sup>a</sup> constant obtained by the initial condition and  $a_{i1}$  represents the equilibrium occupational probability for site  $i$ . Since <sup>the</sup> total probability must be 1,  $P_A + P_{A'}$  is always 1, which gives us

$$a_{11} + a_{21} = 1$$

at  $t = \infty$ . And substitution of Eq. (1-31) in one of Eqs. (1-30) gives

$$a_{11} = a_{21} = 1/2$$

$$a_{12} = a_{22} \equiv m$$

Moreover it is assumed that the rotational group lies on each site completely at  $t = 0$

Therefore,

$$\text{For } P_A(0) = 1 \text{ and } P_{A'}(0) = 0, \quad m = 1/2 \quad (1-32)$$

$$\text{For } P_A(0) = 0 \text{ and } P_{A'}(0) = 1, \quad m = -1/2$$

As seen from Figure 1-2, introducing unit vectors along the x- and y- axes, i.e.,  $\hat{x}$  and  $\hat{y}$ , respectively, the dipole moment of molecule as a whole  $\mu(t)$  at a given time t is

$$\begin{aligned}\mu(t) &= s\hat{y}(P_A + P_{A'}) + uP_A\hat{x}(t) - uP_{A'}\hat{x}(t) \\ &= s\hat{y}(t) + u(P_A - P_{A'})\hat{x}(t)\end{aligned}\quad (1-33)$$

where  $s = \mu\cos\theta$  and  $u = \mu\sin\theta$ . This is because the dipole moment of <sup>the</sup> y axis component does not depend on the group rotation, whereas that of <sup>the</sup> x axis component changes its sign, i.e., + for state A or - for state A'. At the same time, the molecular re-orientation will be considered in terms of the motion of the coordinates. From Eq. (1-32), Eq. (1-33) becomes;

$$\mu(t) = s\hat{y}(t) + 2u\exp(-2kt)\hat{x}(t)\quad (1-34)$$

Therefore from Eqs. (1-32), and (1-34), it follows that

$$\begin{aligned}\mu_A(t) &= s\hat{y}(t) + u\exp(-2kt)\hat{x}(t) \\ \mu_{A'}(t) &= s\hat{y}(t) - u\exp(-2kt)\hat{x}(t)\end{aligned}\quad (1-35)$$

Then the scalar product of  $\mu_i(0)$  and  $\mu_i(t)$  ( $i = A$  and  $A'$ ) is



$$\begin{aligned} \mu_A(o) \cdot \mu_A(t) &= s^2 (y(o) \cdot y(t)) + u^2 \exp(-2kt) (x(o) \cdot x(t)) \\ &\quad + su \exp(-2kt) (y(o) \cdot x(t)) + su (x(o) \cdot y(t)) \\ \mu_{A'}(o) \cdot \mu_{A'}(t) &= s^2 (y(o) \cdot y(t)) + u^2 \exp(-2kt) (x(o) \cdot x(t)) \\ &\quad - su \exp(-2kt) (y(o) \cdot x(t)) - su (x(o) \cdot y(t)) \end{aligned} \tag{1-36}$$

So far we have <sup>been</sup> concerned with <sup>a</sup> one body problem but we are now in a position to solve <sup>the</sup> equation of motion for <sup>an</sup> assembly of molecules. We shall select <sup>the</sup> correlation function treatment as <sup>the</sup> appropriate mechanics to answer <sup>the</sup> problem.

The correlation function  $\phi$  may be given by

$$\phi = \frac{\sum_i^2 P_i \langle \mu_i(o) \cdot \mu_i(t) \rangle}{\sum_i^2 P_i \langle \mu_i(o) \cdot \mu_i(o) \rangle}$$

where  $P_i$  represents the equilibrium occupational probability at site  $i$ . Taking ensemble average for Eqs. (1-36), we have  $\phi(t) = \frac{s^2 \langle y(o) \cdot y(t) \rangle + u^2 \exp(-2kt) \langle x(o) \cdot x(t) \rangle}{s^2 + u^2}$  (1-37)

Now let us assume  $\langle y(o) \cdot y(t) \rangle = \langle x(o) \cdot x(t) \rangle = \exp\left(-\frac{t}{\tau m}\right)$

where  $\tau m$  can be regarded as the molecular relaxation time, because the coordinate system was taken so as to move with the molecule. In this respect,  $\tau g = 1/2 k$  would be connected with

the group relaxation time. Therefore the correlation function becomes;

$$\phi(t) = \frac{s^2}{s^2+u^2} \exp\left(-\frac{t}{\tau_m}\right) + \frac{u^2}{s^2+u^2} \exp\left[-\left(\frac{1}{\tau_m} + \frac{1}{\tau_g}\right)t\right] \quad (1-38)$$

This should give us an equation for dielectric dispersion below; (see Eq. (1-19))

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{C_1}{1+i\omega\tau_1} + \frac{C_2}{1+i\omega\tau_2}$$

where

$$C_1 = \frac{s^2}{s^2+u^2}, \quad C_2 = \frac{u^2}{s^2+u^2}, \quad \tau_1 = \tau_m$$

$$\text{and } \frac{1}{\tau_2} = \frac{1}{\tau_m} + \frac{1}{\tau_g} \text{ or } \tau_2 = \frac{\tau_g}{1 + \left(\frac{\tau_g}{\tau_m}\right)} \quad (1-39)$$

Hence the observed relaxation time of group rotation for the present model should be less than  $\tau_g$ . This model was also applied to inversion of aniline molecule by Williams<sup>8</sup>. If there is no y-component dipole,  $s=0$ , Eq. (1-39) yields a single relaxation process, the observed relaxation time  $\tau^*$  of which is

$$\tau^* = \frac{\tau_g}{1 + \left(\frac{\tau_g}{\tau_m}\right)}$$

This is the case of inversion model of the type NR<sub>3</sub>.

(ii) Hindered Internal Rotation of 1,4-Disubstituted Benzene

This problem was firstly worked out by Williams<sup>9</sup>. We shall consider the same problem with somewhat different approach. Our starting model is shown in Figures 1-3 & 1-4. The occupational probabilities for each state  $i$  are:

$$\begin{aligned}dP_1/dt &= -2kP_1(t) + k'(P_2(t) + P_4(t)) \\dP_2/dt &= -2k'P_2(t) + k(P_1(t) + P_3(t)) \\dP_3/dt &= -2kP_3(t) + k'(P_2(t) + P_4(t)) \\dP_4/dt &= -2k'P_4(t) + k(P_1(t) + P_3(t))\end{aligned}\tag{1-40}$$

The secular determinant

$$\begin{vmatrix}D + 2k & -k' & 0 & -k' \\-k & D+2k' & -k & 0 \\0 & -k' & D+2k & -k' \\-k & 0 & -k' & D+2k'\end{vmatrix} = 0$$

yields  $D = 0$ ,  $-2(k + k')$ ,  $-2k$ , and  $-2k'$ . We can, therefore, write

$$\begin{aligned}P_1(t) &= a_{11} + a_{12}\psi_2(t) + a_{13}\psi_3(t) \\P_2(t) &= a_{21} - a_{12}\psi_2(t) + a_{24}\psi_4(t) \\P_3(t) &= a_{31} + a_{12}\psi_2(t) - a_{13}\psi_3(t) \\P_4(t) &= a_{41} - a_{12}\psi_2(t) - a_{24}\psi_4(t)\end{aligned}\tag{1-41}$$

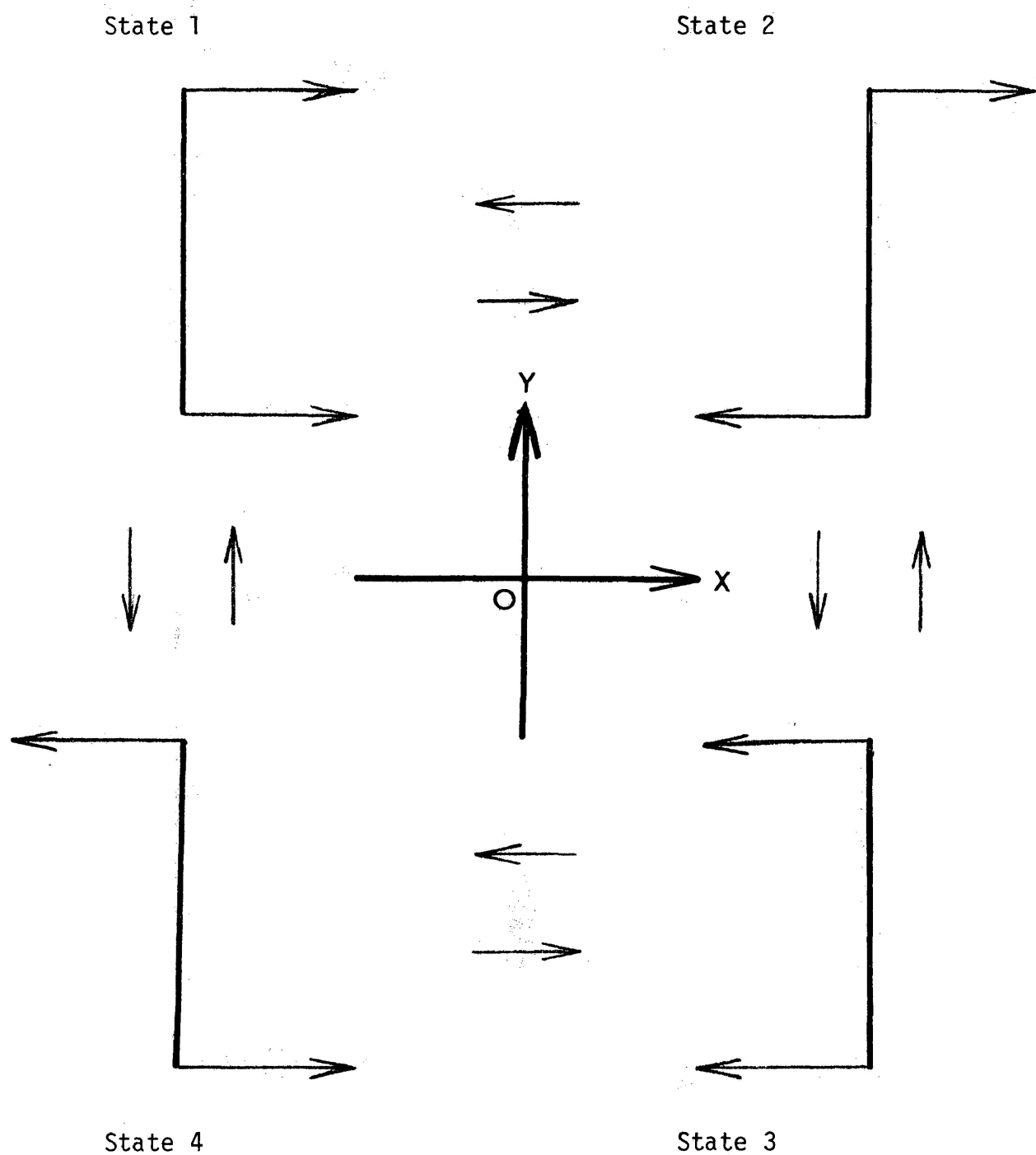


Figure 1-4 (a): Schematic representation of molecular configurations of 1,4-disubstituted benzene and its coordinates with reference to dipole moments. In all states, benzene rings are assumed to be perpendicular to this paper.

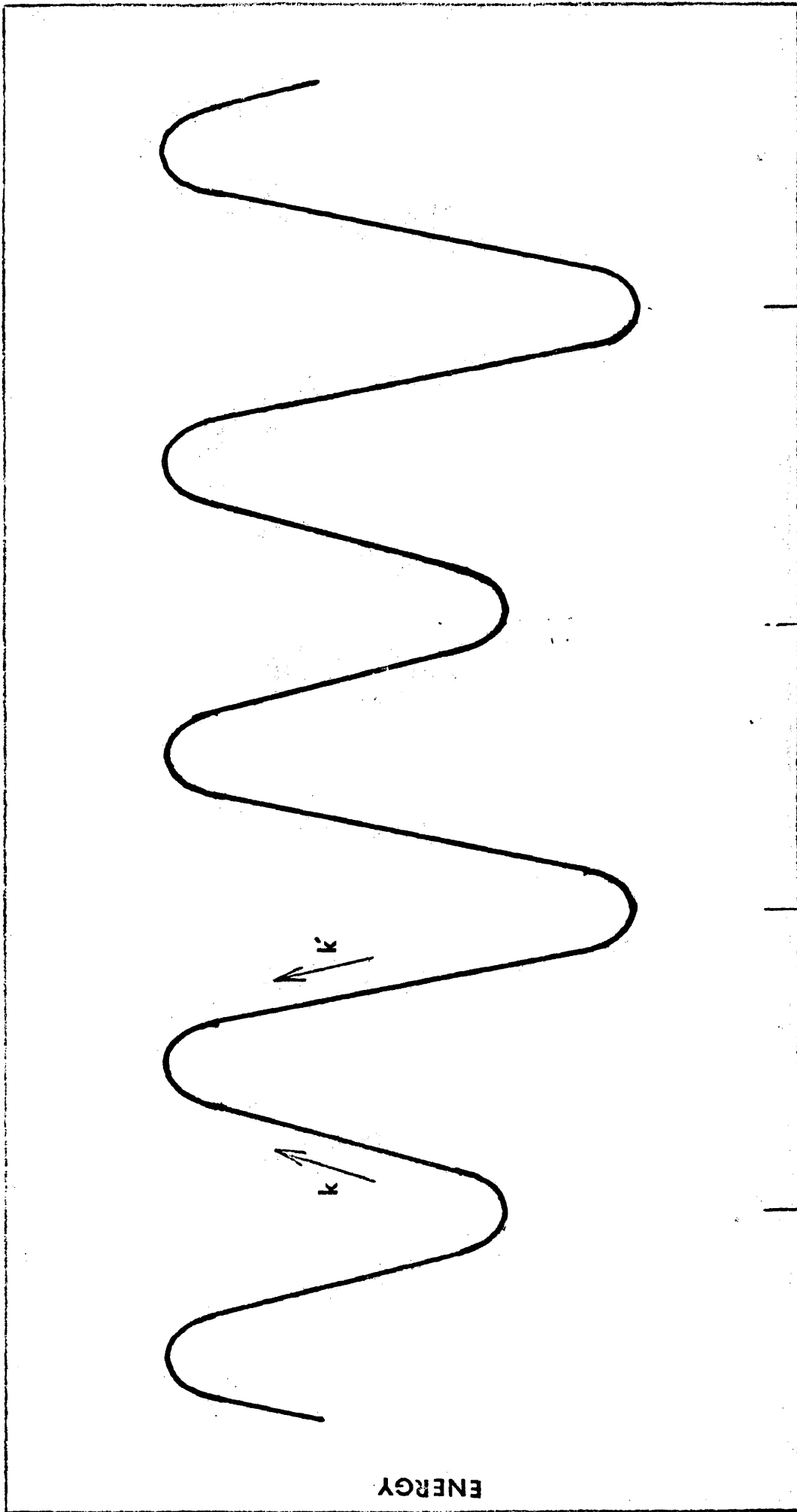


Figure 1-4 (b): Potential curve corresponding to Figure 1-4 (a)

where  $a_{11} = a_{31} = x/2(1+x)$ ,  $a_{21} = a_{41} = 1/2(1+x)$ ,  $x = k'/k = \exp(-\text{potential energy difference}) / (\text{Boltzmann constant}) \times (\text{absolute temperature})$ ,  $\psi_2(t) = \exp(-2(k+k')t)$ ,  $\psi_3(t) = \exp(-2kt)$ , and  $\psi_4(t) = \exp(-2k't)$  and  $a_{i1}$  ( $i = 1, 2, 3$ , and  $4$ ) represents the equilibrium occupational probability for site  $i$ . From Figure 3, it is seen that states 2 and 4 do not contribute to the molecular dipole moment. Suppose the  $x$  component of the dipole moment of group rotation is denoted by  $\mu_x(t)$  the total dipole moment of all states of the molecule is given by:

$$\begin{aligned} \mu(t) &= 2\mu_x P_1(t) - 2\mu_x P_3(t) \\ &= 2\mu_x (P_1(t) - P_3(t)) \end{aligned} \quad (1-42)$$

From Eq. (1-41)

$$\mu(t) = 4a_{13}\mu_x(t)\psi_3(t)$$

Therefore

$$\mu(0) \cdot \mu(t) = 8a_{13}^2 (\mu_x(0) \cdot \mu_x(t)) \psi_3(t) \quad (1-43)$$

For  $t = 0$

$$\mu(0) \cdot \mu(0) = 8a_{13}^2 (\mu_x(0) \cdot \mu_x(0)) \quad (1-44)$$

Hence

$$\Phi = \frac{8a_{13}^2 \mu_x^2 \langle \cos g \rangle \psi_3(t)}{8a_{13}^2 \mu_x^2} = \langle \cos g \rangle \psi_3(t) \quad (1-45)$$

where  $g$  is an angle between  $\mu_x(0)$  and  $\mu_x(t)$ . Assuming the molecular correlation function is  $\exp(-\frac{t}{\tau_m})$  and setting the group relaxation time  $\tau_m = 1/2k$ , we have

$$\phi(t) = \exp\left[-\left(\frac{1}{\tau_m} + \frac{1}{\tau_g}\right)t\right] \quad (1-46)$$

this gives us (see Eq. (1-19))

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau^*}$$

where

$$\tau^* = \frac{\tau_g}{1 + \left(\frac{\tau_g}{\tau_m}\right)} \quad (1-47)$$

Thus we have seen that 1,4-disubstituted benzene should give us a single relaxation time, if the assumptions employed here are satisfactory. This model can be easily extended to  $\text{NR}_2\text{C}_6\text{H}_4\text{NR}_2$  since  $\text{NR}_2$  inversion or internal rotation could be characterized by four equipotential wells<sup>8</sup>. In this case,  $k$  must be equal to  $k'$ . In addition, the present model can be applicable to 1,2-disubstituted ethane<sup>9</sup>.

(iii) Two Equivalent Rotational Groups

We shall extend treatment in (ii) to general internal rotation of two equivalent groups. The starting model is shown in Figures 1-5 & 1-6. It is assumed here that the potential curve is essentially similar to that used in (ii). Therefore Eqs.(1-41) are to be used again. As before, we employ unit vectors to consider re-orientations of molecular and group dipoles. Therefore we need a scalar quantity  $a$  for the unit vector  $\hat{x}(t)$  and a scalar  $b$  for the unit vector  $\hat{y}(t)$  to describe motions of dipoles involved in a molecule. It is beyond doubt that we can always specify  $a$  and  $b$  completely, if <sup>the</sup> molecular structure and suitable group dipole moments of the molecule are known. As an example, consider *m*-dimethoxybenzene. Denoting <sup>the</sup> angles between <sup>the</sup>  $y$ -axis and the directions of  $\mu_{CO}$  and  $\mu_{OCH_3}$  as  $\alpha$  and  $\beta$ , respectively, we have

$$a = 2\mu_{OCH_3} \sin\beta \quad \text{for states 1 and 2}$$

$$= 0 \quad \text{for states 2 and 4}$$

$$b = 2(\mu_{CO} + \mu_{OCH_3} \cos\beta) \cos\alpha \quad \text{for all states}$$

The secular determinant

$$\begin{vmatrix} D+2k & -k' & 0 & -k' \\ -k & D+2k' & -k & 0 \\ 0 & -k' & D+2k & -k' \\ -k & 0 & -k' & D+2k' \end{vmatrix} = 0$$



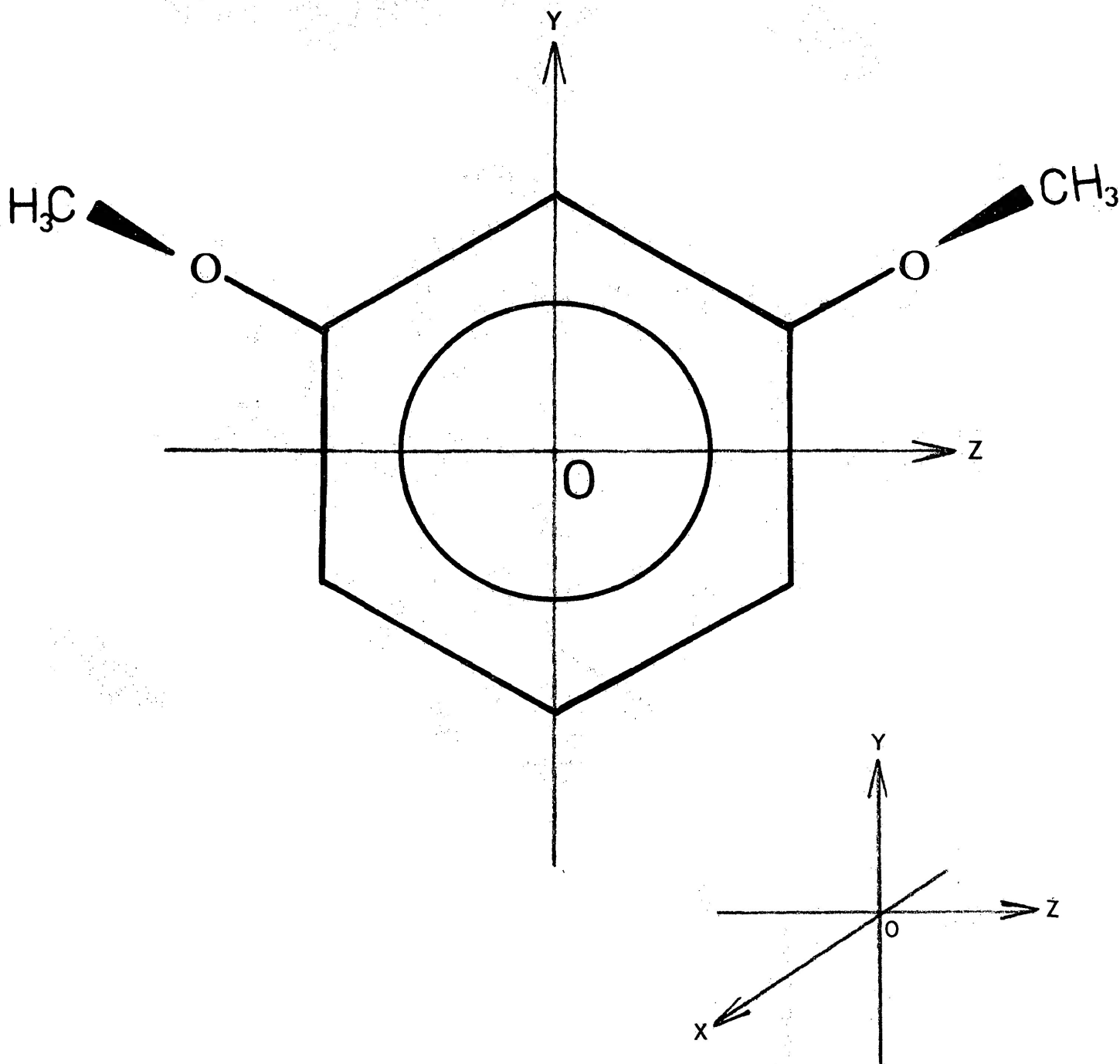


Figure 1-5: Coordinates for *m*-dimethoxybenzene as an example of two equivalent rotators.

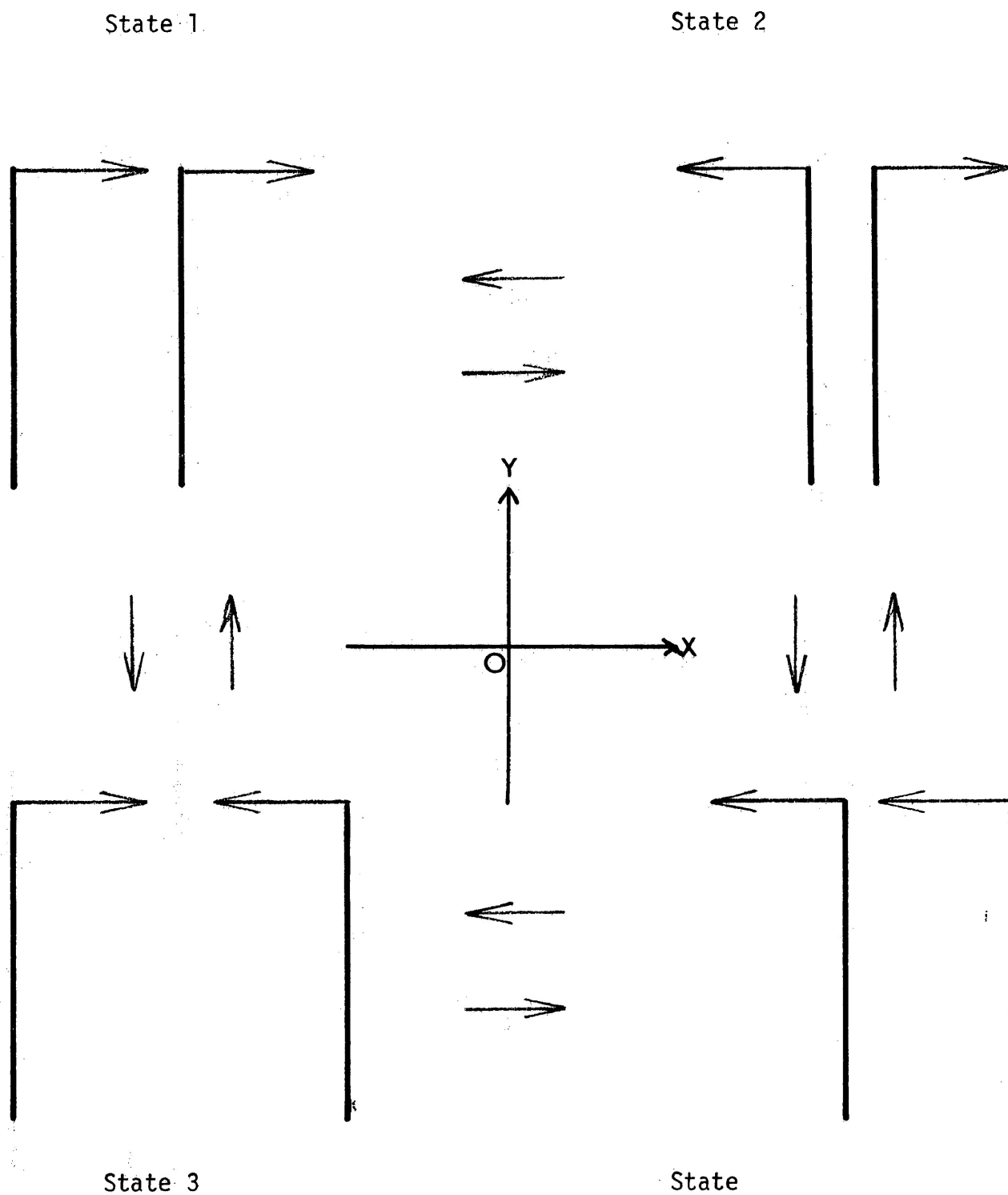


Figure 1-6: Configurations of two equivalent rotators corresponding to Figure 1-5.

where  $a_{11} = a_{31} = x/2(1+x)$ ,  $a_{21} = a_{41} = 1/2(1+x)$ ,  $x = k'/k = \exp(-\text{potential energy difference})/((\text{Boltzmann constant}) \times (\text{absolute temperature}))$ ,  $\psi_2(t) = \exp(-2(k+k')t)$ ,  $\psi_3(t) = \exp(-2kt)$ , and  $\psi_4(t) = \exp(-2k't)$  and  $a_{i1}$  ( $i=1,2,3$ , and  $4$ ) represents the equilibrium occupational probability for site  $i$ . From Figure 1-3, it is seen that states 2 and 4 do not contribute to the molecular dipole moment. Suppose the  $x$  component of the dipole moment of group rotation is denoted by  $\mu_x(t)$  the total dipole moment of all states of the molecule is given by:

$$\begin{aligned} \mu(t) &= 2\mu_x P_1(t) - 2\mu_x P_3(t) \\ &= 2\mu_x (P_1(t) - P_3(t)) \end{aligned} \quad (1-42)$$

From Eq. (1-41),

$$\mu(t) = 4a_{13}\mu_x(t)\psi_3(t)$$

Therefore

$$\mu(0) \cdot \mu(t) = 8a_{13}^2 (\mu_x(0) \cdot \mu_x(t)) \psi_3(t) \quad (1-43)$$

For  $t = 0$

$$\mu(0) \cdot \mu(0) = 8a_{13}^2 (\mu_x(0) \cdot \mu_x(0)) \quad (1-44)$$

Hence

$$\phi = \frac{8a_{13}^2 \mu_x^2 \langle \cos g \rangle \psi_3(t)}{8a_{13}^2 \mu_x^2} = \langle \cos g \rangle \psi_3(t) \quad (1-45)$$

where  $g$  is an angle between  $\mu_x(0)$  and  $\mu_x(t)$ . Assuming the molecular correlation function is  $\exp(-\frac{t}{\tau_m})$  and setting the group relaxation time  $\tau_m = 1/2k$ , we have

$$\Phi(t) = \exp \left[ -\left( \frac{1}{\tau_m} + \frac{1}{\tau_g} \right) t \right] \quad (1-46)$$

This gives us (see Eq. (1-19))

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau^*}$$

where

$$\tau^* = \frac{\tau_g}{1 + \left( \frac{\tau_g}{\tau_m} \right)} \quad (1-47)$$

Now the molecular dipole moment at each state is

$$\begin{array}{ll} a_x(t) + b_y(t) & \text{for state 1} \\ b_y(t) & \text{for state 2} \\ -a_x(t) + b_y(t) & \text{for state 3} \\ b_y(t) & \text{for state 4} \end{array}$$

Hence the total moment at a given time  $t$ , i.e.,  $\mu(t)$  is

$$\begin{aligned} \mu(t) &= (a_x + b_y)P_1 + (b_y)P_2 + (b_y - a_x)P_3 + (b_y)P_4 \\ &= a_x(P_1 - P_3) + b_y \\ &= 2a_{13}x(t)\psi_3(t) + b_y(t) \end{aligned} \quad (1-48)$$

At  $t=0$ , it is assumed that the rotators occupies site  $i$  completely ( $i=1,2,3$ , and  $4$ ).

Then

$$P_1(0) = 1 \text{ and } P_2(0) = P_3(0) = P_4(0) = 0 \quad \text{give } a_{13} = 1/2$$

$$P_2(0) = 1 \text{ and } P_1(0) = P_3(0) = P_4(0) = 0 \quad \text{give } a_{13} = 0$$

$$P_3(0) = 1 \text{ and } P_1(0) = P_2(0) = P_4(0) = 0 \quad \text{give } a_{13} = -1/2$$

$$\text{,and } P_4(0) = 1 \text{ and } P_1(0) = P_2(0) = P_3(0) = 0 \quad \text{give } a_{13} = 0$$

Therefore it follows that

$$\mu_1(t) = a\chi(t)\psi_3(t) + by(t)$$

$$\mu_2(t) = by(t)$$

$$\mu_3(t) = -a\chi(t)\psi_3(t) + by(t)$$

$$\mu_4(t) = by(t)$$

where  $\mu_i(t)$  denotes dipole moment at state  $i$  at  $t=t$ .

The correlation function may be expressed as

$$\phi(t) = \frac{\sum_i^4 P_i \langle \mu_i(0) \cdot \mu_i(t) \rangle}{\sum_i^4 P_i \langle \mu_i(0) \cdot \mu_i(0) \rangle} \quad (1-49)$$

$$\text{where } P_1 = P_3 = \frac{x}{2(1+x)} \quad \text{and } P_2 = P_4 = \frac{1}{2(1+x)}$$

Making scalar products of  $\mu_i(0) \cdot \mu_i(t)$  and  $\mu_i(0) \cdot \mu_i(0)$  and using Eq.(1-49), we finally obtain

$$\phi(t) = \frac{b^2 \langle \chi(0) \cdot \chi(t) \rangle + \frac{x}{1+x} a^2 \psi_3(t) \langle \chi(0) \cdot \chi(t) \rangle}{b^2 + \frac{x}{1+x} a^2} \quad (1-50)$$

Therefore assuming that the molecular re-orientation decays exponentially, we have an equation for dielectric dispersion of Budo's type;

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{c_1}{1+i\omega\tau_1} + \frac{c_2}{1+i\omega\tau_2}$$

where

$$c_1 = \frac{b^2}{b^2 + \frac{x}{1+x} a^2}, \quad c_2 = \frac{\frac{x}{1+x} a^2}{b^2 + \frac{x}{1+x} a^2}, \quad (1-51)$$

$$\frac{1}{\tau_2} = \frac{1}{\tau_m} + \frac{1}{\tau_g}, \quad \text{and } \tau_m = \tau_1$$

Hence it is shown that the molecule which has two equivalent rotational groups should give us two relaxation times, and the dispersion equation is formally same as that for the molecule which has just one rotational group (see (i)). When  $b=0$ , Eq. (1-57) becomes Eq. (1-47), which is necessary, because the present treatment includes all features in (ii). In this sense, the present treatment would be regarded as a generalization of that in (ii). Furthermore it has also shown that  $c_1$  and  $c_2$  depend on temperature and the potential energy difference  $V$  through  $x = \exp(-V/kT)$ .

CHAPTER 2     Evaluation of Molecular Dipole Moments for a Molecule which Contains Two Rotational Groups.

(a) *GENERAL ASPECTS*

Since dipole moments are considered to be vectors, their fundamental properties can be used for dipole moment analysis.

Let us consider a purely geometric problem of two vectors  $\vec{P}$  and  $\vec{Q}$  in which the latter vector  $\vec{Q}$  rotates around the former one  $\vec{P}$  with an angle  $\phi$ .

As shown in Figure 1, we shall introduce two coordinate systems e.g.,  $(x', y', z')$  and  $(x, y, z)$  coordinates, where the two vectors  $\vec{P}$  and  $\vec{Q}$  are assumed to be on both  $x'$ - $y'$ -and  $x$ - $y$ -planes (the paper plane) at  $\phi=0$  (this is always possible as far as we are concerned with the two vectors), and the former coordinates are taken by assuming that  $y'$  axis lies along  $\vec{P}$  vector,  $x'$ -axis makes a right angle with the  $y'$  axis, and  $z'$  and  $z$  axes are perpendicular to the paper plane. Then the dipole moments along the  $x'$ ,  $y'$  and  $z'$ -axes are given by

$$\mu_{x'} = - Q \sin B \cos \phi$$

$$\mu_{y'} = Q \cos B + P$$

$$\mu_{z'} = Q \sin B \sin \phi$$

Therefore dipole moments along the  $x$ -,  $y$ - and  $z$ -axes have the relation shown on the next page <sup>10</sup> ;

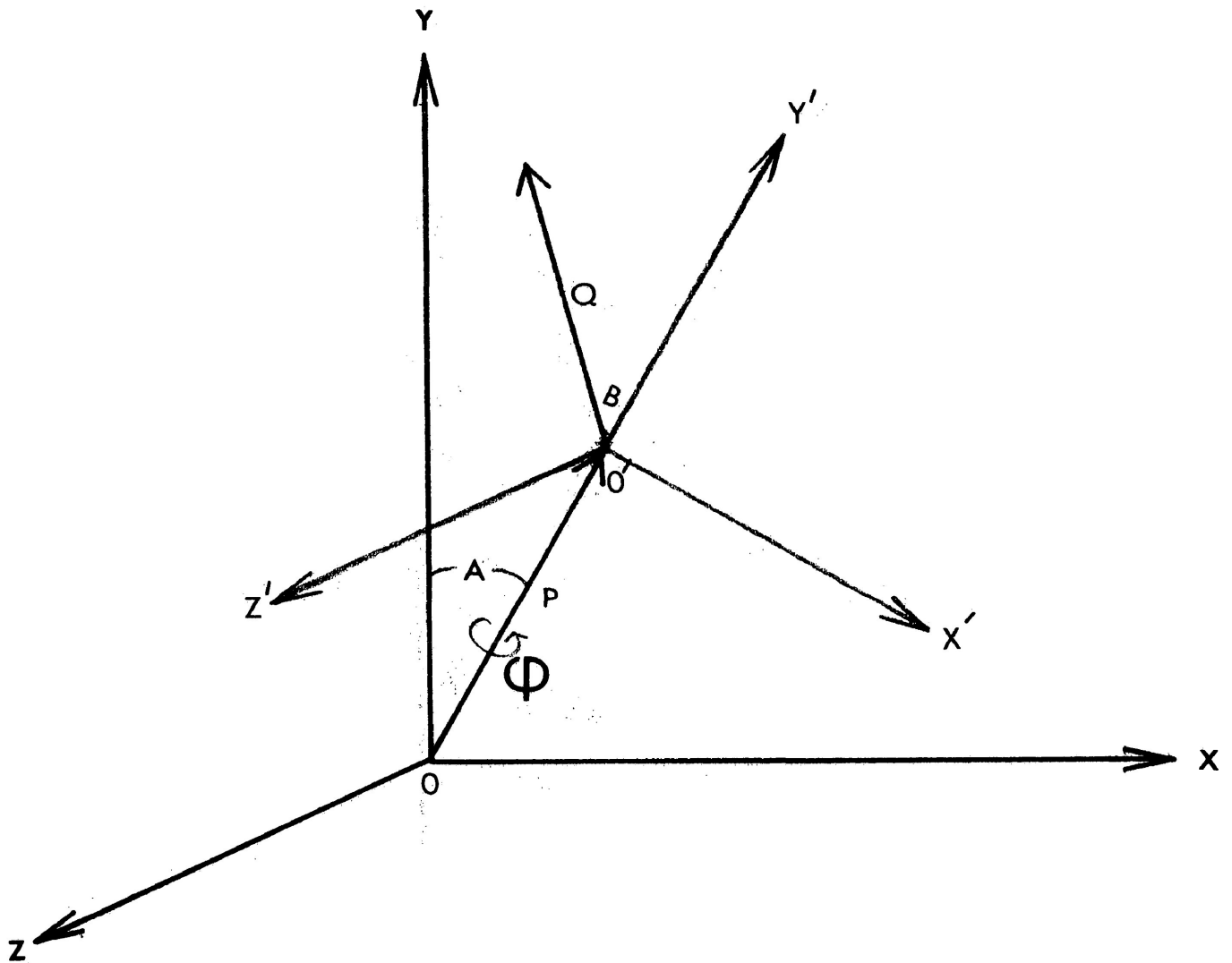


Figure 2-1: Coordinate systems for a single rotator  $Q$ .  $A$  and  $B$  are angles between  $\hat{p}$  and the  $y$ -axis and between  $\hat{p}$  and  $\hat{q}$ , respectively.



$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \cos A & \sin A & 0 \\ -\sin A & \cos A & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mu_{x'} \\ \mu_{y'} \\ \mu_{z'} \end{pmatrix}$$

where A is an angle between the z-axis and  $\mu_{z'}$ . This gives us

$$\begin{aligned} \mu_x &= (\mu_{z'} + \mu_{y'} \cos B) \sin A - \mu_{x'} \sin B \cos A \cos \phi \\ \mu_y &= (\mu_{z'} + \mu_{y'} \cos B) \cos A + \mu_{x'} \sin B \sin A \cos \phi \\ \mu_z &= \mu_{z'} \sin B \sin \phi \end{aligned} \quad (2-1)$$

As an example, in the case of anisole, setting  $A = 0$ ,

$\mu_{z'} = \mu_{\text{C-O}}$  (bond moment of C-O bond), and  $\mu_{y'} = \mu_{\text{OCH}_3}$  (group moment of O-CH<sub>3</sub> group), we have

$$\begin{aligned} \mu_x &= -\mu_{\text{OCH}_3} \sin B \cos \phi \\ \mu_y &= (\mu_{\text{CO}} + \mu_{\text{OCH}_3} \cos B) \\ \mu_z &= \mu_{\text{OCH}_3} \sin B \sin \phi \end{aligned}$$

Then the square of total dipole moment of anisole is

$$\begin{aligned} \mu^2 &= \mu_x^2 + \mu_y^2 + \mu_z^2 \\ &= \mu_{\text{CO}}^2 + 2\mu_{\text{CO}}\mu_{\text{OCH}_3} \cos B + \mu_{\text{OCH}_3}^2 \end{aligned}$$

Therefore it is seen that the total dipole moment of anisole does not depend on the rotational angle  $\phi$ .

Next let us consider two equivalent rotational groups, using Eq. (2-1). The coordinates to be used here are shown in Figure 2.

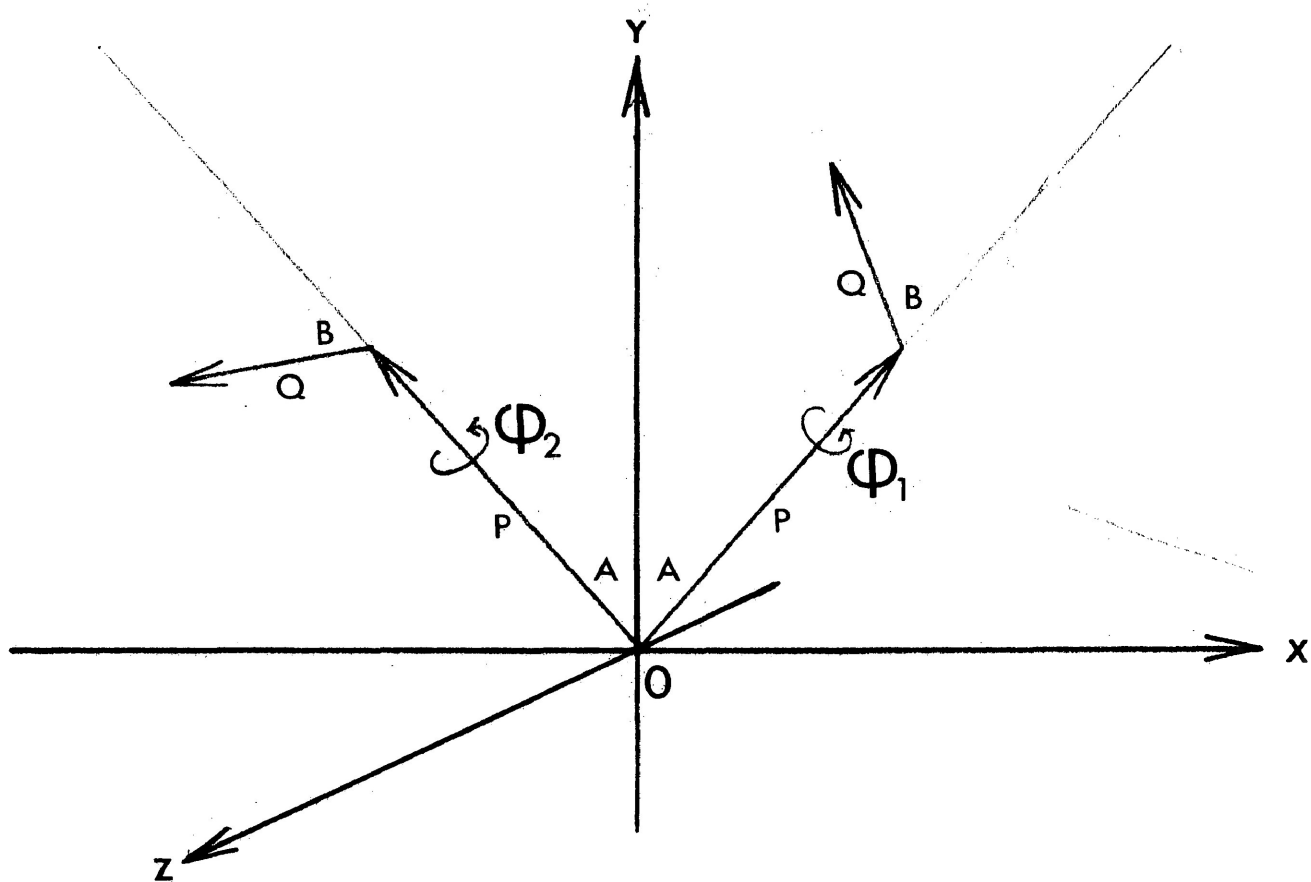


Figure 2-2: Coordinates for two equivalent rotational groups

Assuming that  $P$  vectors of rotators 1 and 2 make an angle  $A$  with the  $y$ -axis, we have the following moments along the  $x$ -,  $y$ - and  $z$ -axes for the rotator 1.

$$\begin{aligned}\mu_{x_1} &= (P + Q\cos B) \sin A - Q \sin B \cos A \cos \phi_1 \\ \mu_{y_1} &= (P + Q\cos B) \cos A + Q \sin B \sin A \cos \phi_1 \\ \mu_{z_1} &= Q \sin B \sin \phi_1\end{aligned}\quad (2-2)$$

where  $\phi_1$  is rotational angle for the rotator 1. Similarly setting  $A = -A$  in Eq. (2-1), we have

$$\begin{aligned}\mu_{x_2} &= -(P + Q\cos B) \sin A - Q \sin B \cos A \cos \phi_2 \\ \mu_{y_2} &= (P + Q\cos B) \cos A - Q \sin B \sin A \cos \phi_2 \\ \mu_{z_2} &= Q \sin B \sin \phi_2\end{aligned}$$

where  $\phi_2$  is rotational angle for the rotator 2. Therefore the overall moments along the  $x$ -,  $y$ - and  $z$ -axes are

$$\begin{aligned}\mu_x &= \mu_{x_1} + \mu_{x_2} = -Q \sin B \cos A (\cos \phi_1 + \cos \phi_2) \\ \mu_y &= \mu_{y_1} + \mu_{y_2} \\ &= 2(P + Q\cos B) \cos A + Q \sin B \sin A (\cos \phi_1 - \cos \phi_2) \\ \mu_z &= \mu_{z_1} + \mu_{z_2} = Q \sin B (\sin \phi_1 + \sin \phi_2)\end{aligned}\quad (2-3)$$

Dependencies of these moments on  $\phi_1$  and  $\phi_2$  are collected in Table 1.

Table 2-1: Dependencies of the component moments  $\mu_x$ ,  $\mu_y$  and  $\mu_z$  along the  $x$ ,  $y$ , and  $z$  axes, in Figure 2, respectively.

$\phi_1$	$0^\circ$	$0^\circ$	$0^\circ$	$0^\circ$	$90^\circ$	$90^\circ$	$90^\circ$	$90^\circ$
$\phi_2$	$0^\circ$	$90^\circ$	$180^\circ$	$270^\circ$	$0^\circ$	$90^\circ$	$180^\circ$	$270^\circ$
$\mu_x$	$2a_x$	$a_x$	$0$	$a_x$	$a_x$	$0$	$-a_x$	$0$
$\mu_y$	$a_{y0}$	$a_{y0} + a_y$	$a_{y0} + 2a_y$	$a_{x0} + a_y$	$a_{y0} - a_y$	$a_{y0}$	$a_{y0} + a_y$	$a_{y0}$
$\mu_z$	$0$	$a_z$	$0$	$-a_z$	$a_z$	$2a_z$	$a_z$	$0$
$\phi_1$	$180^\circ$	$180^\circ$	$180^\circ$	$180^\circ$	$270^\circ$	$270^\circ$	$270^\circ$	$270^\circ$
$\phi_2$	$0^\circ$	$90^\circ$	$180^\circ$	$270^\circ$	$0^\circ$	$90^\circ$	$180^\circ$	$270^\circ$
$\mu_x$	$0$	$-a_x$	$-2a_x$	$-a_x$	$a_x$	$0$	$-a_x$	$0$
$\mu_y$	$a_{y0} - 2a_y$	$a_{y0} - a_y$	$a_{y0}$	$a_{y0} - a_y$	$a_{y0} - a_y$	$a_{x0}$	$a_{y0} + a_y$	$a_{x0}$
$\mu_z$	$0$	$a_z$	$0$	$-a_z$	$-a_z$	$0$	$-a_z$	$-2a_z$

where  $a_x = -Q \sin B \cos A$ ,  $a_{y0} = 2(P + Q \cos B) \cos A$   
 $a_y = Q \sin B \sin A$ , and  $a_z = Q \sin B$

(b) DIPOLE MOMENT FOR FREE ROTATION MODEL

If the potential energy curves for the rotators 1 and 2 do not depend on the rotational angles  $\phi_1$  and  $\phi_2$ , i.e., the potential energy  $V$  is constant for  $0 \leq \phi_1 \leq 2\pi$  and  $0 \leq \phi_2 \leq 2\pi$ , then the average value for  $\mu^2$  ( $\mu$  is the total dipole moment) can be expressed as

$$\begin{aligned}
 \langle \mu^2 \rangle &= \frac{\int_0^{2\pi} \int_0^{2\pi} \mu^2 \exp(-V/kT) d\phi_1 d\phi_2}{\int_0^{2\pi} \int_0^{2\pi} \exp(-V/kT) d\phi_1 d\phi_2} \\
 &= \frac{\int_0^{2\pi} \int_0^{2\pi} \mu^2 d\phi_1 d\phi_2}{\int_0^{2\pi} \int_0^{2\pi} d\phi_1 d\phi_2} \tag{2-4}
 \end{aligned}$$

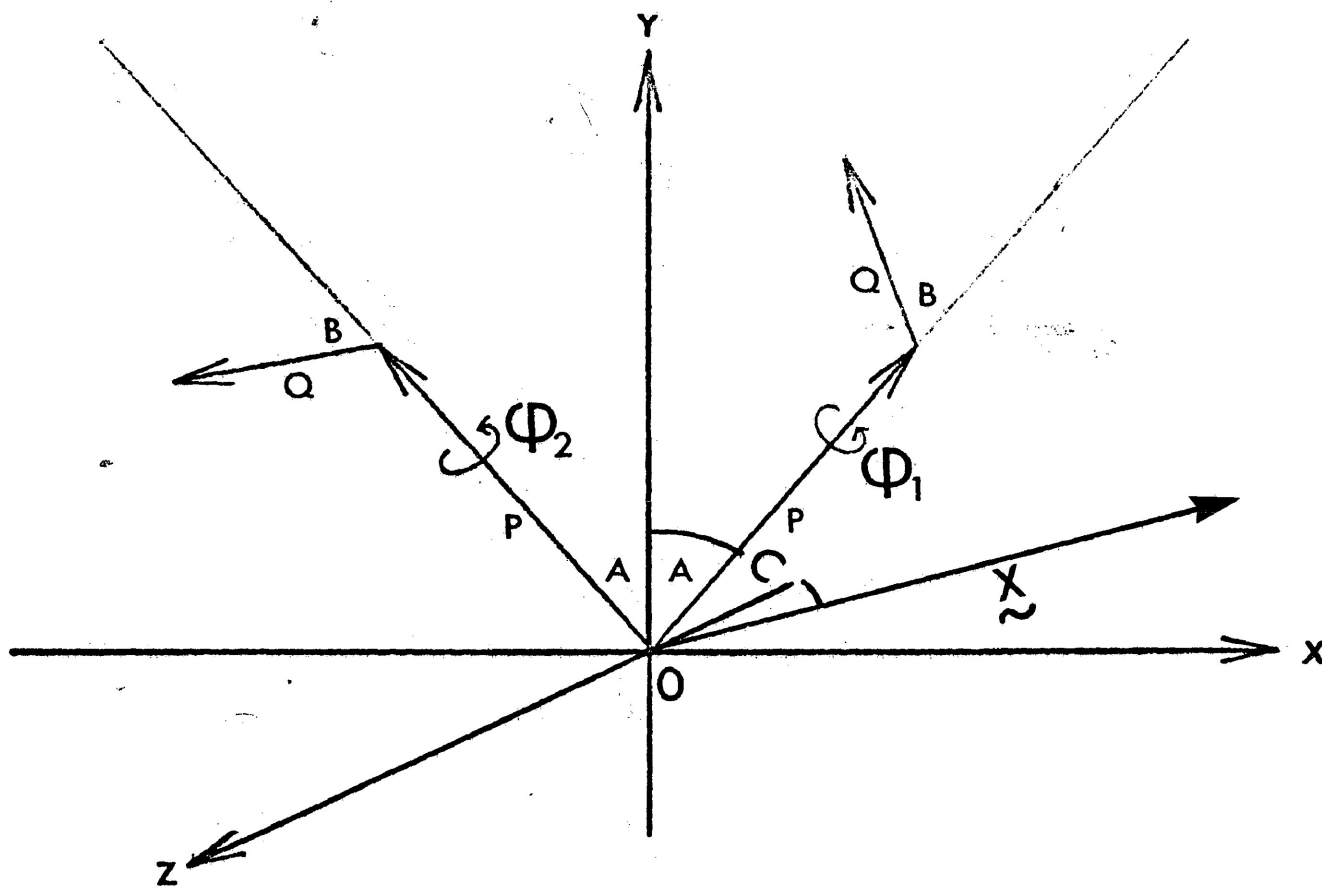


Figure 2-3: Coordinates for a rigid group and two equivalent rotational groups.  $X_2$  is the dipole moment of the rigid group, and  $C$  is its angle from the  $y$ -axis.

From Eqs. (2-3)

$$\mu^2 = \mu_x^2 + \mu_y^2 + \mu_z^2$$

Therefore for two equivalent rotators,  $\langle \mu^2 \rangle$  becomes

$$\langle \mu^2 \rangle = 4(P + Q\cos B)^2 \cos^2 A + 2Q^2 \sin^2 B \quad (2-5)$$

For <sup>a</sup> molecule which contains a rigid group in addition to the two equivalent rotational groups, <sup>the</sup> dipole moment coordinates may be taken as in Figure 3.

In this case,  $x\sin C$  and  $x\cos C$  are added to  $\mu_x$  and  $\mu_y$  in Eq. (2-3) respectively. Hence using Eq. (2-4) we have

$$\begin{aligned} \langle \mu^2 \rangle &= [2(P+Q\cos B)\cos A + x\cos C]^2 \\ &\quad + 2Q^2 \sin^2 B + x^2 \sin^2 C \end{aligned} \quad (2-6)$$

In the case when the rotational group of 2 exhibits free rotation while that of 1 is fixed at an angle  $\phi_1$ , then  $\langle \mu^2 \rangle$  may have the relation

$$\begin{aligned} \langle \mu^2 \rangle &= \frac{\int_0^{2\pi} \mu^2 d\phi_2}{\int_0^{2\pi} d\phi_2} \\ &= M_x^2 + M^2 + 2Q^2 \sin^2 B + 2Q\sin B (M\sin A - M_x \cos A) \cos \phi_1 \end{aligned} \quad (2-7)$$

where  $M_x = X\sin C$ ,  $M = 2(P+Q\cos B)\cos A + X\cos C$

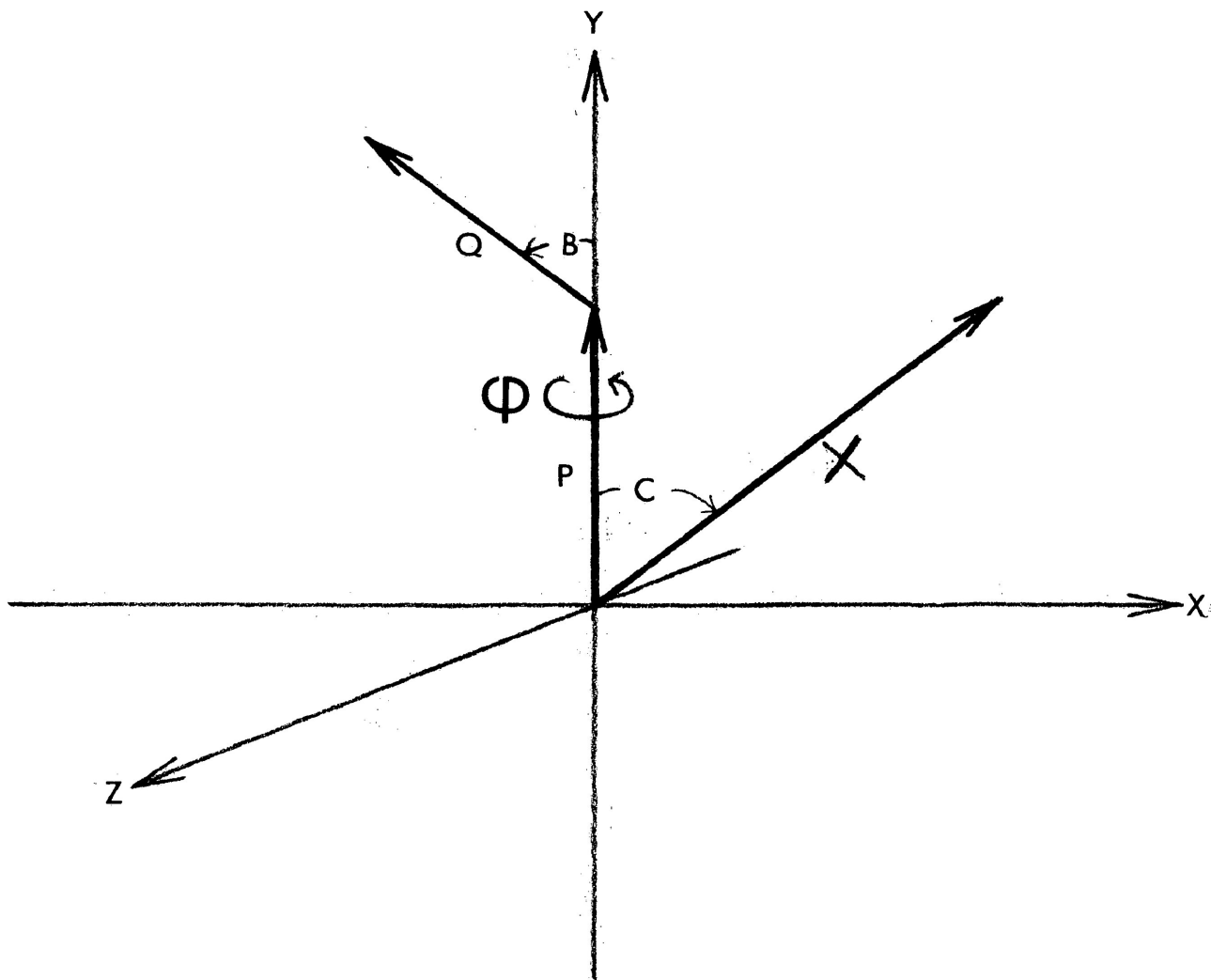


Figure 2-4: Coordinate system for a rotator and a rigid dipole.

For a molecule which has a rotational group and a rigid group, setting  $A = 0$  in Eq. (2-1) and taking <sup>the</sup> coordinate system as in Figure (2-4),  $\langle \mu^2 \rangle$  is given by

$$\langle \mu^2 \rangle = (P + Q\cos B + x\cos C)^2 + x^2\sin^2 C + Q^2\sin^2 B$$

In the case when two equivalent rotational groups have identical equilibrium potential minima at  $\phi_i = 0^\circ$  and  $180^\circ$  ( $i = 1$  and  $2$ ), then the total dipole moment would have the relation below;

$$\mu^2 = \frac{1}{4} \mu^2_{\substack{\phi_1=0^\circ \\ \phi_2=0^\circ}} + \frac{1}{4} \mu^2_{\substack{\phi_1=0^\circ \\ \phi_2=180^\circ}} + \frac{1}{4} \mu^2_{\substack{\phi_1=180^\circ \\ \phi_2=0^\circ}} + \frac{1}{4} \mu^2_{\substack{\phi_1=180^\circ \\ \phi_2=180^\circ}} \quad (2-8)$$

where  $\mu^2_{\substack{\phi_1=0^\circ \text{ or } 180^\circ \\ \phi_2=0^\circ \text{ or } 180^\circ}}$  stands for the square of dipole

moment at the corresponding angles.

From Table 2

$$\begin{aligned} \mu^2_{\substack{\phi_1=0^\circ \\ \phi_2=0^\circ}} &= (2a_x + M_x)^2 + (a_{y0} + M_y)^2 \\ \mu^2_{\substack{\phi_1=0^\circ \\ \phi_2=180^\circ}} &= (M_x^2 + (a_{y0} + M_y + 2a_y)^2 \\ \mu^2_{\substack{\phi_1=180^\circ \\ \phi_2=0^\circ}} &= M_x^2 + (a_{y0} + M_y - 2a_y)^2 \\ \mu^2_{\substack{\phi_1=180^\circ \\ \phi_2=180^\circ}} &= (M_x - 2a_x)^2 + (a_{y0} + M_y)^2 \end{aligned} \quad (2-9)$$

Where  $M_y = x\sin C$



Substitutions of Eqs. (2-9) in Eq. (2-8) give exactly the same equation as the right hand side of Eq. (2-6), i.e.,

$$\mu^2 = (a_{y0} + M_x)^2 + 2(a_x^2 + a_y^2) + M_x^2 \quad (2-10)$$

Similarly in the case when the rotational groups have identical equilibrium potential minima at  $\phi_i = 90^\circ$  and  $270^\circ$ , the total dipole moment has the relation;

$$\mu^2 = \frac{1}{4} \mu^2_{\substack{\phi_1=90^\circ \\ \phi_2=90^\circ}} + \frac{1}{4} \mu^2_{\substack{\phi_1=90^\circ \\ \phi_2=270^\circ}} + \frac{1}{4} \mu^2_{\substack{\phi_1=270^\circ \\ \phi_2=90^\circ}} + \frac{1}{4} \mu^2_{\substack{\phi_1=270^\circ \\ \phi_2=270^\circ}} \quad (2-11)$$

where notations will be seen from Eq. (2-8).

From table 1

$$\begin{aligned} \mu^2_{\substack{\phi_1=90^\circ \\ \phi_2=90^\circ}} &= \mu^2_{\substack{\phi_1=270^\circ \\ \phi_2=270^\circ}} = M_x^2 + (a_{y0} + M_y)^2 + 4a_z^2 \\ \mu^2_{\substack{\phi_1=90^\circ \\ \phi_2=270^\circ}} &= \mu^2_{\substack{\phi_1=270^\circ \\ \phi_2=90^\circ}} = M_x^2 + (a_{y0} + M_y)^2 \end{aligned} \quad (2-12)$$

Substitutions of Eq. (2-12) in Eq. (2-11) lead to Eq. (2-10).

Therefore it is seen that Eq. (2-6) which results from the assumption of "free rotation" can be simultaneously derived from the above two cases so that in<sup>a</sup> discussion of dipole moment such a fact should be taken into account. It is readily shown that this result is also applicable to the dipole moment analysis of a molecule which has a rotational group and a rigid group.

(c) DIPOLE MOMENT FOR "FREE OSCILLATION"

In the previous section, we have introduced a horizontal potential energy line against rotational angle to obtain the average of dipole moment assuming "free rotation". But here we shall introduce a square pulse potential whose height  $W$  is very large in comparison with the agitation energy  $kT$ .

In order to introduce an idea of "free oscillation" and to understand it, let us consider internal rotation of <sup>the</sup> methoxy group of *o*-chloro anisole as an example. From Eq. (2-1), the square of dipole moment for the molecule is given by

$$\mu^2 = M_x^2 + Q^2 \sin^2 B + \mu_y^2 + 2M_x Q \sin B \cos \phi \quad (2-13)$$

where  $M_x = M_{C-Cl} \sin 60^\circ$ ,  $M_y = \mu_{C-Cl} \cos 60^\circ$ ,  $Q = -\mu_{OCH_3}$ ,  $P = \mu_{CO}$ ,

$B = 180^\circ - \angle COC$ , and  $\mu_y = P + Q \cos B + M_y$

In this molecule, the steric repulsion near  $\phi = 0^\circ$  would be expected so that a square pulse potential as in Figure 1 may be approximately taken into account for rotation of the methoxy group with neglect of possible mesomeric effect.

The average square dipole moment in this case is, therefore, given by;

$$\langle \mu^2 \rangle = \frac{\int_0^{\frac{\pi}{2}-\Delta} \mu^2 e^{-\frac{W}{kT}} d\phi + \int_{\frac{\pi}{2}-\Delta}^{\frac{3\pi}{2}+\Delta} \mu^2 e^{-\frac{V}{kT}} d\phi + \int_{\frac{\pi}{2}+\Delta}^{2\pi} \mu^2 e^{-\frac{W}{kT}} d\phi}{\int_0^{\frac{\pi}{2}-\Delta} e^{-\frac{W}{kT}} d\phi + \int_{\frac{\pi}{2}-\Delta}^{\frac{3\pi}{2}+\Delta} e^{-\frac{V}{kT}} d\phi + \int_{\frac{\pi}{2}+\Delta}^{2\pi} e^{-\frac{W}{kT}} d\phi}$$

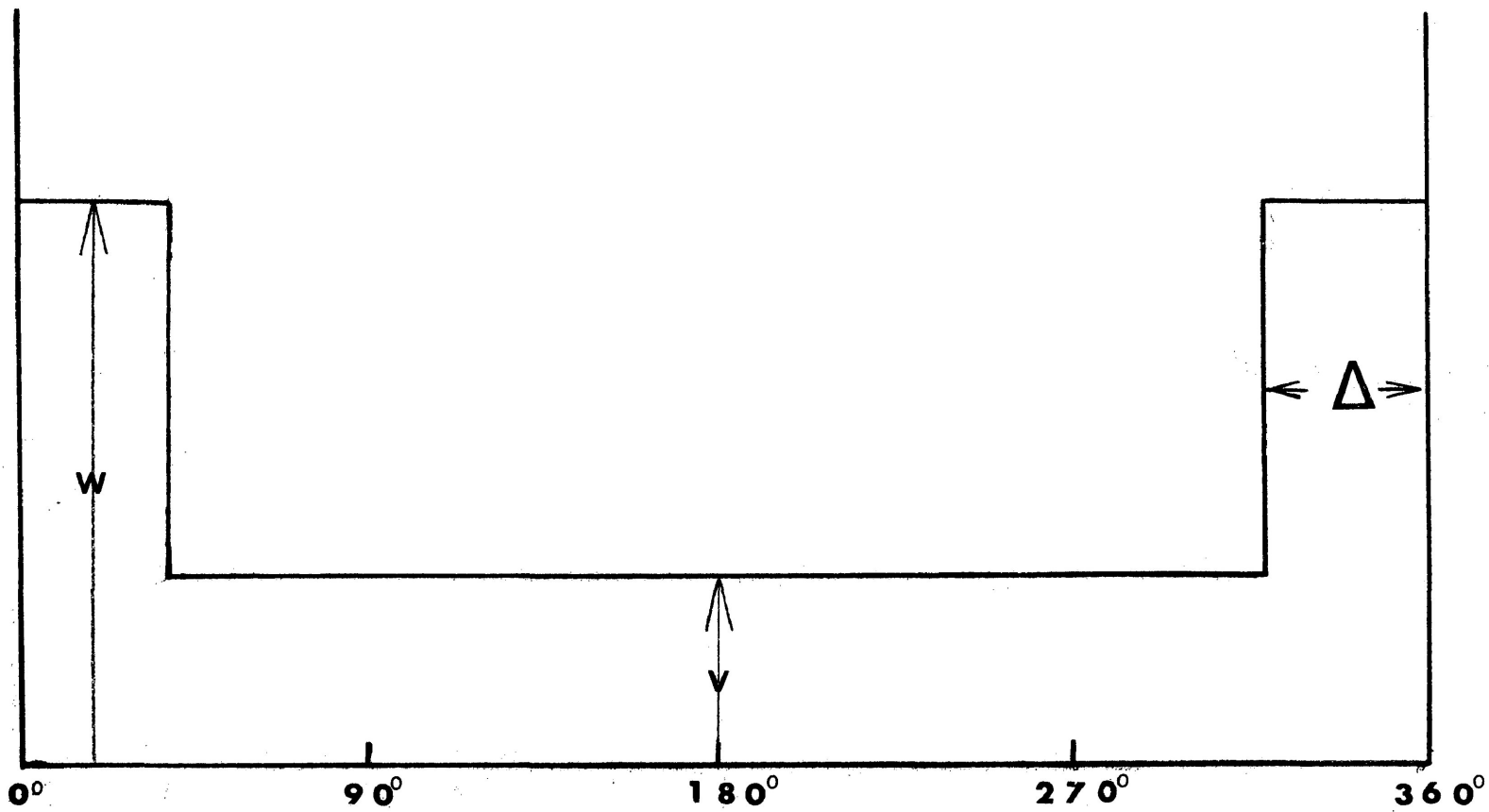


Figure 1: A square pulse potential.

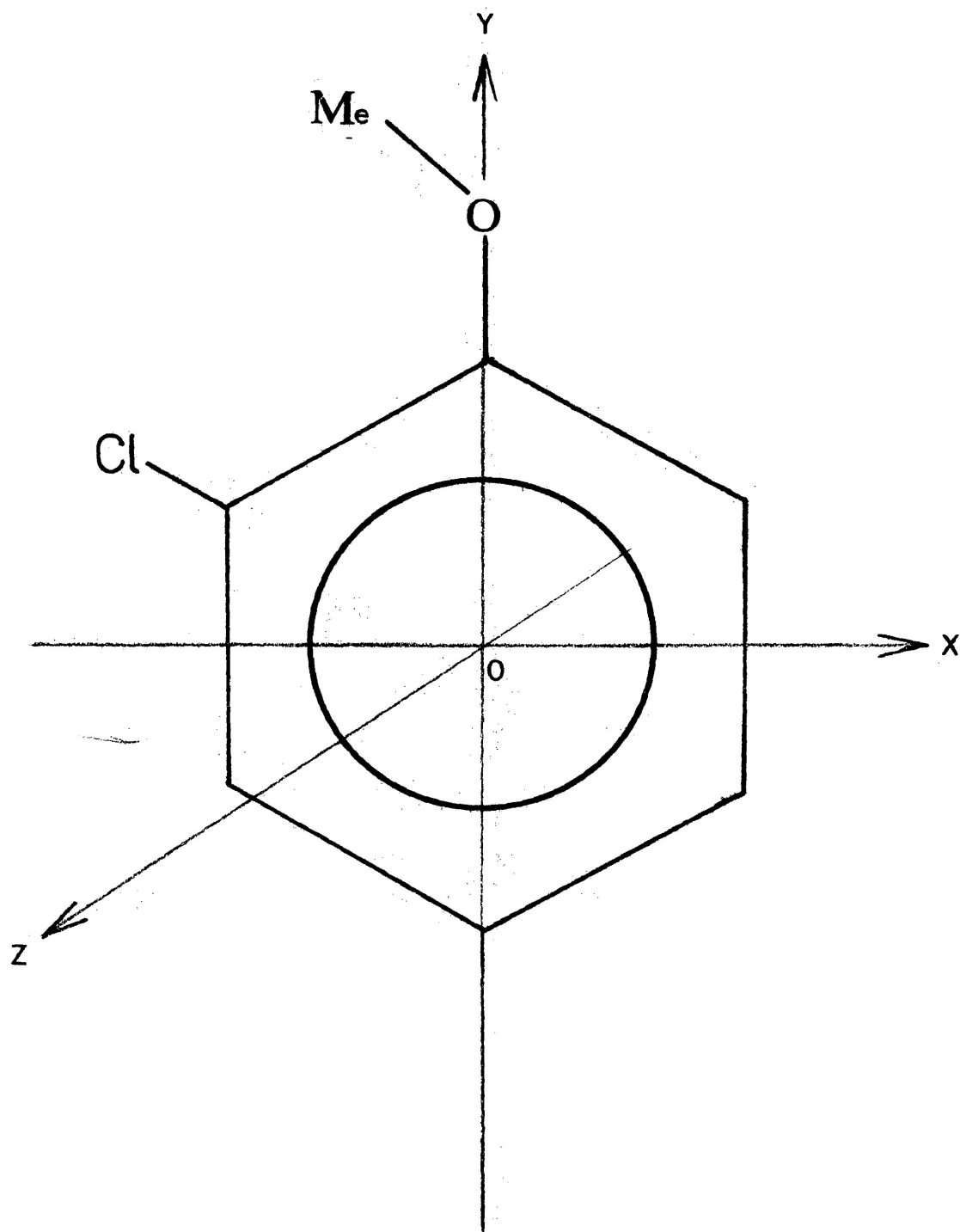


Figure 2: Coordinate system of o-chloroanisole corresponding to  $\phi = 0$

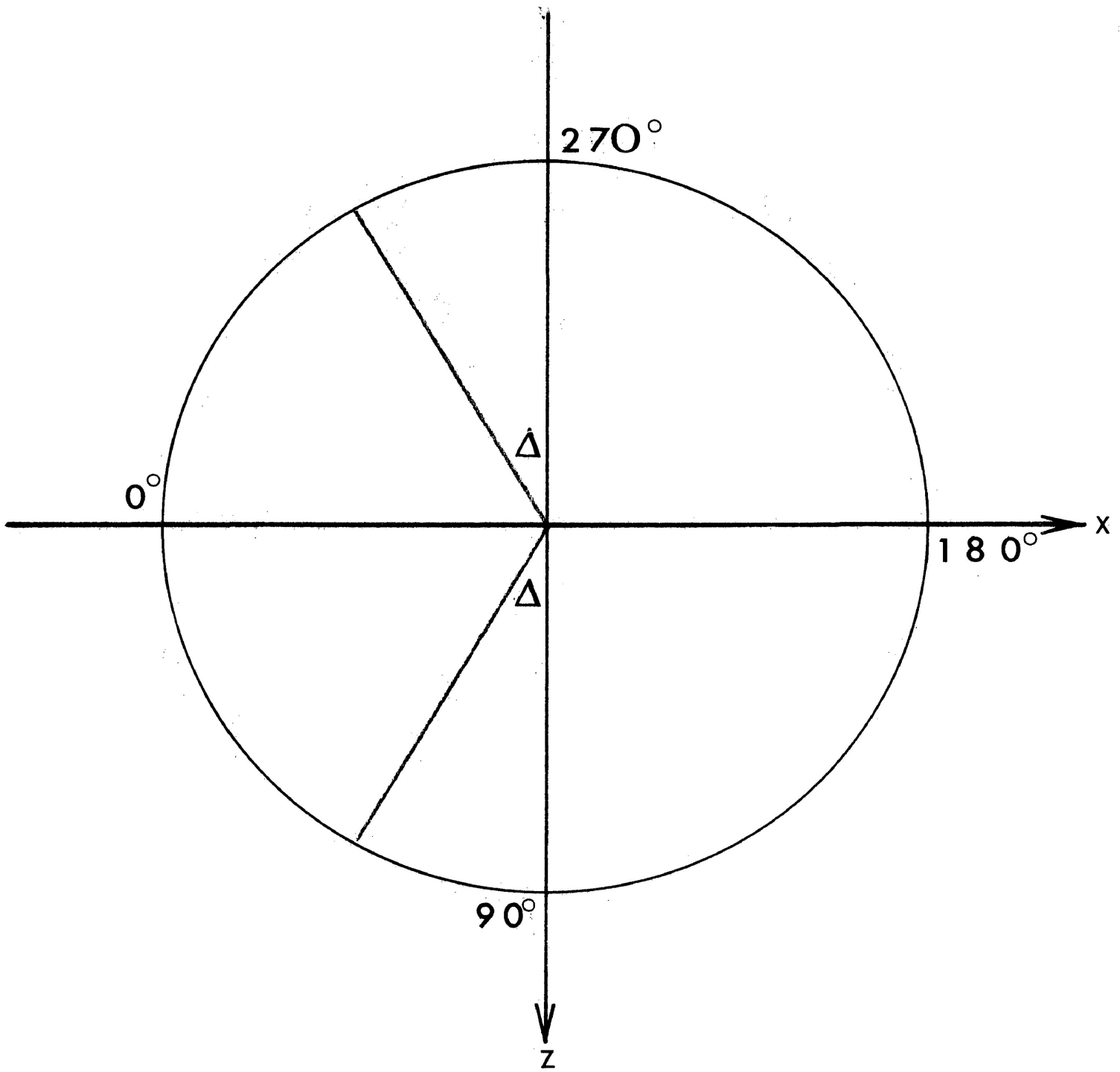


Figure 3: Definition of  $\Delta$

Now if it is assumed that  $W \gg kT$ , then

$$\langle \mu^2 \rangle = \frac{\int_{\frac{\pi}{2}-\Delta}^{\frac{3\pi}{2}+\Delta} \mu^2 e^{-\frac{V}{kT}} d\phi}{\int_{\frac{\pi}{2}-\Delta}^{\frac{3\pi}{2}+\Delta} e^{-\frac{V}{kT}} d\phi} = \frac{\int_{\frac{\pi}{2}-\Delta}^{\frac{3\pi}{2}+\Delta} \mu^2 d\phi}{\int_{\frac{\pi}{2}-\Delta}^{\frac{3\pi}{2}+\Delta} d\phi}$$

$$= M_x^2 + \mu_y^2 + Q^2 \sin^2 B - 4M_x Q \sin B \cdot \frac{\cos \Delta}{\pi + 2\Delta} \quad (2-14)$$

It is clear that  $\Delta=90^\circ$  gives  $\langle \mu^2 \rangle$  for free rotation. Hence it will be seen from Eq. (2-14) that the observed dipole moment of this molecule would be greater than the moment for free rotation, if the above assumptions are satisfactory. ( $Q < 0$  and  $\cos \Delta \geq 0$  for  $-90^\circ < \Delta \leq 90^\circ$ ). This is satisfied for o-haloanisoles and o-halothioanisoles as seen from Tables I and II. Using observed moments and Eq. (2-14), it is possible to evaluate  $\Delta$  values, which are also collected in Tables I and II. It is interesting to note that  $(90^\circ - \Delta)$  increases with the atomic radius of <sup>the</sup> o-substituent, which is expected from the steric repulsion. Eq. (2-14) is also applied to similar evaluations for m-halothioanisoles

Table I: Observed Dipole Moments  $\mu_{\text{obs}}$ , Dipole Moments for Free Rotation  $\sqrt{\langle \mu^2 \rangle}$ , and  $\Delta$ 's of o-haloanisoles, X  $\text{C}_6\text{H}_5\text{OCH}_3$ .

X	F	Cl	Br
$\mu_{\text{C-X}} \text{ (D)}^{12}$	1.46	1.58	1.54
$\mu_{\text{obs}} \text{ (D)}^{13}$	2.31	2.50	2.47
$\sqrt{\langle \mu^2 \rangle} \text{ (D)}$	2.09	2.19	2.16
$\Delta^\circ$	37	18	16

$\mu_{C-O} = 0.95$  (D),  $\mu_{O-CH_3} = 1.11$  (D), and  $\text{COC} = 110^\circ$  are used.

Table II: Observed Dipole Moments  $\mu_{\text{obs}}$ , Dipole Moments for Free Rotation  $\sqrt{\langle \mu^2 \rangle}$ , and  $\Delta$ 's of o-halothioanisole X  $\text{C}_6\text{H}_5\text{SCH}_3$ .

X	Cl	Br
$\mu_{\text{obs}}$ (D) <sup>14</sup>	2.56	2.53
$\sqrt{\langle \mu^2 \rangle}$ (D)	2.23	2.20
$\Delta^\circ$	27	26

(Dipole moment of 1.38 (D) for thioanisole and group moment angle of  $75^\circ$  for  $-\text{SH}_3$  are used<sup>15</sup>) and m-halothiophenols with small changes of calculation procedures. These are collected in Tables III and IV. It should be pointed out that for all these compounds,  $\Delta$  becomes almost  $90^\circ$ . Therefore it can be said that the steric repulsions for these compounds are negligible so that the rotational groups ( $-\text{SCH}_3$  and  $-\text{S-H}$ ) may mainly exhibit free rotation. This may also be supported by agreement between the observed moment of p- $\text{CH}_3\text{S-C}_6\text{H}_5\text{-SCH}_3$ <sup>14</sup> (1.85 D) and  $\sqrt{\langle \mu^2 \rangle} = 1.89$  (D) for free rotation.

Table III: Observed Dipole Moments  $\mu_{\text{obs}}$  and Dipole Moments for Free Rotation  $\sqrt{\langle \mu^2 \rangle}$  of m-halothioanisoles, M - X  $\text{C}_6\text{H}_5\text{SCH}_3$ .

X	Cl	Br
$\mu_{\text{obs}}$ (D) <sup>14</sup>	1.89	1.85
$\sqrt{\langle \mu^2 \rangle}$ (D)	1.96	1.93

Table IV: Observed Dipole Moments  $\mu_{\text{obs}}$  and Dipole Moments for Free Rotation of m-halothiophenols, M - X C<sub>6</sub>H<sub>5</sub>SH.

X	Cl	Br
$\mu_{\text{obs}}$ (D) <sup>14</sup>	1.56	1.51
$\sqrt{\langle \mu^2 \rangle}$ (D)	1.61	1.59

Dipole moment of 1.19 (D) and group moment angle of <sup>15</sup> 46° for -SH are used.

Table V: Observed Dipole Moments  $\mu_{\text{obs}}$  and Dipole Moments for Free Rotation of o-halothiophenols, O - X C<sub>6</sub>H<sub>5</sub>SH.

X	Cl	Br
$\mu_{\text{obs}}$ (D) <sup>14</sup>	1.98	1.96
$\sqrt{\langle \mu^2 \rangle}$ (D)	2.28	2.25

Similar calculations are made for o-halothiophenols and the results are listed in Table V. It will be seen from Table V that  $\mu < \sqrt{\langle \mu^2 \rangle}$ , which suggests that the assumptions used to derive Eq. (2-14) are no longer valid for o-halothiophenols. This may be due to intramolecular hydrogen bonding.

Now let us apply the above considerations to a molecule which has two equivalent rotational groups and one rigid substituent. (for example 6-chloro-1,4-dimethoxybenzene (Chap. 4 (b))).



It is assumed that one of the two rotational groups exhibits free rotation and the other (2) <sup>undergoes</sup> free oscillation. From Eq. (2-3)

$$\begin{aligned}\mu_x &= X \sin C - Q \sin B \cos A (\cos \phi_1 + \cos \phi_2) \\ \mu_y &= 2(P + Q \cos B) \cos A + X \cos C + Q \sin B \sin A (\cos \phi_1 - \cos \phi_2) \\ \mu_z &= Q \sin B (\sin \phi_1 + \sin \phi_2)\end{aligned}\quad (2-15)$$

In this case,  $\langle \mu^2 \rangle$  corresponding to the left hand side of Eq. (2-4) may be defined by

$$\langle \mu^2 \rangle = \frac{\int_0^{2\pi} d\phi_2 \int_{\frac{\pi}{2} - \Delta}^{\frac{3\pi}{2} + \Delta} \mu^2 d\phi_1}{\int_0^{2\pi} d\phi_2 \int_{\frac{\pi}{2} - \Delta}^{\frac{3\pi}{2} + \Delta} d\phi_1}\quad (2-16)$$

$\mu^2 = \mu_x^2 + \mu_y^2 + \mu_z^2$  can be calculated from Eq. (2-15), and substitution of  $\mu^2$  in Eq. (2-16) gives

$$\begin{aligned}\langle \mu^2 \rangle &= M_x^2 + M^2 + 2Q^2 \sin^2 B \\ &\quad \pm 4Q \sin B (M_x \cos A - M \sin A) \frac{\cos \Delta}{\pi + 2\Delta}\end{aligned}\quad (2-17)$$

where  $M_x = X \sin C$ ,  $M = 2(P + Q \cos B) \cos A + M_y$ , and + for  $C \leq A$  and - for  $C \geq A$ .

For 6-chloro-1,4-dimethoxybenzene,  $X = 1.6$  (D),  $B = 70^\circ$ ,  $P = 0.95$  (D),  $C = 30^\circ$ ,  $Q = -1.11$  (D),  $A = 90^\circ$ , and  $\mu_{\text{obs}} = 2.47$  (D) =  $\sqrt{\langle \mu^2 \rangle}$  gives  $\Delta = 22^\circ$ , which is in good agreement with  $\Delta = 18^\circ$  of o-chloroanisole (see Table I).

The above models are only a few applications of the "free oscillation" <sup>treatment</sup>. It can be also used for other systems without meeting mathematical difficulties.

## CHAPTER 3 Experimental

### (a) *APPARATUS*

The dielectric constant and loss were measured at 145, 70, 35.11, 23.98, 16.2, 9.313 (GHz) and 2 (MHz) as well as 1 ~ 3 (MHz) range with the apparatus<sup>16-25</sup> available in this laboratory. The experimental techniques required for the measurements are excellently described by some of the workers in this laboratory. The results are collected in "Appendices".

### (b) *PURIFICATION OF MATERIAL*

P-Xylene (solvent) was distilled with sodium wire, and kept in amber bottles with sodium wire. Liquids (solute) were dried by suitable drying agents and distilled under vacuum. 2-2'- and 3-3'-difuryl mercuries were synthesized by Mr. Bordan Drupay, Department of Chemistry, Lakehead University, Canada. Other chemicals were obtained commercially.

### (c) *DIELECTRIC PARAMETERS*

The experimentally obtained dielectric constant  $\epsilon'$  and loss  $\epsilon''$  were corrected with usual procedure and fitted to Cole-Cole equation<sup>26</sup> firstly.

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

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

(3-1)

From these equations,  $\tau_0$ ,  $\alpha$ , and  $\epsilon_\infty$  were determined. Using this  $\epsilon_\infty$ , the same data were also fitted to Budd's equation<sup>27</sup>.

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

(3-2)

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

where  $C_1 + C_2 = 1$ .

For a system of  $\alpha \approx 0$ , the above calculation procedures necessarily requires the following approximation;

$$\frac{1}{1 + i\omega\tau_0} \approx \frac{C_1}{1 + i\omega\tau_1} + \frac{C_2}{1 + i\omega\tau_2}$$

$$C_1 + C_2 = 1 \tag{3-3}$$

The right and left hand sides in Eq. (3-3) are Debye's and Budd's equations, respectively. Eq. (3-3) leads to

$$(\tau_0 - C_1\tau_1 - C_2\tau_2) i\omega + \left\{ \tau_1\tau_2 - \tau_0(C_1\tau_2 + C_2\tau_1) \right\} \omega^2 \approx 0 \quad (3-4)$$

In order to satisfy Eq. (3-4), irrespective of frequency  $0 < \omega < \infty$ , it is necessary that the first and second terms in brackets should be zero simultaneously.

Therefore,

$$\tau_0 \approx C_1\tau_1 + C_2\tau_2 \quad (3-5)$$

$$\tau_0 \approx \frac{\tau_1\tau_2}{C_1\tau_2 + C_2\tau_1} \quad (3-6)$$

These two equations can be used to the above Cole-Cole and Budd's analyses to avoid improbable results. Setting "=" in the places of "≈" in Eqs. (3-3), (3-4), (3-5) and (3-6), we have exact answers, e.g.,  $\tau_0 = \tau_2$  and  $C_1 = 1$  or  $\tau_0 = \tau_1$  and  $C_2 = 1$ , which do not tell anything useful.

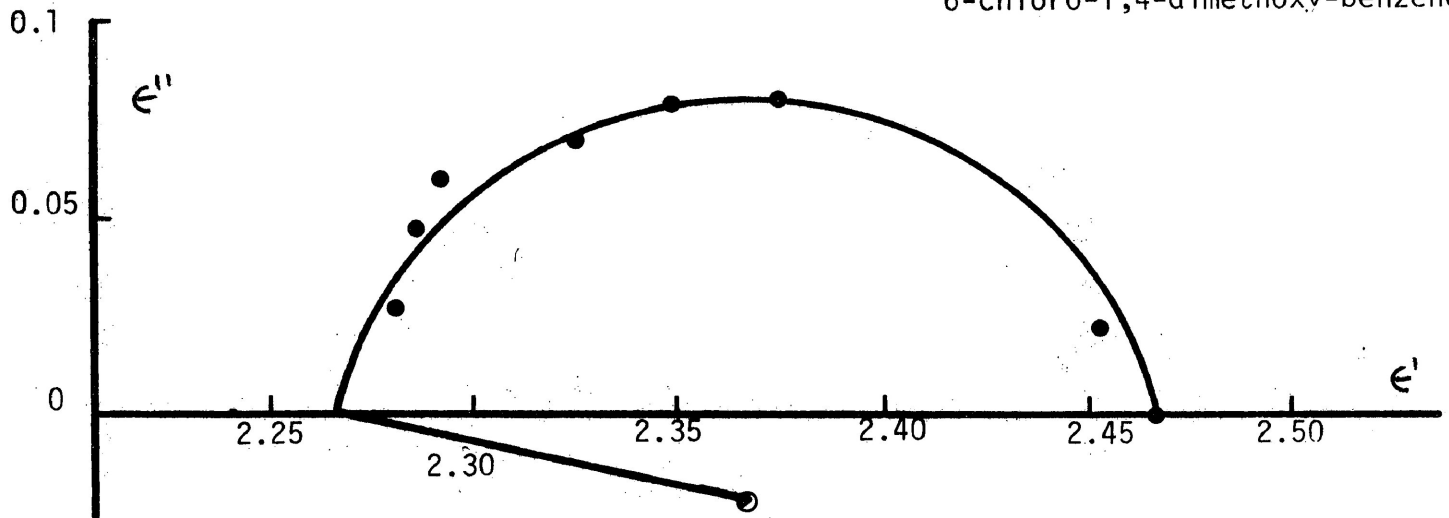
In calculating the above dielectric parameters, the usual procedures<sup>16-28</sup> in this laboratory were used.

Dipole moment  $\mu$  was evaluated with the help of the equation<sup>16-25</sup>,

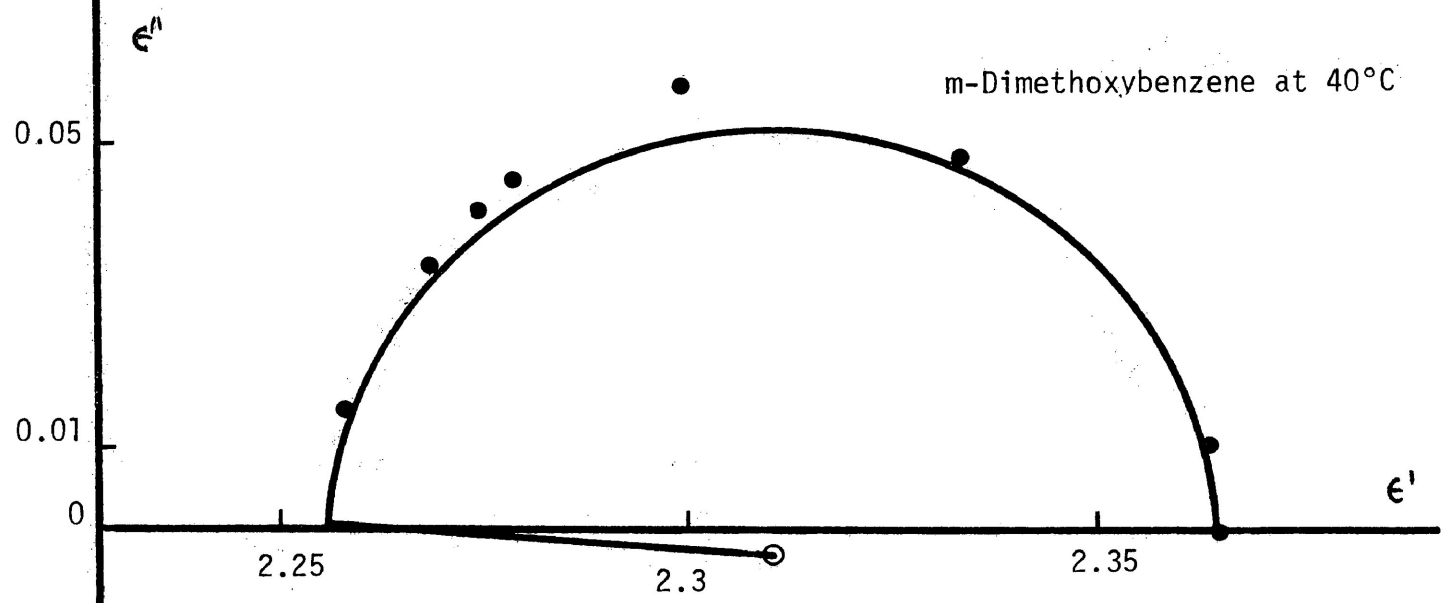
$$\mu = \sqrt{\frac{3T(\epsilon_0 - \epsilon_\infty)M_2}{(\epsilon_1 + 2)^2 W_2 d_1}}$$

where  $M_2$  is the molecular weight of solute,  $W_2$  the weight fraction of solute, and  $d_1$  and  $\epsilon_1$  are the density and dielectric constant of solvent, respectively.

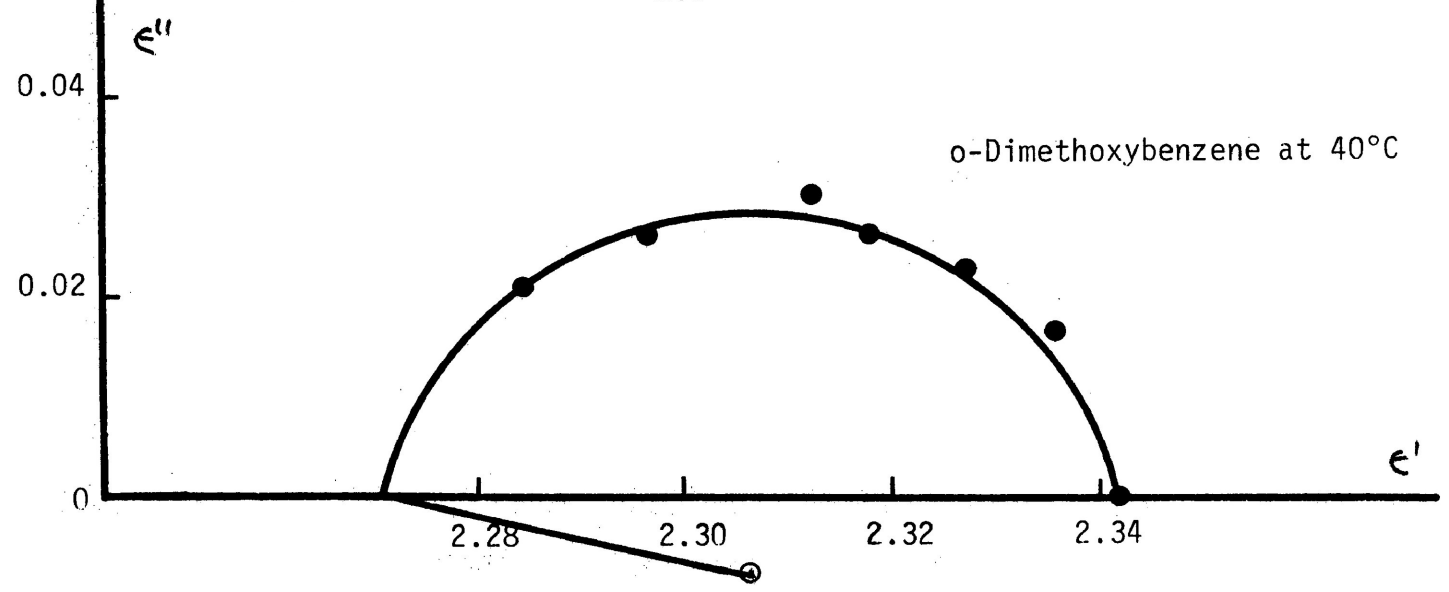
6-chloro-1,4-dimethoxy-benzene

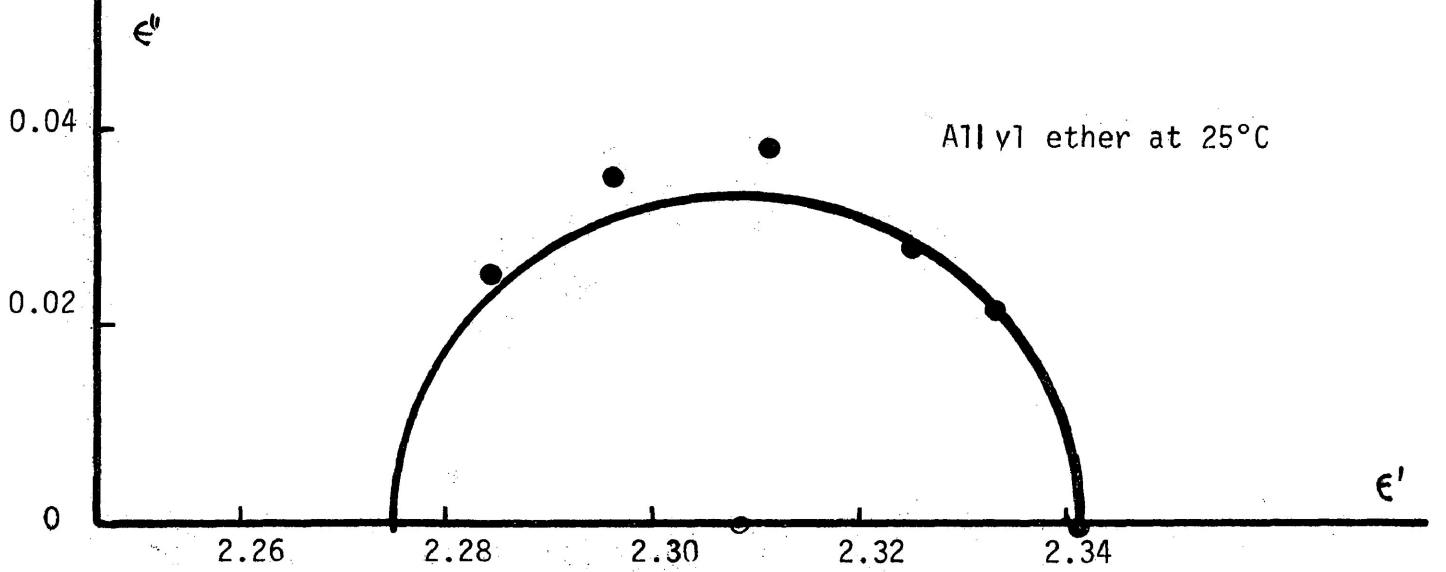
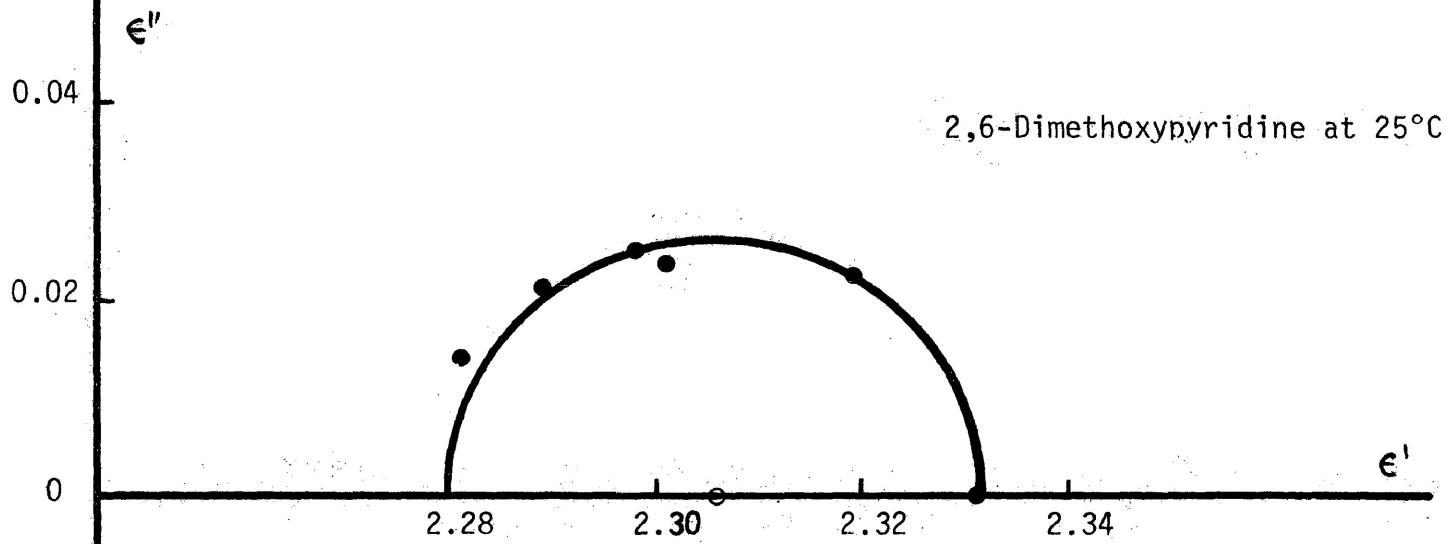
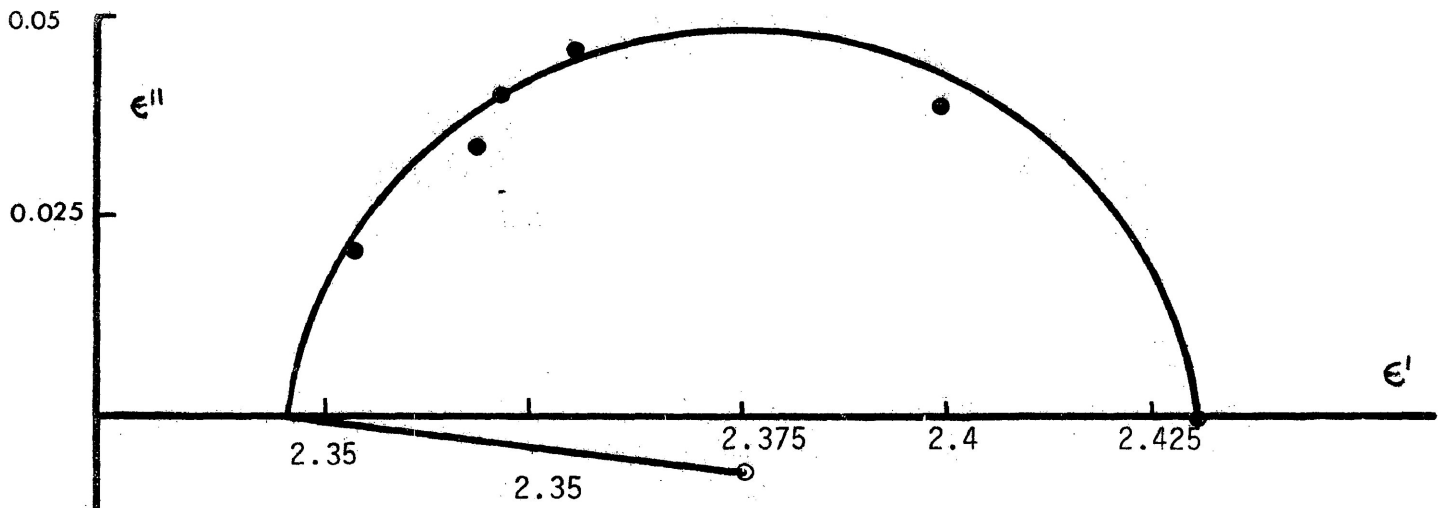


m-Dimethoxybenzene at 40°C



o-Dimethoxybenzene at 40°C







## (a) INTRODUCTION

The methoxy group attached to benzene usually exhibits hindered rotation<sup>20,21</sup>. Anisole should be firstly considered here. One of most important features for the molecule is <sup>that</sup> two values for Budo's  $C_1$  exist in the literature, i.e., Farmer and Walker<sup>29</sup>, Forest and Smyth<sup>30</sup>, and Klages and Krauss<sup>31</sup> report  $C_1 = 0.33$  or  $0.15$ , (in p-xylene),  $C_1 = 0.20$  (in benzene) and  $C_1 = 0.17$  (in mesitylene, benzene and carbon disulphide), respectively, whereas Vaughan and Smyth<sup>32</sup>, Vaughan, Roeder and Provder<sup>33</sup>, Garg and Smyth, Kranbuehl, Klug and Vaughan<sup>35</sup> report  $C_1 = 0.80, 0.77, 0.78$  (pure liquid anisole) and  $0.8$  (in benzene), respectively. The last authors measured the dielectric parameters of anisole-benzene mixtures, changing concentration, temperature and frequency to examine <sup>the</sup> internal field effect on  $C_1$  and concluded that the contribution from the effect is very small. As seen from Table 4-1, the  $\tau_2$  value for anisole is about  $7 \sim 8$  psec at room temperature. Farmer<sup>20</sup> reported that the relaxation times of diethyl ether and diethyl ketone are  $2.7$  and  $2.9$  psec. respectively, in cyclohexane at  $15^\circ\text{C}$ . In addition, he also reported the  $\tau_2$  values of benzylchloride are  $2.6, 4.7,$  and  $3.6$  psec at  $15, 25$  and  $50^\circ\text{C}$ , respectively, in p-xylene. In view of the molecular shape and size, the  $\tau_2$

of anisole accounted for the relaxation time of methoxy group, therefore, appears to be too long. P-dimethoxybenzene is expected to have a single relaxation time (Chap. 1 (c) (ii)) which is mainly connected with the re-orientation of the methoxy group. Literature values of relaxation times for the compound are given in Table 4-2. It is seen that the relaxation time of the compound is about 6 ~ 7 psec. in normal solvent (benzene, p-xylene, cyclohexane and carbontetrachloride etc.) at room temperature. This value is very close to the  $\tau_2$  of anisole so that it is assigned to the relaxation time of <sup>the</sup> methoxy group. This conclusion is drawn from the variation of the mean relaxation time of p-dimethoxybenzene upon the viscous solvents like nujol and decalin. If the relaxation is due to the dipole orientation of the over all molecule by an introduction of electric field, the relaxation time would be dependent on viscosity of a solvent directly, while if the relaxation results from the orientation of intramolecular dipole, the relaxation time would not depend on the viscosity so strong as the former case.

Klages and Knobloch report  $\tau_2 = 1.7$  for 1-methoxy-naphthalene ( $C_1=0.93$ ) and  $\tau_2 = 1.1$  for 2-methoxynaphthalene ( $C_1=0.8$ ) in benzene at 20°C, while Vaughan, Roeder and Provder report  $\tau_2 = 2.3$  ( $C_1=0.87$ ) at 20°C and  $\tau_2 = 1.0$  ( $C_1=0.8$ ) at 80°C for 1-methoxy-naphthalene and 2-methoxynaphthalene, respectively, as pure liquid (see Table 1). The literature values for the relaxation

times of o- and m-dimethoxybenzenes are collected, in Table 4-3. It is of interest to note that the  $\tau_2$  value of <sup>the</sup> o-compound is about 3 (psec.) while that of <sup>the</sup> m-compound is about 2 (psec.). The  $\tau_2$  values for both compounds are roughly 1/2 of that for anisole or shorter.

Roberti and Smyth<sup>37</sup> (D. M. Roberti and C. P. Smyth, J. Am. Chem. Soc., 82, 2106 (1960)) obtained two discrete Cole-Cole arcs for pure o-dimethoxybenzene at 25°C and assigned 3.7 psec. and 69 psec. to the high and low frequency relaxations.

TABLE 4-1: Dielectric Parameters of Anisole

Mole fraction	Solvent	t(°C)	$\tau_0$ (psec)	$\tau_1$	$\tau_2$	$C_1$	Ref.
	p-xylene	15	10.8	79	9.6	0.15	29
	p-xylene	25	9.0	40	8.0	0.15	
	p-xylene	40	7.7	14	6.8	0.15	
	p-xylene	50	6.7	11	5.8	0.15	
	p-xylene	60	5.8	12	4.9	0.15	
	p-xylene	15	10.8	13.3	9.1	0.33	
	p-xylene	25	9.0	14.6	7.0	0.33	
	p-xylene	40	7.7	11.4	5.9	0.33	
	p-xylene	50	6.7	9.6	5.1	0.33	
	p-xylene	60	5.8	9.2	4.3	0.33	
1.000	B <sub>Z</sub>	20		12.2	1.17	0.81	35
0.856	B <sub>Z</sub>	20		11.5	0.80	0.79	
0.721	B <sub>Z</sub>	20		12.4	2.28	0.75	
0.549	B <sub>Z</sub>	20		13.5	4.09	0.62	
0.329	B <sub>Z</sub>	20		11.1	2.18	0.70	
1.000	B <sub>Z</sub>	40		10.3	1.43	0.76	
0.846	B <sub>Z</sub>	40		9.0	0.85	0.78	
0.721	B <sub>Z</sub>	40		10.0	2.34	0.69	
0.549	B <sub>Z</sub>	40		9.1	1.49	0.72	
0.329	B <sub>Z</sub>	40		10.2	2.34	0.57	

TABLE 4-2: Literature Value of Relaxation of p-Dimethoxybenzene

Solvent	t°	$\tau_0$ (psec)	$\tau_1$ (psec)	$\tau_2$ (psec)	C <sub>1</sub>	Ref.
B <sub>Z</sub>	20	6.2				39
B <sub>Z</sub>	40	5.2				39
B <sub>Z</sub>	60	4.6				39
B <sub>Z</sub>	20	9.7				37
B <sub>Z</sub>	40	6.4				37
B <sub>Z</sub>	60	4.6				37
B <sub>Z</sub>	20		8.5	0.75	0.73	40
B <sub>Z</sub>	25	6.9				41
B <sub>Z</sub>	20			8.35		31
Xylene	15	6.3				
Decalin	20	17.5	31.6	13.8	0.19	42
Decalin	40	13.3	27.5	11.0	0.17	42
Decalin	60	9.8	21.9	9.6	0.16	42
Nujol	20	20.0	112	14.0	0.22	42
Nujol	40	14.8	97	10.5	0.18	42
Nujol	60	11.6	40	7.2	0.15	42
Pure	60		8.5	0.7	0.87	33
Liquid	80		6.2	0.9	0.88	33
Cyclohexane	15	8.3				20
Cyclohexane	25	6.9				20
Cyclohexane	40	5.7				20
Cyclohexane	50	4.9				20
Mesitylene	70			5.1		31
Mesitylene	20			10.9		31
Mesitylene	0			16.7		31
Mesitylene	-30			36.2		31

TABLE 4-3: Dielectric Parameters for o- and m-dimethoxybenzenes  
in the Literature

o-dimethoxybenzene

<u>t(°C)</u>	<u><math>\tau_1</math>(psec)</u>	<u><math>\tau_2</math>(psec)</u>	<u>C<sub>1</sub></u>	<u>Ref.</u>
25	53.1	3.7	0.25	32
20*	12.8	1.3	0.76	36
25	48.5	3.5	0.30	33
40	39.4	3.4	0.24	33
60	25.2	2.3	0.22	33

<u>m-dimethoxybenzene</u>	<u><math>\tau_1</math>(psec)</u>	<u><math>\tau_2</math>(psec)</u>	<u>C<sub>1</sub></u>	<u>Ref.</u>
60	15.9	2.3	0.80	32
20*	14.7	0.6	0.16	36
20	32.8	2.1	0.89	33
40	24.6	2.4	0.81	33
60	16.3	2.7	0.79	33

\* were measured in benzene solution.

TABLE 4-4: Dielectric Parameters of Dimethoxy Compounds in  
p-xylene

	$t$	$\tau_0$	$\alpha$	$\tau_1$	$\tau_2$	$C_1$	$\mu$
Dimethoxymethane	25	3.5	0				0.58
1,2-Dimethoxyethane	25	3.0	0				1.55
4-4 Dimethoxybiphenyl	25	5.2	0				1.86
o-Dimethoxybenzene	40	3.8	0.12	6.26	1.43	0.63	1.30
m-Dimethoxybenzene	40	10.1	0.07	13.7	3.6	0.71	1.54
6-chloro-1,4-dimethoxybenzene	40	14	0.16	17.2	4.2	0.78	2.47
2,6-Dimethoxyridine	25	9.0	0.05	12.7	4.8	0.67	0.94
4,4-Dimethoxythio- benzophenone	25	46.6	0	62.1	10.	0.87	3.83
5,6-Dimethoxy-1-indanone	25			50 45	2.94 5.7*	0.90	3.30
2,5-Dimethoxy-2,5-dihydro- furan	25	11.0	0				1.63
2,5-Dimethoxytetra- hydrofuran	40	9.7	0	10.4	2.2	0.73	1.12

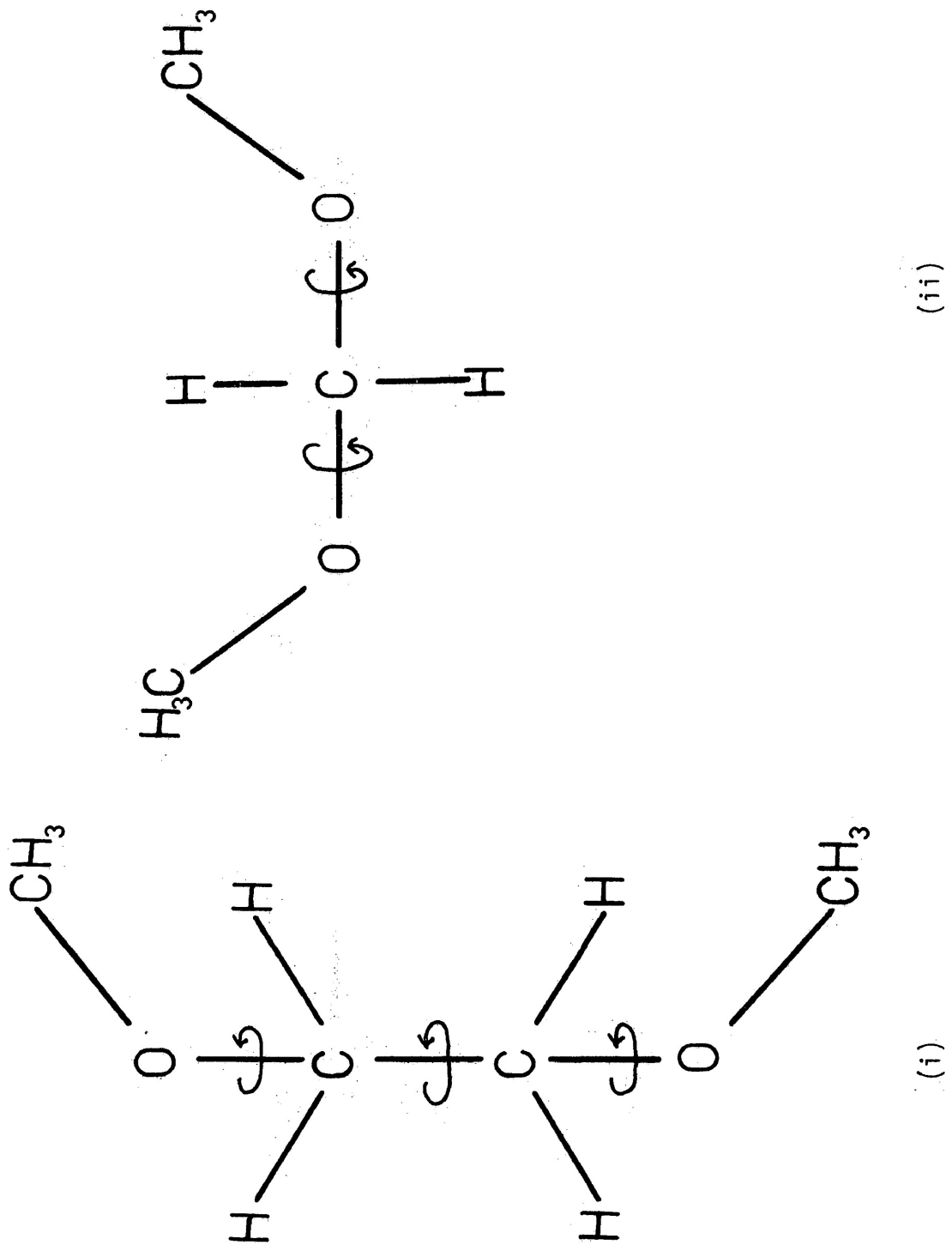
(b) *RESULTS AND DISCUSSION*

The results of the present work for dimethoxy compounds are collected in Table 4-4.

Dimethoxymethane has  $\tau_0 = 3.5$  (psec),  $\alpha \sim 0$  and  $\mu = 0.58$  (D) at 25°C in p-xylene while 1,2-dimethoxyethane has  $\tau_0 = 3.0$  (psec)

$\alpha \sim 0$  and  $\mu = 1.55$  (D) at the same conditions. In view of molecular volume, the latter compound is expected to have a longer relaxation time than the former. Dimethoxymethane has two degrees of freedom for its internal rotation which influences the value of the observed dipole moment as seen from Figure 4-1, whereas, 1,2-dimethoxyethane has three degrees of freedom. In 1,2-dimethoxyethane the steric effect and electrostatic repulsion make the internal rotation around  $-\text{CH}_2 - \text{O}'$  highly improbable so that two  $-\text{CH}_2 - \text{O}'^{\text{CH}_3}$  groups may be fixed at most probable positions. Therefore we should take into account the internal rotation around C-C bond. In this case, the dipole moment along the direction of the C-C bond should be cancelled out so that a single relaxation time connected with group rotation ( $-\text{CH}_2\text{OCH}_3$ ) would be predominant. But for dimethoxymethane, such a cancellation would not occur so that the contribution from the molecular re-orientation as well as the group rotation should be also taken into account. The molecular re-orientation leads to longer relaxation time than  $-\text{CH}_2\text{OCH}_3$  group relaxation time.  $\alpha \sim 0$  for 1,2-dimethoxyethane supports the above considerations of the internal rotation, on the other hand,  $\alpha \sim 0$  for dimethoxymethane suggests that the internal rotation may be very hindered so that this compound could be essentially regarded as the rigid molecule.





(ii)

(i)

Figure 4-1: Possible internal rotations which change total dipole moments of (i) 1,2-dimethoxyethane, and (ii) dimethoxymethane

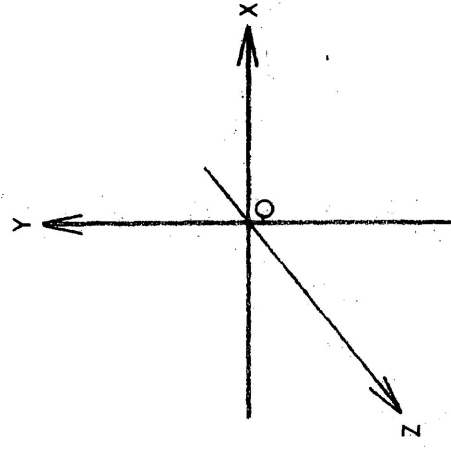
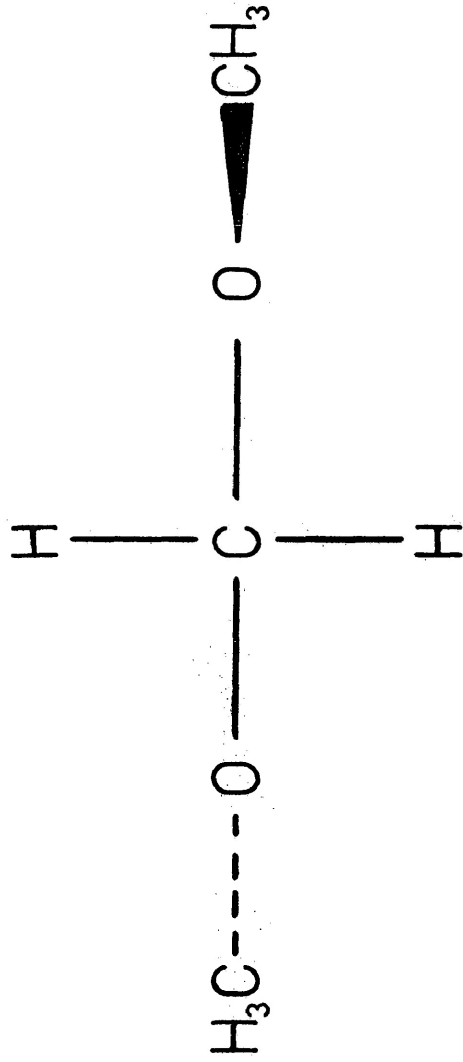


Figure 4-2: Proposed molecular configuration of dimethoxymethane from the present work.

This arises from the steric effect and electrostatic repulsion. The dipole moment for free rotation is calculated for this molecule from Eq. (2-5) to give us 1.62 (D), ( $\mu_{C-O} = 0.95$  (D),  $\mu_{OCH_3} = 1.11$  (D),  $\angle COC = 110^\circ$  and  $\angle OCO = 110^\circ$  are used) and 1.70 (D) (from the group moment of  $\mu_{CH_3OCH_3} = 1.25$  (D),  $P = 0$ ,  $Q = 1.25$  (D) and  $\angle OCO = 110^\circ$ ). Therefore it is seen that the calculated dipole moment for free rotation is about three times of the observed one, which again suggests that the internal rotation of dimethoxymethane may be very hindered. Making use of Table 2-1 and Eqs. (2-3),  $\phi_1 = 90^\circ$  ( $270^\circ$ ) and  $\phi_2 = 270^\circ$  ( $90^\circ$ ) give us the calculated dipole moment of 0.65 (D), which is in good agreement with the observed one of 0.58 (D). The molecular configuration corresponds to these angles is schematically shown in Figure 2. It is of interest to note that this molecular configuration has not dipole moments along the x and z axes but has a y component dipole which does not change with the rotation around C-O bonds. (see Table 2-1 and Eqs. (2-3)). In other words, the molecular re-orientation would mainly contribute to the dielectric relaxation, which necessarily implies  $\alpha \sim 0$ .

With respect to calculation of the dipole moment for free rotation in 1,2-dimethoxyethane,  $\mu_{CH_3OCH_3} = 1.25$  (D),  $\angle COC = 110^\circ$  and  $\angle OCC = 110^\circ$  give us 1.58 (D), which is well compared to the observed one of 1.55 (D). In calculation, the rotation

around C - OCH<sub>3</sub> bond is neglected in accordance with the above assumption. From the observed dipole moment alone, it is difficult to determine whether the moment is originated from internal rotation or freezing of the rotation (see Chap. 2 (b)). There are three possibilities about this calculated value. (i) The free rotations of two rotational groups, (ii) equal probabilities for the cis and trans forms, and (iii)  $\phi_1 + \phi_2 = 90^\circ$ . In view of the electrostatic repulsion of two oxygen atoms, the first two possibilities may be excluded.

It is well-known that 1,2-dichloroethane has two forms of rotational isomers, i.e., the trans and the gauche isomers<sup>38</sup>.

The observed dipole moment  $\mu_{\text{obs}}$  of this molecule was given by<sup>38</sup>

$$\begin{aligned} \mu_{\text{obs}}^2 &= x_g \mu_g^2 + x_t \mu_t^2 \\ x_g + x_t &= 1 \end{aligned} \quad (4-1)$$

where  $x_g$  and  $x_t$  are the mole fractions of the gauche and the trans forms, respectively, and  $\mu_g$  and  $\mu_t$  are the corresponding dipole moments. In addition, the energy difference  $\Delta E$  between the trans and gauche isomers would be characterized by

$$\frac{x_g}{2x_t} = \exp\left(\frac{-\Delta E}{RT}\right) \quad (4-2)$$

where R is the gas constant and T is the absolute temperature.

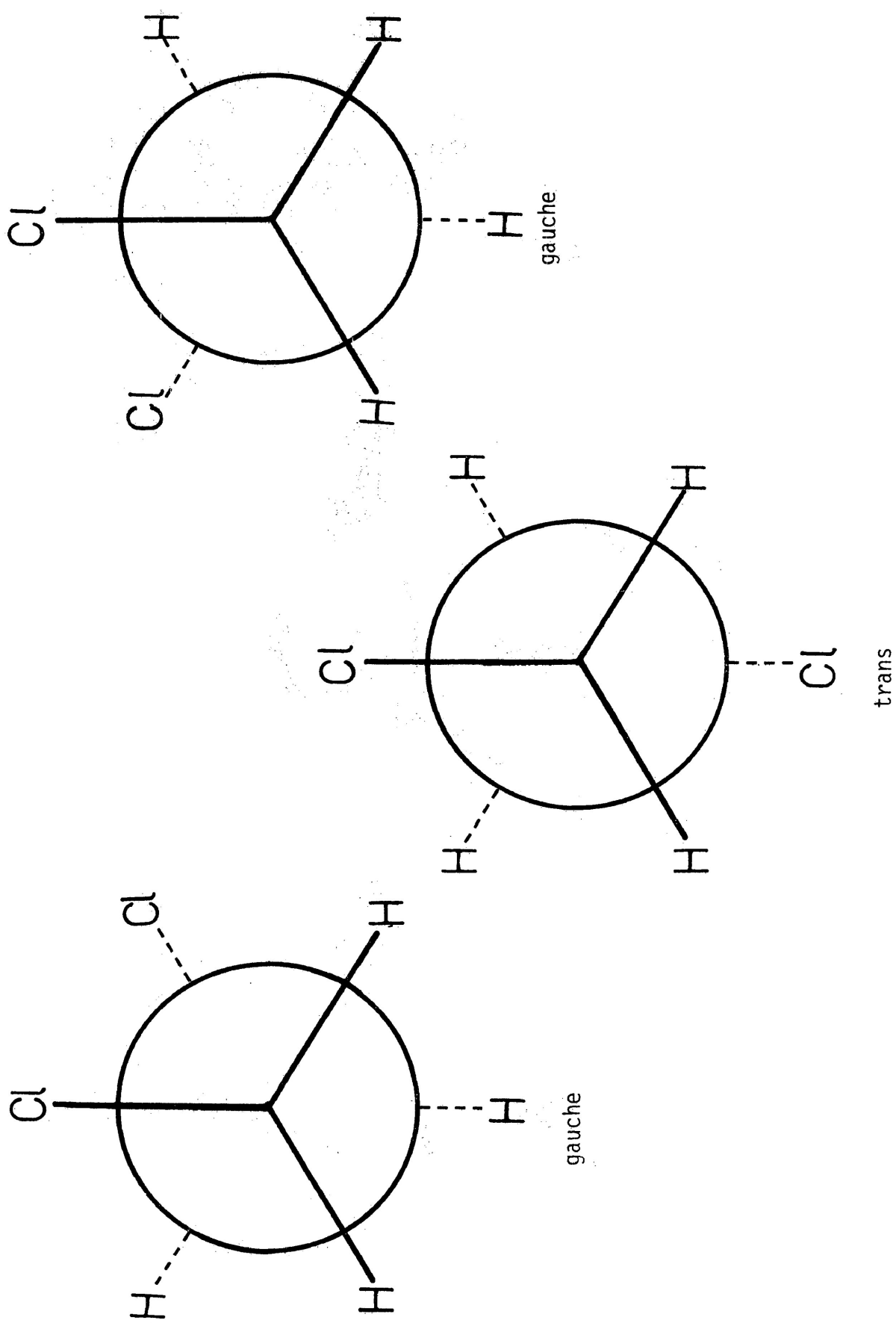


Figure 4-3: Rotational isomers of 1,2-dichloroethane

In this particular case,  $\mu_t = 0$  so that Eq. (4-1) would become

$$\mu_{\text{obs}}^2 = \chi_g \mu_g^2 \quad (4-3)$$

In a similar manner, Eq. (4-3) may be applicable to 1,2-dimethoxyethane. In this case, using  $\chi_g = 2.03$  (D), we have  $\mu_g = 0.59$  and  $\Delta E = 0.20$  Kcal/mole. Because of  $\Delta E < RT \sim 0.6$  Kcal/mole at room temperature, the barrier would not be significant. The relaxation time of diethyl ether, at 19°C in cyclohexane is reported to be 2.9 (psec)<sup>20</sup>. Although we need some corrections to compare this value to the present results,  $\tau_o$  value of 1,2-dimethoxyethane is very close to this value. 4-4'-Dimethoxybiphenyl is measured at 25°C in p-xylene to have  $\tau_o = 5.2$  (psec),  $\alpha \sim 0$  and  $\mu = 1.86$  (D). These parameters are in good agreement with those of p-dimethoxybenzene  $\tau_o = 6.9$  (psec),  $\alpha = 0.04$  and  $\mu = 1.68$  (D) at 2.5°C in cyclohexane<sup>20</sup>. Therefore, since the molecular relaxation times of these molecules would differ appreciably, the dielectric relaxation of this molecule is likely to be the re-orientation of methoxy group (see Chap. I (c) (ii)). It is interesting to note that <sup>the</sup>  $\tau_o$  value of 4-4'-dimethoxybiphenyl is slightly shorter than that of p-dimethoxybenzene and the dipole moment of the former compound is greater than that of the latter. Without considering the mesomeric effect between the lone pair electrons of the oxygen atom and the phenyl ring, the

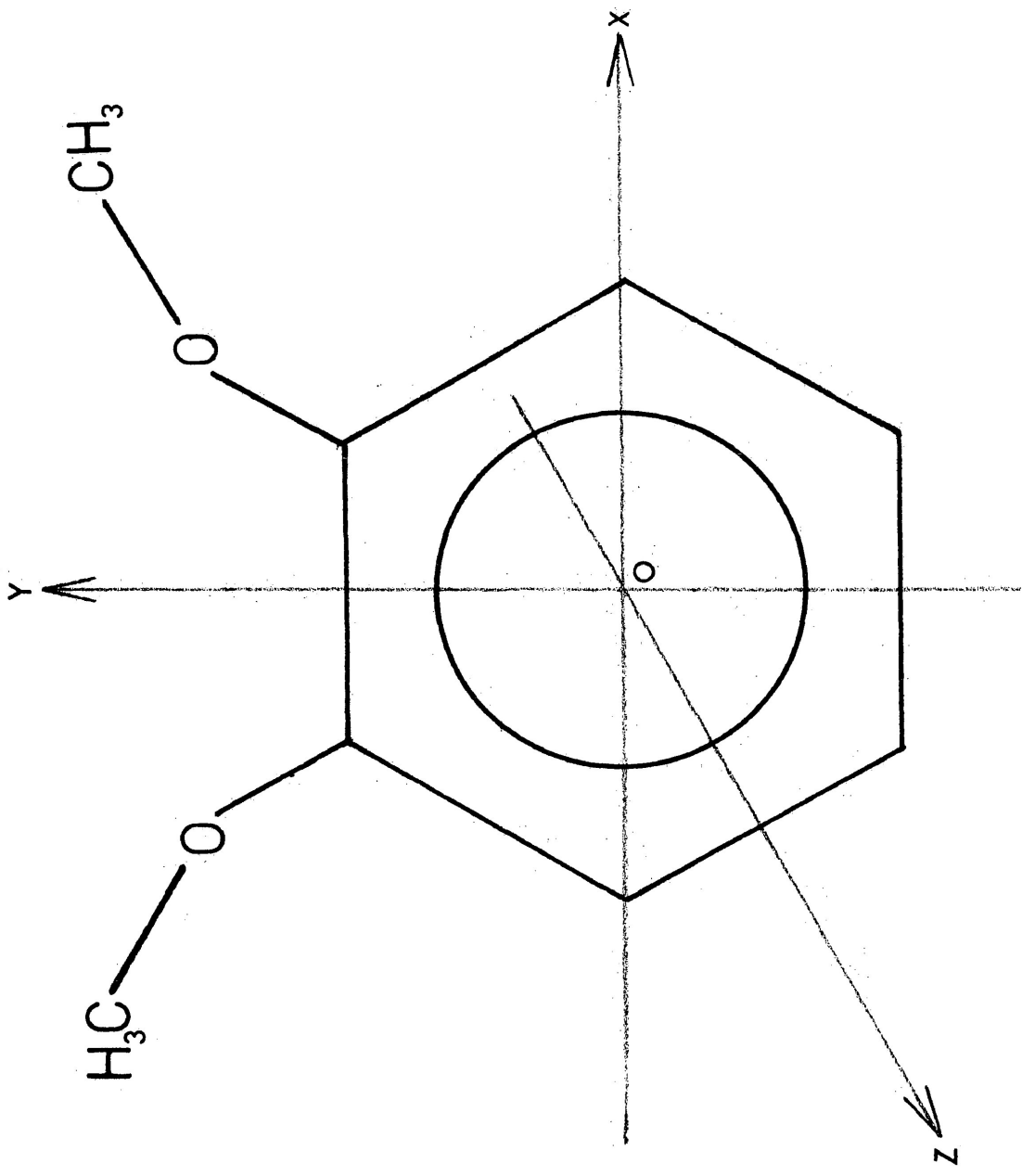


Figure 4-4: Coordinates for o-dimethoxybenzene

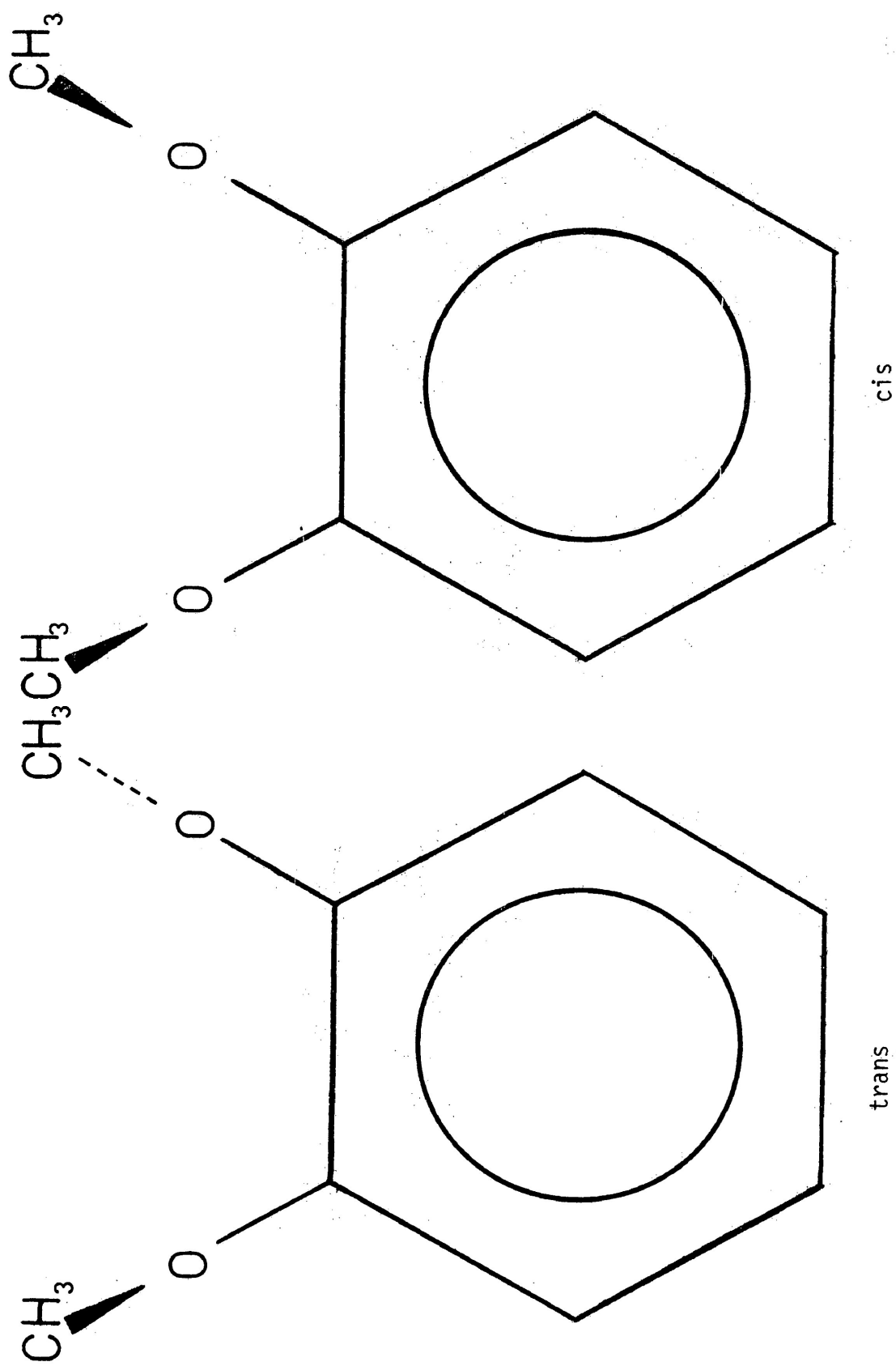


Figure 4-5: Configurations for o-dimethoxybenzene



dipole moment for free rotation is calculated to become 1.46 (D) for both 4-4'-dimethoxybiphenyl and p-dimethoxybenzene.

o-Dimethoxybenzene is found to have very short relaxation time ( $\tau_0 = 3.8$  (psec)),  $\alpha = 0.12$  and  $\mu = 1.30$  (D) at 40°C in p-xylene. The dipole moment based on a free rotation model is obtained to be 1.78 (D), which is not in good agreement with the observed one. Apparently the steric hinderance of this molecule would reach maximum at  $\phi_1 = 0$  and  $\phi_2 = 180^\circ$  (see Figure 2-2 where rotational angles  $\phi_1$  and  $\phi_2$  are defined).

These angles lead to the calculated dipole moment of 0.06 (D) and Budd's  $C_1$  of 1, which do not agree with the experimental results. However,  $\phi_1 = 0^\circ$  and  $\phi_2 = 90^\circ$  and  $270^\circ$  or  $\phi_1 = 90^\circ$  and  $270^\circ$ , and  $\phi_2 = 180^\circ$  give the calculated dipole moment of 1.46 (D), which is very close to the experimental one. But the molecular configuration corresponds to these angles is unlikely to exist, because of steric hinderance between one of the methyl group and the oxygen atom of another. On the other hand, the methyl groups are also possible to touch the nearest hydrogen atom attached to the benzene ring. Therefore the configurations given in Figure 4-5 may be most probable, i.e.,  $\phi_1 = 90^\circ$  ( $270^\circ$ ) and  $\phi_2 = 270^\circ$  ( $90^\circ$ ): trans form, and  $\phi_1 = 90^\circ$  ( $270^\circ$ ) and  $\phi_2 = 90^\circ$  ( $270^\circ$ ): cis form.

In this case, Eq. (4-1) can be re-written as

$$\mu_{\text{obs}}^2 = x_t \mu_t^2 + x_{\text{cis}} \mu_{\text{cis}}^2 \quad (4-4)$$

Making use of  $\mu_{\text{cis}} = 2.31$  (D) and  $\mu_t = 0.99$  (D), we have  $x_t = 0.84$  for o-dimethoxybenzene. The same calculations were made for m-dimethoxybenzene ( $\mu_{\text{obs}} = 1.52$  (D),  $\mu_t = 0.57$  (D) and  $\mu_{\text{cis}} = 2.16$  (D)), and p-dimethoxybenzene ( $\mu_{\text{obs}} = 1.68$ ,  $\mu_t = 0$  (D) and  $\mu_{\text{cis}} = 2.09$  (D)), and  $x_t = 0.54$  and  $x_t = 0.35$  were obtained for the former and the latter compounds, respectively. At the same time, the dipole moments for free rotation were also evaluated, and 1.78 (D), 1.57 (D) and 1.46 (D) were obtained for o-, m- and p-dimethoxybenzenes, respectively.

It is noted that especially in <sup>the</sup> m-compound, the calculated value for free rotation is in good agreement with the observed one. In order to estimate the energy difference between the cis and the trans forms, we can use <sup>a</sup> similar equation to Eq. (4-2), i.e.,

$$\frac{x_{\text{cis}}}{x_t} = \exp \left( - \frac{\Delta E}{RT} \right) \quad (4-5)$$

substitution of  $x_t = 0.84$  and  $x_{\text{cis}} = 0.16$  in Eq. (4-5) gives  $\Delta E = 0.96$  Kcal/mole for o-compound. Therefore it becomes clear that the rotation of the methoxy group of the compound is very hindered and it appears to exist mostly in the trans form.

We could see another evidence to support the above conclusion from temperature dependence of the observed dipole moment of o-dimethoxybenzene<sup>43</sup>. According to the theory treated in Chap 1 (c) (iii),  $C_1$  may be given by

$$C_1 = \frac{b^2}{\frac{x}{1+x} a^2 + b^2} \quad (4-6)$$

(see Eq. (1-51))

and

$$x = \frac{x_{cis}}{x_t} \quad (4-7)$$

since

$$\Delta E = V$$

Eqs. (4-6) and (4-7) give  $C_1 = 0.54$  for o-compound. (the observed  $C_1 = 0.63$ ).

This good agreement of the calculated  $C$  with the observed one suggests the validity of the starting model based on two sites of the cis and the trans configurations. The relaxation times ( $\tau_1 = 6.3$  (psec) and  $\tau_2 = 1.4$  (psec) at 40°C in p-xylene) of o-dimethoxybenzene can be used to estimate the relaxation time of the methoxy group  $\tau_g$  from the site model

$$\frac{1}{\tau_g} = \frac{1}{\tau_2} - \frac{1}{\tau_1}$$

This gives  $\tau_g = 1.9$  (psec) at 40°C in p-xylene.

Roberti and Smyth attributed the short relaxation time of the o-compound ( $\tau_2 = 3.7$  (psec) and  $\tau_1 = 69$  (psec) at 25°C pure liquid) to a cooperative motion of the methoxy group

rotation which becomes similar to an oscillation about an equilibrium, because of steric hinderance to rotation, each methoxy group influences the rotation of the other<sup>37</sup>. In view of molecular size and shape, the  $\tau_1$  value of the compound can be compared with that of o-xylene at 50°C in cyclohexane ( $\tau_1 = 6.4$  (psec),  $\tau_2 = 4.0$  (psec),  $C_1 = 0.8$  and  $\tau_0 = 6.1$  (psec))<sup>44</sup>. Also note that o-xylene has  $\tau_0 = 8.3$  (psec),  $\tau_1 = 11.0$  (psec),  $\tau_2 = 4.3$  (psec), and  $C_1 = 0.70$  at 25°C in cyclohexane, while o-dichlorobenzene has  $\tau_0 = 9.4$  (psec) at 25°C in cyclohexane<sup>44</sup>.

m-Dimethoxybenzene was measured at 40°C in p-xylene to have  $\tau_0 = 10.1$  (psec),  $\alpha = 0.07$ ,  $\tau_1 = 13.7$  (psec),  $\tau_2 = 3.6$  (psec) and  $C_1 = 0.71$  (for comparison with the literature values, see Table 4-3). Eqs. (4-6) and (4-7) give  $C_1 = 0.13$ , which does not agree with the observed one. However, the conformational analysis indicates that  $\phi_1 = 90^\circ$  (180° and 270°) and  $\phi_2 = 0^\circ$  (90° and 0°) give the calculated  $\mu = 1.88$  (D) and  $C_1 = 0.61$ . The molecular configurations correspond<sup>ing</sup> to these angles may be originated from repulsion of the methoxy group at  $\phi_1 = 0^\circ$  and  $\phi_2 = 180^\circ$ . From calculations of the dipole moments for this compound, there would exist two points of view about the internal rotation (i) free rotation, and (ii) four stable sites (see Chap.2 (b)(ii)) and the energies of them

are almost identical ( $\Delta E \approx 0$ ). It is of interest to note that the  $\tau_2$  value of this compound is close to  $\tau_0$  value of 1,2-dimethoxyethane. Therefore the  $\tau_2$  value may be regarded as the relaxation time of the methoxy group.

6-chloro-1,4-dimethoxybenzene was measured at 40°C in p-xylene to have  $\tau_0 = 14$  (psec),  $\alpha = 0.16$ ,  $\tau_1 = 17.2$  (psec),  $\tau_2 = 4.2$  (psec),  $C_1 = 0.78$  and  $\mu = 2.47$  (D). The dipole moment for free rotation is calculated to have 2.18 (D) ( $\mu_{C-C_1} = 1.60D$ ) is used, see ref. (12)), which is not in good agreement with the observed one. The calculated dipole moments for the cis and the trans forms (see Fig. 4-6) are 2.63 (D) and 1.60 (D), respectively, which give  $\chi_t = 0.19$  and  $\chi_{cis} = 0.81$ . However these  $\chi$  values are not likely, when we take into account the environment of the dimethoxy group at 4 position upon internal rotation. In other words, we may predict  $\chi_t = \chi_{cis} = 1/2$  in this case.

Now setting the coordinates of this compound as in Figure 4-6 and fixing  $\phi_1 = 180^\circ$ , we have the calculated dipole moments  $\mu_0 = 3.56$  (D) and  $\mu_{180} = 1.60$  (D) for  $\phi_2 = 0^\circ$  and  $\phi_2 = 180^\circ$ , respectively. And defining the mole fractions at  $\phi_2 = 0$  and  $\phi_2 = 180^\circ$  by  $\chi_0$  and  $\chi_{180}$ , respectively, we may have the equation similar to Eq. (4-1);

$$\mu_{obs}^2 = \chi_0 \mu_0^2 + \chi_{180} \mu_{180}^2$$

This equation gives  $\chi_0 = 0.65$  and  $\chi_{180} = 0.35$ , which is more probable than the previous calculation.

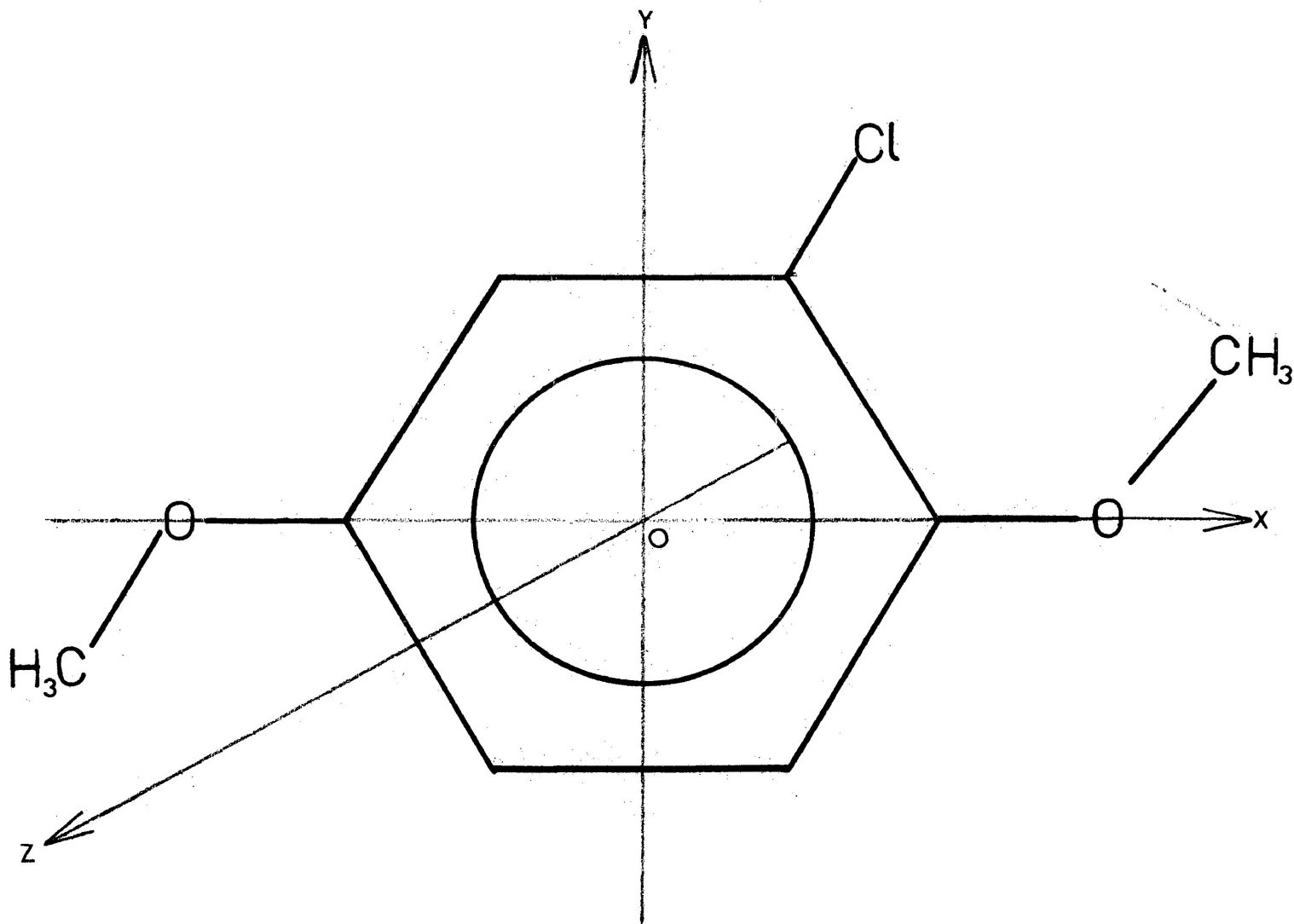


Figure 4-6: Coordinates of 6-chloro-1,4-dimethoxybenzene for calculation of its dipole moment.

Let us introduce  <sup>$\theta$</sup>  "free oscillation model" (Chap. 2 - (c))  
 (i) the methoxy group at <sup>the</sup> 4 position is assumed to rotate freely, while the methoxy group at <sup>the</sup> 1 position remains at  $\phi_1 = 180^\circ$ , and (ii) the methoxy groups at 1 and 4 positions are assumed to rotate freely with the regions  $90^\circ - \Delta \leq \phi_1 \leq 270^\circ + \Delta$  and  $0 \leq \phi_2 \leq 360^\circ$  where  $90^\circ \geq \Delta \geq 0^\circ$ . These assumptions are made taking into account the steric hindrance near  $\phi_1 = 0^\circ$ .

From Eqs. (2-3),  $\Delta = 90^\circ$  gives

$$\mu_x = X \sin C$$

$$\mu_y = X \cos C + Q \sin B (\cos \phi_1 - \cos \phi_2)$$

$$\mu_z = Q \sin B (\sin \phi_1 + \sin \phi_2)$$

where  $X = \mu_{C-C1}$  and  $C = 30^\circ$  in accordance with Figure 5.

Therefore the total dipole moment  $\mu$  becomes

$$\begin{aligned} \mu^2 = & X^2 + 2Q^2 \sin^2 B - 2Q^2 \sin^2 B \cos(\phi_1 + \phi_2) \\ & + 2QX \sin B \cos C (\cos \phi_1 - \cos \phi_2) \end{aligned}$$

For the assumption (i), the average of the square of the total dipole moment  $\langle \mu^2 \rangle$  is given by;

$$\langle \mu^2 \rangle = \frac{\int_0^{2\pi} \mu^2 d\phi_2}{\int_0^{2\pi} d\phi_2} = X^2 + 2Q^2 \sin^2 B + 2QX \sin B \cos C \cos \phi_1 \quad (4-8)$$

It should be noted that  $\phi_1 = 90^\circ$  or  $270^\circ$  gives the same calculated dipole moment as the case of the double free rotation (see Eqs. (2-6), (2-10) and (2-12)).  $\phi_1 = 180^\circ$  gives  $\sqrt{\langle \mu^2 \rangle} = 2.76$  (D), which is the same value as  $\phi_1 = 90^\circ, 180^\circ$  and  $270^\circ$  and  $\phi_2 = 0^\circ, 270^\circ$  and  $0^\circ$ , respectively, while  $\sqrt{\langle \mu^2 \rangle} = \mu_{\text{obs}}$  gives  $\phi_1 = 118^\circ$  or  $242^\circ$ . On the other hand, for the assumption (ii),

$$\langle \mu^2 \rangle = \frac{\int_0^{2\pi} d\phi_2 \int_{\frac{3\pi}{2} + \Delta}^{\frac{1}{2}\pi - \Delta} \mu^2 d\phi_1}{\int_0^{2\pi} d\phi_2 \int_{\frac{3\pi}{2} + \Delta}^{\frac{1}{2}\pi - \Delta} d\phi_1}$$

$$= x^2 + 2Q^2 \sin^2 B - \frac{4QX \sin B \cos C \cos A}{\pi + 2\Delta}$$

$\Delta = 90^\circ$  corresponds to the double free rotation.  $\Delta = 0^\circ$  gives  $\sqrt{\langle \mu^2 \rangle} = 2.56$  (D), while setting  $\langle \mu^2 \rangle = \mu_{\text{obs}}^2$ , we have  $\Delta = 22^\circ$ , i.e.  $68^\circ \leq \phi_1 \leq 290^\circ$ , (This is very close to the one obtained from o-chloroanisole ( $18^\circ$ ) see Chap. 2-(c)). Such a rotation may lead to  $\alpha \neq 0$ . Both assumptions seem to be likely, however, we cannot decide which one is more probable from the observed dipole moment alone.

Maier<sup>45</sup> reported that  $\tau_0$  of 2,6-dichloroanisole in benzene at  $20^\circ\text{C}$  is 19.9 (psec), which may be compared with  $\tau_1$  of 6-chloro-1,4-dimethoxybenzene, ( $\tau_1 = 17.2$  (psec)). At the same time this



may be also compared with  $\tau_0$  values of o-diiodobenzene<sup>21</sup> ( $\tau_0 = 14.6$  (psec) in p-xylene at 60°C), o-bromiodobenzene<sup>21</sup> ( $\tau_0 = 12.0$  (psec) in p-xylene at 60°C) and o-chloriodobenzene<sup>21</sup> ( $\tau_0 = 11.0$  (psec) at 60°C), because anisole is considered to be intermediate in size between that of bromo and iodobenzene<sup>46</sup>.

Mountain, measuring relaxation times of o-haloanisoles, concluded that relaxation processes of these compounds except fluoroanisole were mainly due to the molecular re-orientation<sup>21</sup>. If this is the case, it would be expected that the  $\tau_2$  value of 6-chloro-1,4-dimethoxybenzene would become similar to that of anisole ( $\tau_0 = 7.7$  (psec),  $\tau_1 = 11.4$  (psec),  $\tau_2 = 5.9$  (psec) and  $C_1 = 0.33$  at 40°C in p-xylene)<sup>29</sup>. And if it is not, the  $\tau_2$  of the former compound would be close to  $\tau_0$  of p-dimethoxybenzene ( $\tau_0 = 5.7$  (psec) at 40°C in cyclohexane)<sup>29</sup>. Because the methoxy relaxation times in the both cases are almost similar, it is difficult to attribute the observed  $\tau_2$  value of 6-chloro-1,4-dimethoxybenzene to one of the above two cases.

The dielectric parameters of 2,6-dimethoxypyridine are  $\tau_0 = 9.03$  (psec),  $\alpha = 0.05$ ,  $\tau_1 = 12.7$  (psec),  $\tau_2 = 4.8$  (psec),  $C_1 = 0.67$  and  $\mu = 0.94$  (D) at 25°C in p-xylene. The dipole moment for free rotation is calculated to become 3.12 (D), which suggests that the internal rotation should be hindered. While the conformational analysis indicates that  $\phi_1 = 0$  and  $\phi_2 = 180^\circ$  give us the calculated moment of 0.99 (D), ( $\mu_{\text{pyridine}} = 2.23$  (D) is used. Ref. (41)), which is in good

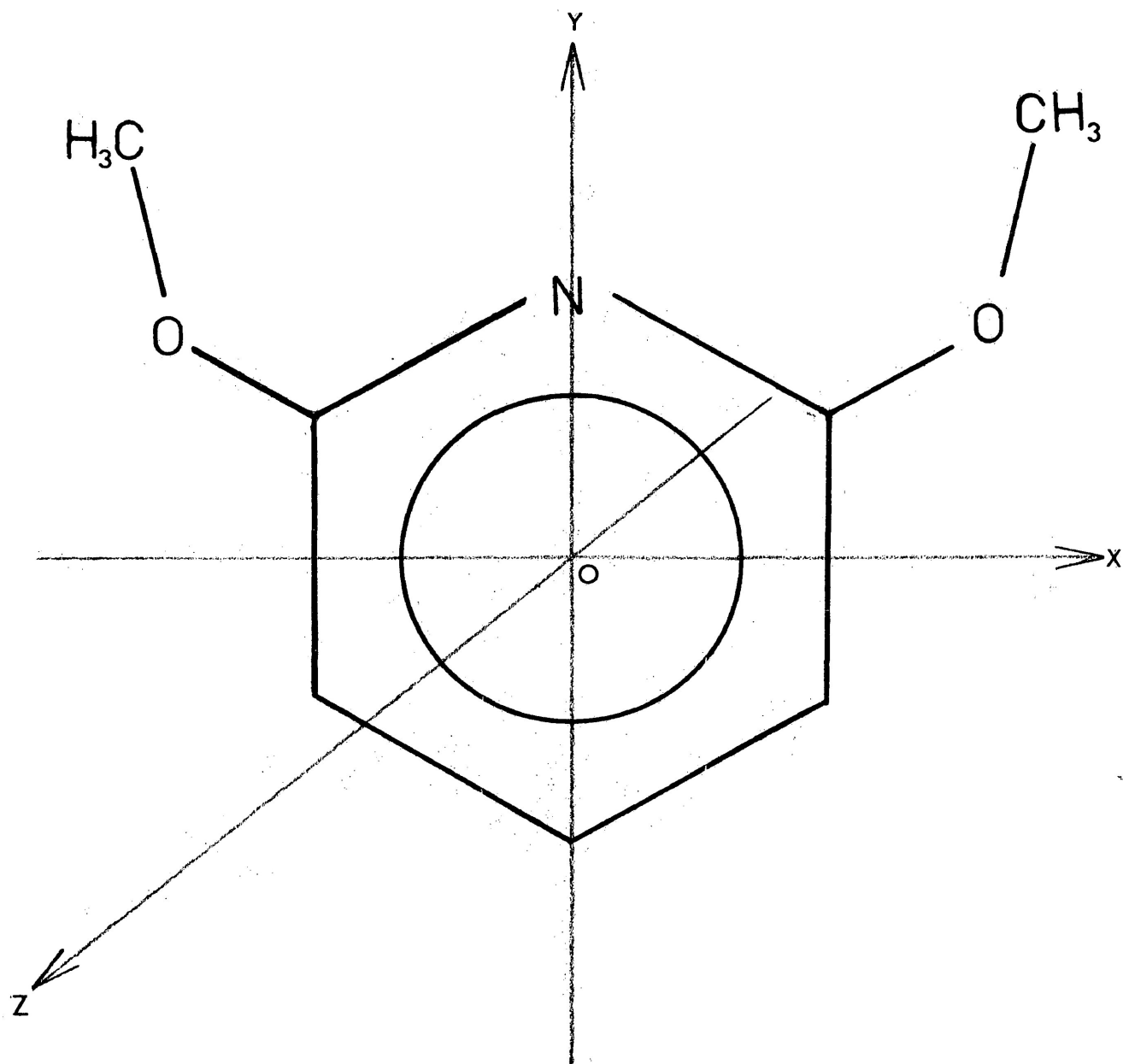


Figure 4-7: Molecular configuration of 2,6-dimethoxyuridine proposed from dipole moment measurement.

agreement with the observed one. The configuration corresponds to these angles is shown in Figure 4-7. It suggests that the repulsions at  $\phi_1 = 180^\circ$  and  $\phi_2 = 180^\circ$  of the methyl groups with the hydrogen atoms at 3 and 5 positions may lead the two methoxy groups to the configuration in Figure 6, since the nitrogen atom at <sup>the</sup> 1 position has no hydrogen <sup>atom</sup> so that there would be no appreciable steric effect in this configuration. At the same time, the configuration would be favoured by the mesomeric effect. Therefore it will be seen that internal motion of the methoxy groups in the compound is very different from that in m-dimethoxybenzene.

The  $\tau_1$  value may be compared with  $\tau_1$  of m-xylene ( $\tau_1 = 12.0$  (psec),  $\tau_2 = 4.0$  (psec)  $C_1 = 0.67$  and  $\tau_0 = 9.3$  (psec) at  $25^\circ\text{C}$  in cyclohexane)<sup>44</sup> as well as  $\tau_0$  of m-dichlorobenzene (10.0 (psec) at  $25^\circ\text{C}$  in cyclohexane)<sup>44</sup>.  $\tau_0$  of pure pyridine was reported to be 7.3 (psec) at  $20^\circ\text{C}$ <sup>65</sup>.

4-4'-Dimethoxythiobenzophenone was measured at  $25^\circ\text{C}$  in p-xylene to have  $\tau_0 = 46.6$  (psec),  $\alpha = 0$ ,  $\tau_1 = 62.1$  (psec),  $\tau_2 = 10.2$  (psec),  $C_1 = 0.87$  and  $\mu = 3.83$  (D). The mean relaxation time of benzophenone is reported to have  $\tau_0 = 19.0$  (psec) at  $25^\circ\text{C}$  in cyclohexane solution. It is interesting to note that the  $\tau_2$  value of 4-4'-dimethoxythiobenzophenone is in the order of <sup>the</sup> value of anisole ( $\tau_0 = 9.0$  (psec) at  $25^\circ\text{C}$  in p-xylene)<sup>29</sup>.

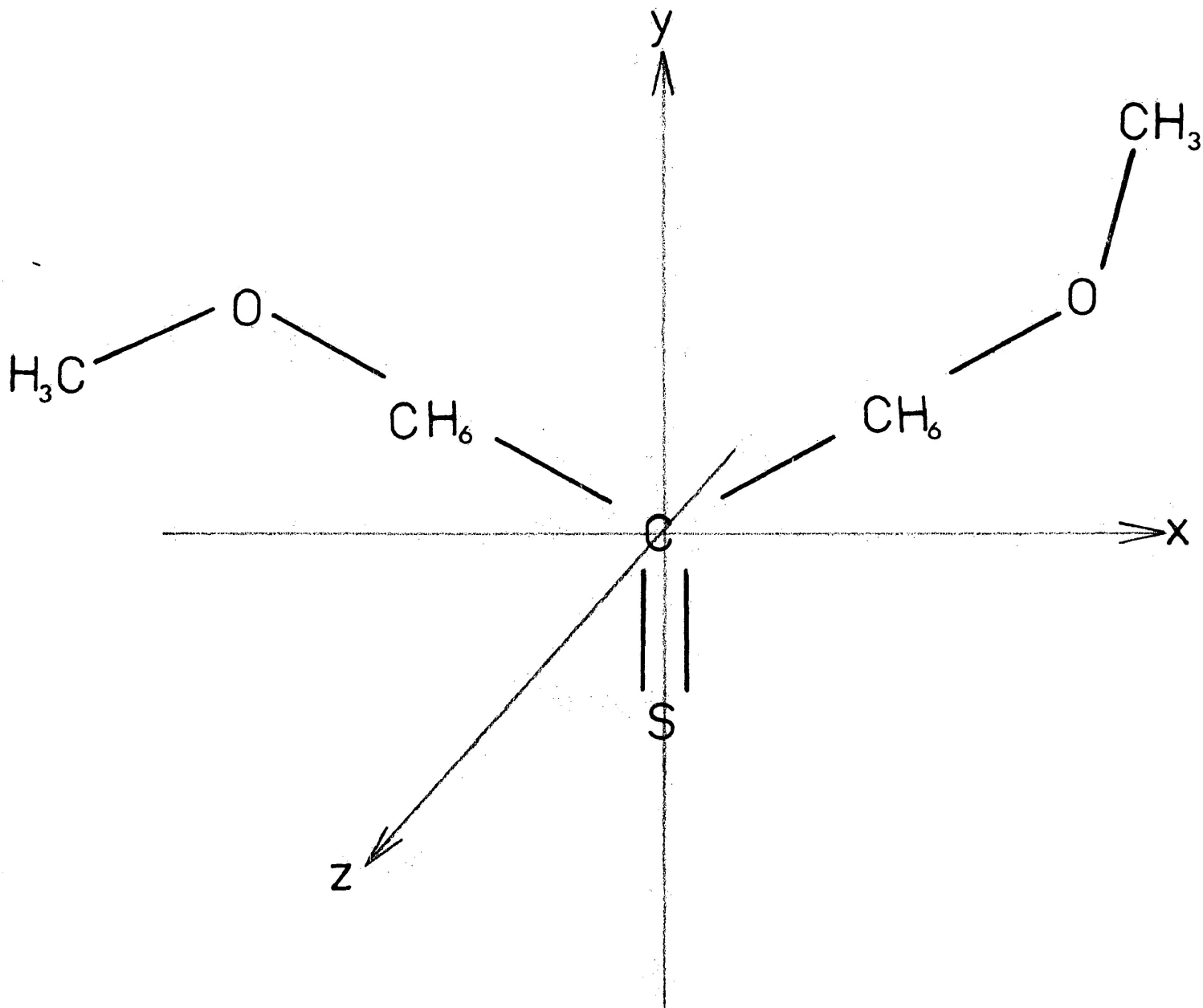


Figure 4-8: Coordinates of 4,4'-dimethoxythiobenzophenone.

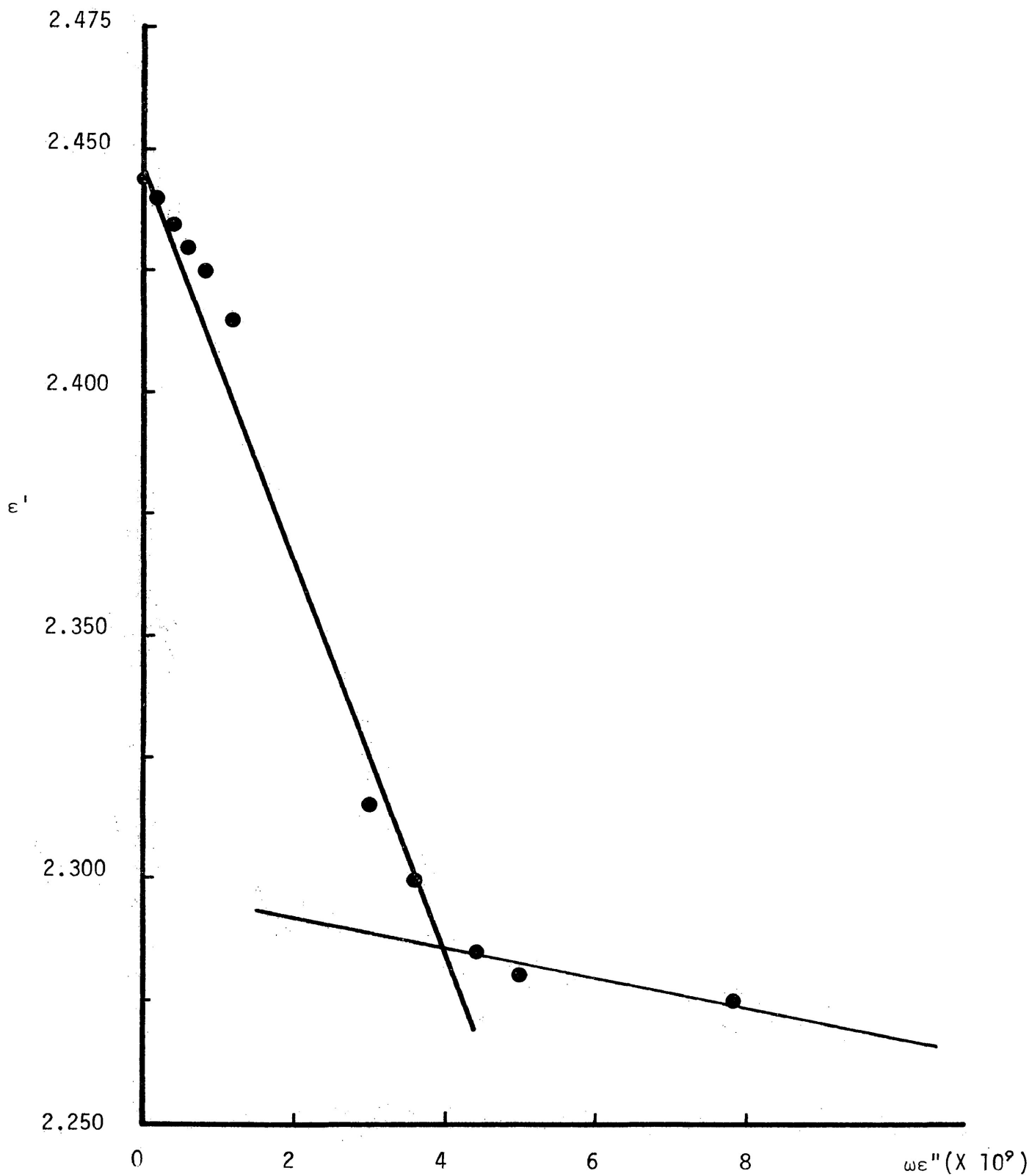
The dipole moment for free rotation of this compound is found to be 2.51 (D), which is too small to account for the observed value, ( $\mu_{C=S} = 2.60$  (D) is used. Ref. (12)) while  $\phi_1 = 0^\circ$  and  $\phi_2 = 180^\circ$  give the calculated dipole moment of 3.84 (D), which is in good agreement with the observed one. In <sup>this</sup> calculation, the mesomeric effect is totally ignored so that the configuration of the benzene ring cannot be determined by the present analysis, however, the molecular configuration may be simplified and shown as in Figure 4-9. This configuration also gives the calculated Budd's  $C_1 = 1$ , which might explain the observed  $\alpha \sim 0$  for this molecule.

5,6-Dimethoxy-1-indanone was observed at 25°C in p-xylene to show two separate lines of  $\epsilon'$  versus  $\omega\epsilon''$  plot, which gives  $\tau_1 = 45$  (psec) and  $\tau_2 = 5.7$  (psec).  $\epsilon_\infty$  was evaluated from the relation;

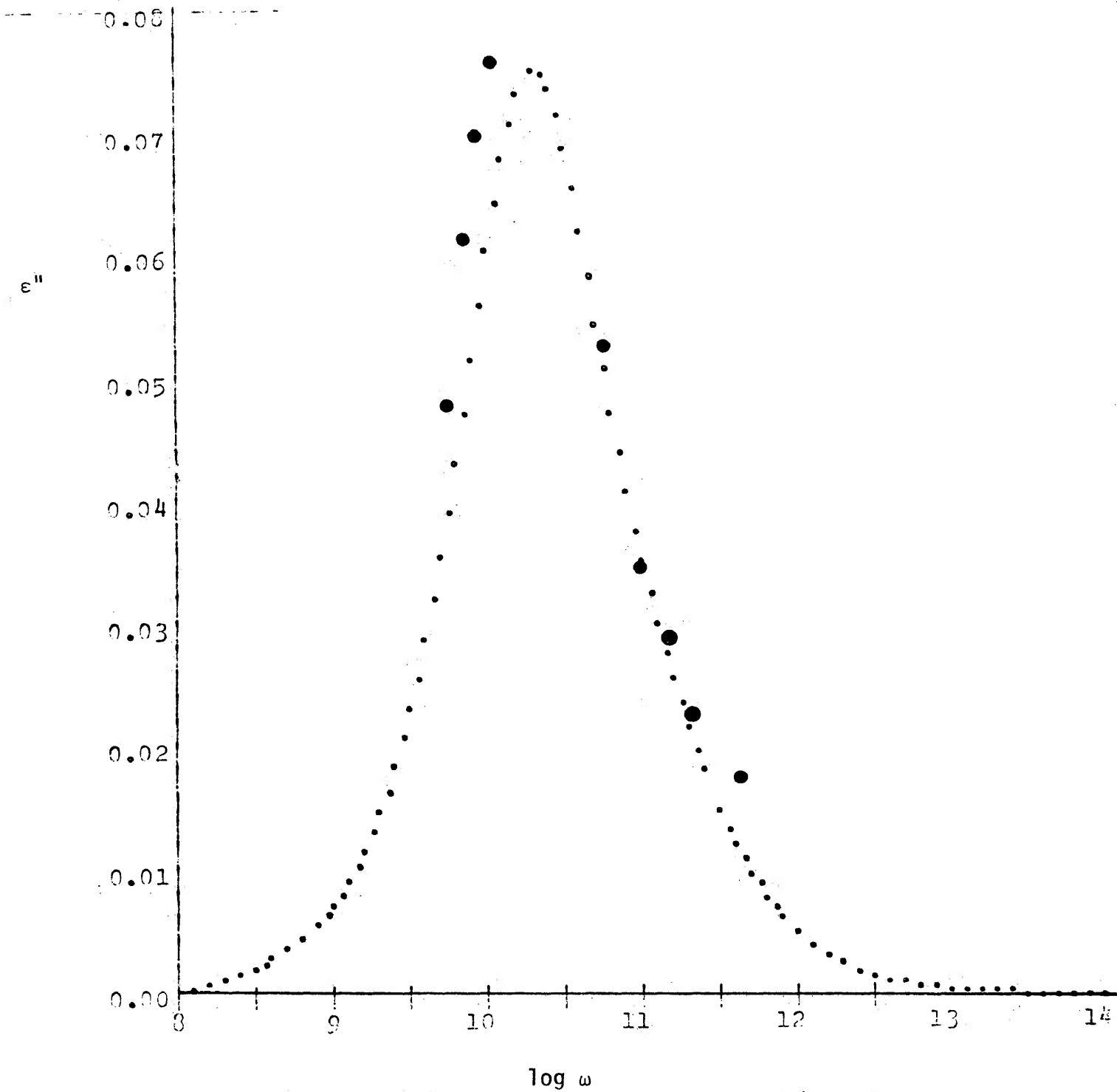
$$\epsilon' = \frac{1}{\tau_2} \left( \frac{\epsilon''}{\omega} \right) + \epsilon_\infty$$

Here ( $\epsilon'$ ,  $\epsilon''$ ) points of the second relaxation process were selected to give  $\epsilon_\infty = 2.278$ , from which dipole moment of the compound was obtained to be 3.30 (D). At the same time, using the  $\epsilon_\infty$ ,  $\tau_1 = 51$  (psec),  $\tau_2 = 7.0$  (psec) and  $C_1 = 0.90$  were obtained by computer analysis.

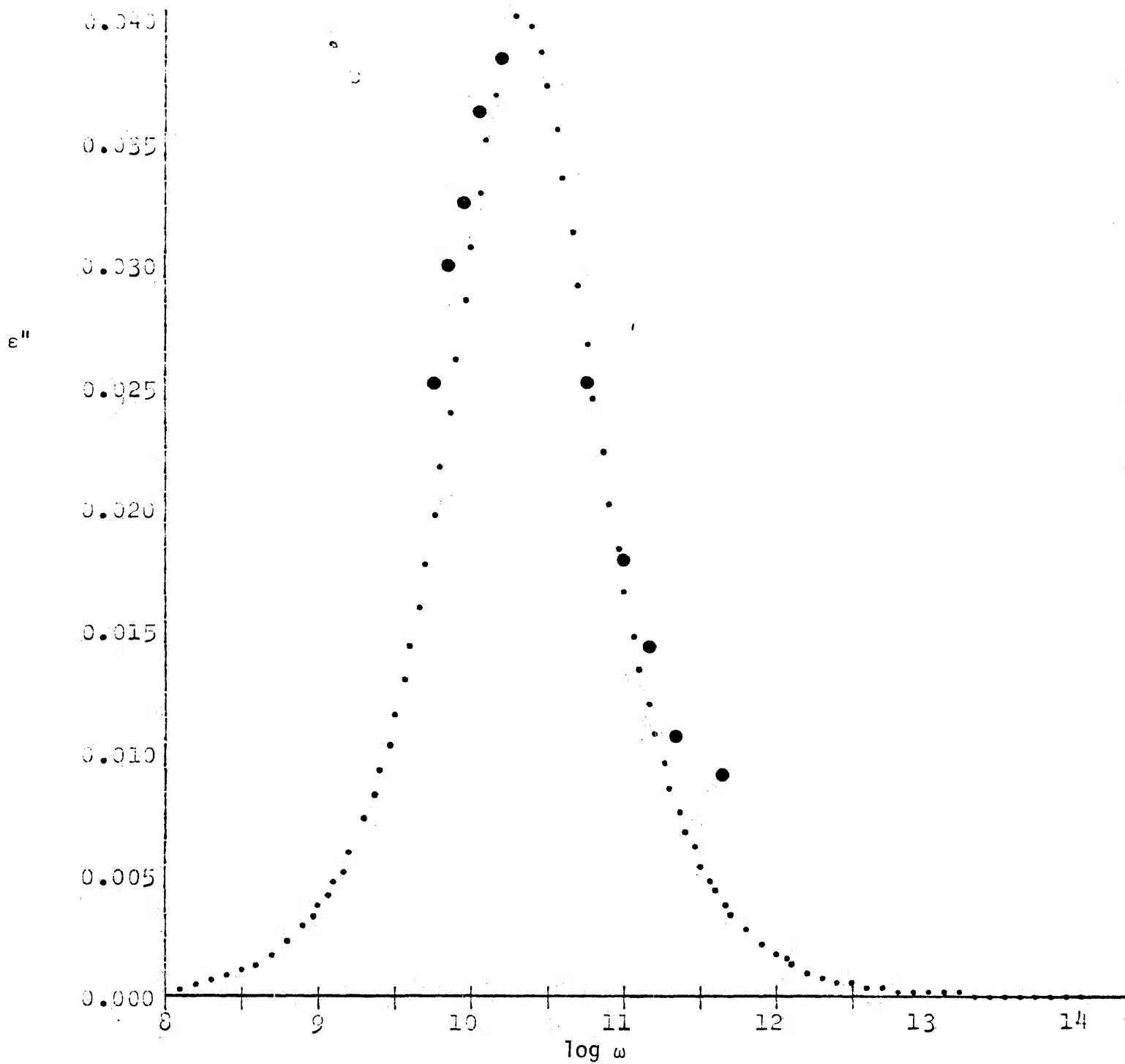
This compound is expected to indicate internal rotation of methoxy group similar to o-dimethoxybenzene. The dipole



$\epsilon'$  versus  $\omega\epsilon''$  plot for 5,6-dimethoxy-1-indanone.

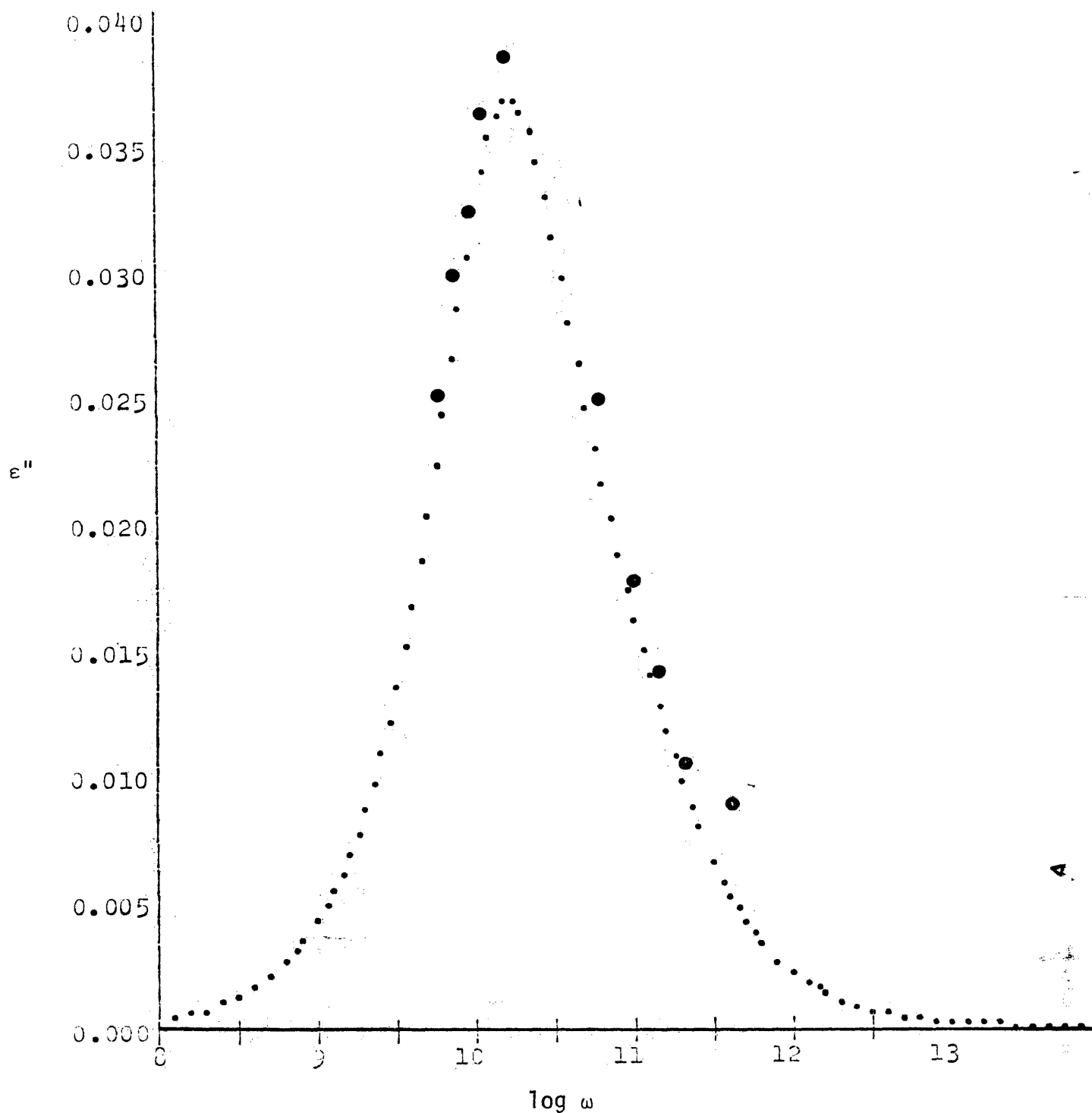


$\epsilon''$  versus  $\log \omega$  plot for 5,6-dimethoxy-1-indanone (big points represent the observed values while the small ones were obtained from Budó's equation assuming  $C_1 = 0.9$ ,  $\tau_1 = 5.1$  (psec), and  $\tau_2 = 7.0$  (psec)).



$\epsilon''$  versus  $\log \omega$  plot for 4-4'-dimethoxythiobenzophenone  
 (Big points represent the observed values while the small ones  
 were obtained from Debye equation assuming  $\tau_0 = 46.6$  (psec))





$\epsilon''$  versus  $\log \omega$  plot for 4-4'-dimethoxythiobenzophenone  
 (Big points represent the observed values while the small ones  
 were obtained from Budd's equation assuming  $\tau_1 = 62.1$  (psec),  
 $\tau_2 = 10.2$  (psec) and  $C_1 = 0.87$ )

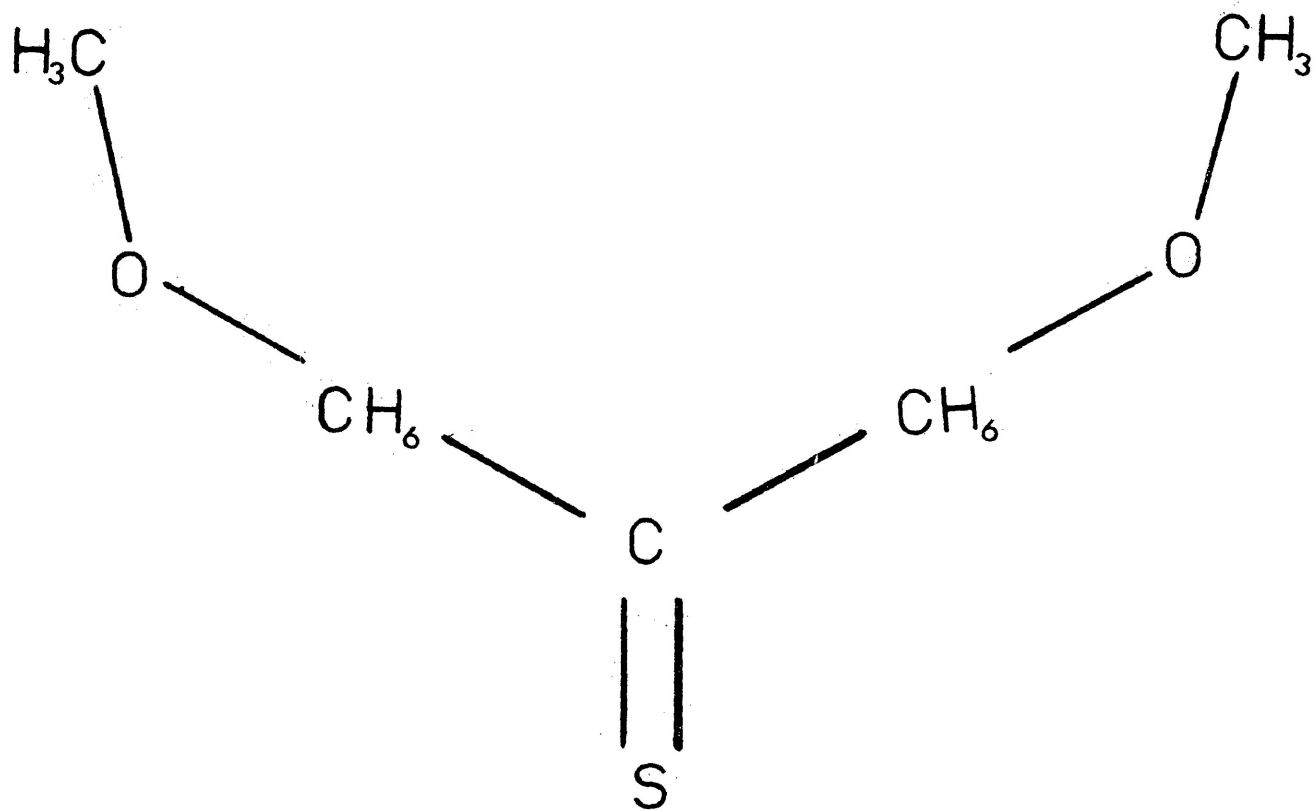


Figure 4-9: Simplified molecular configuration of 4-4'-dimethoxythiobenzophenone.

moment for free rotation is evaluated to be 3.34 (D), which is very close to the observed one. ( $\mu_{C=O} = 2.83$  (D) is used in calculation, see Ref. (47)). At the same time, making use of the calculated dipole moments 3.65 (D) and 3.00 (D) of the cis and the trans configurations, respectively, and  $\chi_{cis} = 0.16$  and  $\chi_t = 0.84$  of o-dimethoxybenzene, we obtain the calculated dipole moment of 3.11 (D), which is also close to the observed one within the errors involved in these treatments. On the other hand, using the observed moment of 3.30 (D) and Eq. (4-1), we have  $\chi_t = 0.56$  and  $\chi_{cis} = 0.44$ .

Here it should be pointed out that this calculation is very sensitive to the observed dipole moment as well as the group moment of  $\mu_{C=O}$ . (In this molecule,  $\mu_{cis} - \mu_t = 0.65$  (D) and  $\mu_{obs} = 3.30$  (D), while in o-dimethoxybenzene,  $\mu_{cis} - \mu_t = 1.32$  (D) and  $\mu_{obs} = 1.30$  (D)). The  $C_1$  calculation from the site model would be possible, using

$$C_1 = \frac{b^2 + \mu_{C=O}^2}{(b^2 + \mu_{C=O}^2) + \frac{\chi}{1+\chi} a^2}$$

Eq (4-7) and  $\chi_t = 0.56$  give  $C_1 = 0.95$ , which suggests that the observed relaxation time may be mainly due to the molecular relaxation process. Therefore, the internal rotation of methoxy group in 5,6-dimethoxy-1-indanone is very similar

to that in o-dimethoxybenzene. Since the  $\tau_1$  and  $\tau_2$  of the former compound are very different, the coupling of the molecular relaxation time  $\tau_1$  with the group relaxation time  $\tau_g$  would be very small so that  $\tau_g \approx \tau_1$ . Therefore  $\tau_g$  of o-dimethoxybenzene, 1.85 (psec) at 40°C may be compared with that of 5,6-dimethoxy-1-indanone, 2.94 (psec) at 25°C.

2,5-Dimethoxy-2,5-dihydrofuran was measured at 25°C in p-xylene to have  $\tau_0 = 11.0$  (psec),  $\alpha = 0$  and  $\mu = 1.63$  (D), while 2,5-dimethoxytetrahydrofuran was also measured at 40°C in p-xylene to have  $\tau_0 = 9.7$  (psec),  $\alpha = 0$ ,  $\tau_1 = 10.4$  (psec),  $\tau_2 = 2.2$  (psec),  $C_1 = 0.73$ , and  $\mu = 1.12$  (D).

It is noted that  $\tau_0$  values of the both compounds are very similar. The  $\tau_2$  value of the latter compound may be regarded as the methoxy group relaxation time. There are three possible molecular configurations in cyclopentane, i.e., the planar, the envelope, and the half-chair forms<sup>48</sup>.

### (c) VARIATION OF RELAXATION TIME OF METHOXY GROUP

It has been pointed out that the relaxation time of methoxy group changes with its circumstances. Now let us consider anisole as an example to see the reason of this change.

Let us consider the relaxation process in terms of four potential sites with the same method. The starting molecular model can be constructed by taking account of both steric

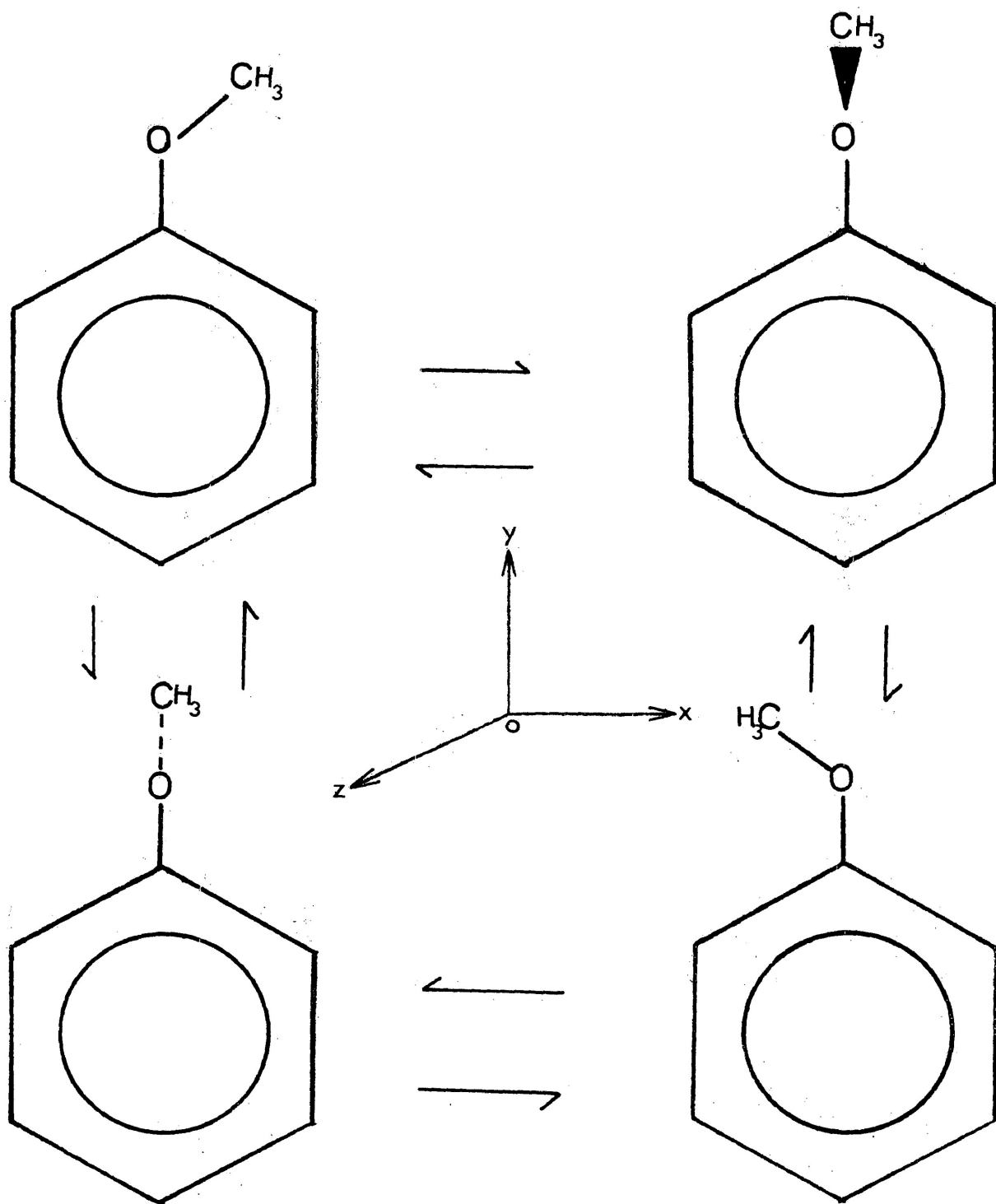


Figure 4-10: Molecular model of anisole for internal rotation of the methoxy group

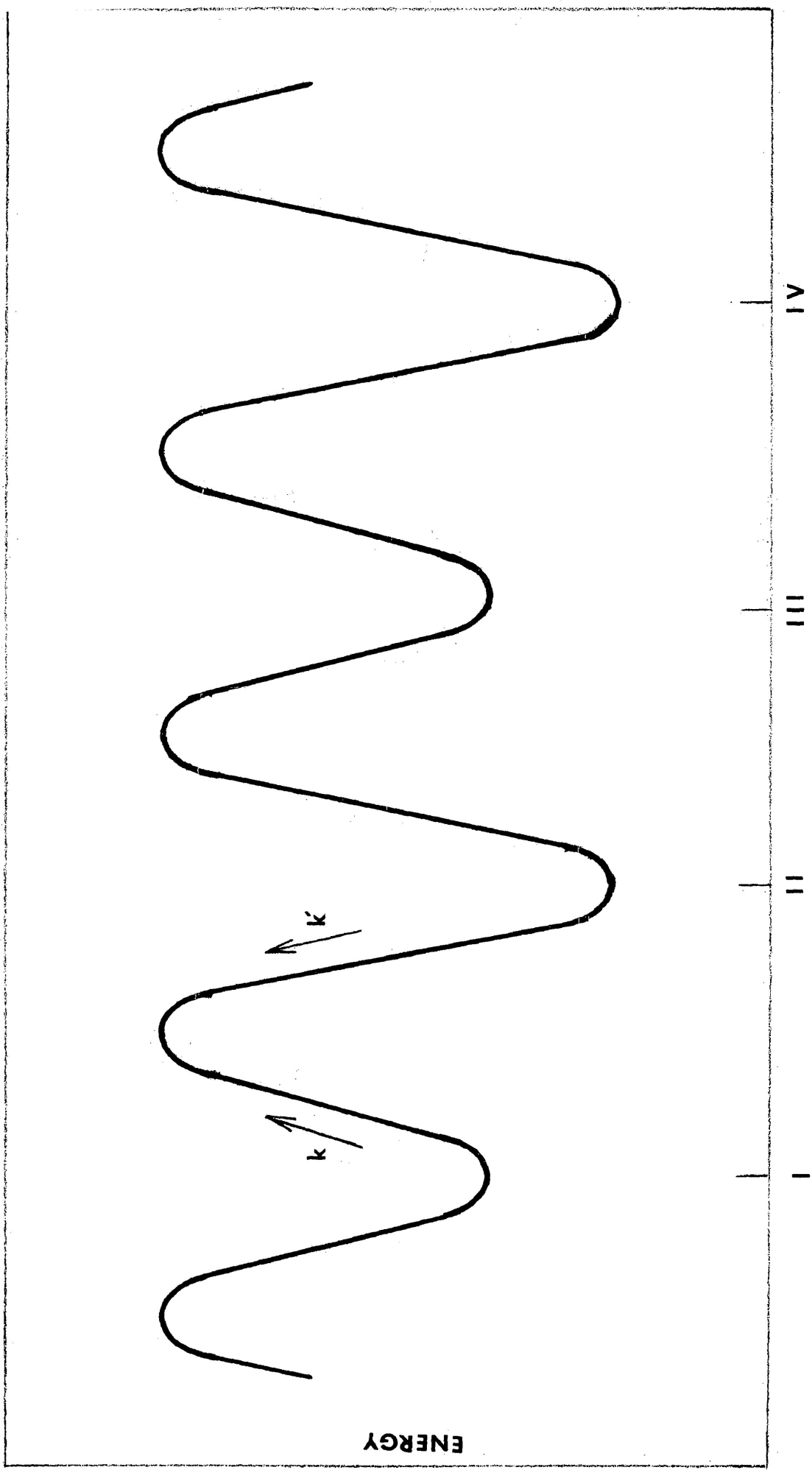


Figure 4-11: Potential energy curve corresponding to Figure 4-10

and mesomeric effects as shown in Figure 4-10.

The occupational probability of each site has already worked out in Chap. 1 (c) (ii). The results are

$$\begin{aligned}
 P_1(t) &= a_{11} + a_{12}\psi_2(t) + a_{13}\psi_2(t) \\
 P_2(t) &= a_{21} - a_{12}\psi_2(t) + a_{24}\psi_4(t) \\
 P_3(t) &= a_{11} + a_{12}\psi_2(t) - a_{13}\psi_3(t) \\
 P_4(t) &= a_{21} - a_{12}\psi_2(t) - a_{24}\psi_4(t)
 \end{aligned}
 \tag{4-9}$$

where  $a_{11} = X/2(1+X)$ ,  $a_{21} = 1/2(1+X)$ ,  $\chi = (k'/k) = \exp(-V/k'P)$ ,  $\psi_2(t) = \exp(-2(k+k')t)$ ,  $\psi_3(t) = \exp(-2kt)$ , and  $\psi_4(t) = \exp(-2k't)$ .

When each site is assumed to be occupied completely, the dipole moment  $\mu_i$  ( $i=1,2,3$  and  $4$ ) at the site is given by

$$\begin{aligned}
 \mu_1(0) &= \mu_y \underline{y}(0) + \mu_x \underline{x}(0) \\
 \mu_2(0) &= \mu_y \underline{y}(0) + \mu_x \underline{z}(0) \\
 \mu_3(0) &= \mu_y \underline{y}(0) - \mu_x \underline{x}(0) \\
 \mu_4(0) &= \mu_y \underline{y}(0) - \mu_x \underline{z}(0)
 \end{aligned}
 \tag{4-10}$$

where  $\mu_x = (\text{dipole moment of } -\text{OCH}_3 \text{ group}) \times \sin\theta$ ,  $\mu_y = (\text{dipole moment of } -\text{OCH}_3 \text{ group}) \times \cos\theta + (\text{dipole moment of O-C})$ , and  $\underline{x}(0)$ ,  $\underline{y}(0)$ , and  $\underline{z}(0)$  are the unit vectors along the x, y, and z axes, respectively.

The total dipole moment  $\mu(t)$  at an arbitrary time can be expressed in terms of occupational probabilities as follows:

$$\mu(t) = \sum_i^4 P_i(t) \mu_i(0)$$

From Eqs. (4-9) and (4-10), this is given by  $\mu(t) = \mu_y \chi(t) + \mu_x (2a_{13}) \psi_3(t) \chi(t) + \mu_x (2a_{24}) \psi_4(t) z(t)$

(4-11)

At the same time,

$P_1 = 1$  and  $P_2 = P_3 = P_4 = 0$  give  $a_{13} = \frac{1}{2}$  and  $a_{24} = 0$   
 $P_2 = 1$  and  $P_1 = P_3 = P_4 = 0$  give  $a_{13} = 0$  and  $a_{24} = \frac{1}{2}$   
 $P_3 = 1$  and  $P_1 = P_2 = P_4 = 0$  give  $a_{13} = -\frac{1}{2}$  and  $a_{24} = 0$ , and  
 $P_4 = 1$  and  $P_1 = P_2 = P_3 = 0$  give  $a_{13} = 0$  and  $a_{24} = -\frac{1}{2}$

(4-12)

Therefore  $\mu(t)$  at each site becomes:

$$\begin{aligned} \mu_1(t) &= \mu_y \chi(t) + \mu_x \psi_3(t) \chi(t) \\ \mu_2(t) &= \mu_y \chi(t) + \mu_x \psi_4(t) z(t) \\ \mu_3(t) &= \mu_y \chi(t) - \mu_x \psi_3(t) \chi(t) \\ \mu_4(t) &= \mu_y \chi(t) - \mu_x \psi_4(t) z(t) \end{aligned}$$

(4-13)

It is obvious that substitutions of  $t = 0$  in Eqs. (4-13) give Eqs. (4-10).



The correlation function  $\Gamma(t)$  may be written

$$\Gamma(t) = \frac{\sum_{i=1}^{i=4} {}^{\circ}P_i \langle \mu_i(0) \cdot \mu_i(t) \rangle}{\sum_{i=1}^{i=4} {}^{\circ}P_i \langle \mu_i(0) \cdot \mu_i(0) \rangle} \quad (4-14)$$

where  ${}^{\circ}P_i$  represents the equilibrium occupational probability, i.e., in this case,  ${}^{\circ}P_1 = {}^{\circ}P_3 = a_{11}$  and  ${}^{\circ}P_2 = {}^{\circ}P_4 = a_{21}$ .

It follows from Eqs. (4-9), (4-10), and (4-14) that,

$$\begin{aligned} \Gamma(t) = & \frac{\mu^2}{\mu_x^2 + \mu_y^2} \langle \chi(0) \cdot \chi(t) \rangle + \frac{\mu^2 x}{\mu_x^2 + \mu_y^2} \frac{x}{1+x} \psi_3(t) \langle \chi(0) \cdot \chi(t) \rangle \\ & + \frac{\mu^2 x}{\mu_x^2 + \mu_y^2} \frac{1}{1+x} \psi_4(t) \langle \zeta(0) \cdot \zeta(t) \rangle \end{aligned} \quad (4-15)$$

Now it is assumed that the molecular correlation function

$$\begin{aligned} & \exp\left(-\frac{t}{\tau_m}\right) \\ & = \langle \chi(0) \cdot \chi(t) \rangle = \langle \chi(0) \cdot \chi(t) \rangle \\ & = \langle \zeta(0) \cdot \zeta(t) \rangle \end{aligned}$$

Then Eq. (4-15) should give the following equation for dielectric relaxation;

$$\frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{A_1}{1 + i\omega\tau} + \frac{A_2}{1 + i\omega\tau_3} + \frac{A_3}{1 + i\omega\tau_4} \quad (4-16)$$

where  $\frac{1}{\tau_3} = \frac{1}{\tau_m} + (2k)$ ,  $\frac{1}{\tau_4} = \frac{1}{\tau_m} + (2k')$

$$A_1 = \frac{\mu^2 y}{\mu_x^2 + \mu_y^2}, \quad A = \frac{\mu^2 x}{\mu_x^2 + \mu_y^2} \frac{X}{1+X}, \quad \text{and}$$

$$A_3 = \frac{\mu^2 x}{\mu_x^2 + \mu_y^2} \frac{1}{1+X}$$

If the dielectric data are analysed by Budd's equation, viz,

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{C_1}{1 + i\omega\tau_1} + \frac{C_2}{1 + i\omega\tau_2} \quad (4-17)$$

where  $\tau = \tau_m$ ,  $C_1 = A_1$  and  $C_2 = \frac{\mu^2}{\mu^2 - \mu^2}$

then,

$$\frac{1}{1 + i\omega\tau_2} = \frac{X}{1+X} \frac{1}{1 + i\omega\tau_3} + \frac{1}{1+X} \frac{1}{1 + i\omega\tau_4} \quad (4-18)$$

This equation is formally similar to Eq. (4-17) so that approximately (see Chap. 3 - (c))

$$\tau_2 = \frac{X}{1+X} \tau_3 + \frac{1}{1+X} \tau_4 \quad (4-19)$$

Therefore,

$$\begin{aligned} \frac{\tau_2}{\tau_4} &= \frac{X}{1+X} \left(\frac{\tau_3}{\tau_4}\right) + \frac{1}{1+X} \\ &\approx \frac{X^2}{1+X} + \frac{1}{1+X} = \frac{1+X^2}{1+X} \end{aligned}$$

This corresponds to

$$(X - 1) \left[ X + 1 - \left( \frac{\tau_2}{\tau_4} \right) \right] = 0$$

This gives

$$X = 1 \tag{4-20}$$

and

$$\frac{\tau_2}{\tau_4} = X + 1 \tag{4-21}$$

Eq. (4-20) corresponds to the case when all the potential sites are identical to each other, whereas Eq. (4-21) corresponds to the case when the observed relaxation time  $\tau_2$  from Budó's equation is greater than the group relaxation time. In the particular case of  $X = 1$ , the observed relaxation time becomes twice of the group relaxation time.

This may explain the variation of relaxation time of methoxy group. According to the present considerations, the dielectric data should be analysed in terms of three relaxation times and weight factors so that the approximations in Eqs. (4-19) and (4-21) can be avoided. However, Budó's equation is usually used, because of the experimental limitations and calculation procedures.

The potential energy at sites II and IV may depend on the steric repulsion (o-substituent), while the energy at sites I and III may be independent of it, because the energy

is mainly based on the mesomeric effect. If the steric repulsion between methoxy group and o-substituent is great in comparison to the mesomeric effect, i.e., ( $k'/k - X \approx 0$ ), the  $\tau_2/\tau_4$  may explain the above conclusion that the steric effect shortens methoxy relaxation time. On the other hand, if the potential energy of the mesomeric effect and the steric repulsion is almost identical to each other ( $V \approx 0$ ), then  $X \approx 1$ , which leads to the result that the observed  $\tau_2$  should be twice the group relaxation time. This might be the case of anisole. In other words, anisole may be characterized by almost identical energy of the steric repulsion and the mesomeric effect.

Therefore we have seen that the observed  $\tau_2$  for methoxy group depends on the relative importance of the steric repulsion to the mesomeric effect. This conclusion may be applicable not only to methoxy group relaxation but also to other rotational groups which have the possibility of mesomeric effect.

## CHAPTER 5 Dielectric Relaxation of Other Ether Compounds

### (a) *ANOMALOUSLY SHORT RELAXATION TIME OF DIPHENYL ETHER*

Fisher found that relaxation times of diphenyl ether and benzophenone in benzene solution at 23°C were 2.8 and 20.4 (psec) respectively<sup>49</sup>. If the relaxation times are considered to be mainly due to Stokes' type friction of dipolar molecule as proposed by Debye, the former relaxation time would be anomalously short compared to the latter one by taking account of Debye's relation, i.e., relaxation time is proportional to the molecular volume in the same solvent and at the same temperature.

The existing data regarding to diphenyl ether and other related compounds are listed in Table 5-1.

There are two main interpretations about this phenomenon (i) mesomeric effect due to overlap of  $\pi$  electrons of oxygen atom with those of benzene rings, proposed by Higasi and Smyth<sup>50</sup>, and (ii) double internal rotation mechanism suggested by Fong<sup>51</sup>.

Let us review these mechanisms briefly.

Table 5-1: Literature values in connection with "anomalously short relaxation time of diphenyl ether".

(1) SYMMETRIC MOLECULES

<u>COMPOUND</u>	<u>SOLVENT</u>	<u>TEMP. (°C)</u>	<u><math>\tau_0</math> (psec)</u>	<u><math>\alpha</math></u>	<u><math>\mu</math> (D)</u>	<u>REF.</u>
Diphenyl Ether	Benzene	20	4		1.12	57
	Benzene		2.8			49
Dinaphthyl ether	Benzene	20	15.4		1.14	57
Dinaphthyl sulfide	Benzene	20	9.2		1.55	57
	Benzene	20	10.0	0.08		53
	Nujol	20	28.8	0.44		53
	Nujol	40	13.5	0.36		53
	Nujol	60	9.1	.29		53
Diphenyl methane		30	6.5		0.26	52
		40	5.4		0.26	52
		40	13	0.08	0.22	53
		60	3.9		0.26	52
		60	7	0.08	0.22	53
		20	20.1		0.36	57
Dibenzyl ether	Benzene	20	18			54
	Benzene	20	27.6		1.12	52
	Benzene	40	15			54
	Benzene	40	18.7		1.11	52
	Benzene	60	13			54
	Benzene	60	13.2		1.11	52
Bibenzyl		60	13.3		0.36	52
		75	10.5		0.34	52
Dicyclohexyl ether	Benzene	20	17			54
	Benzene	40	13			54
	Benzene	60	9			54
Benzophenone	Cyclohexane	25	19.0	0.04	2.93	20
	Cyclohexane	40	15.2	0.03	2.92	20
	Benzene	20	21.2		2.98	57
	Benzene	23	20.4			49
Dicyclohexyl ketone	cyclohexane	25	14.8	0.08	2.69	20
	cyclohexane	40	11.2	0.04	2.69	20
Decafluorobenzophenone	p-xylene	15	30.0	0	1.31	20
	p-xylene	25	27.4	0	1.30	20
	p-xylene	40	20.0	0	1.30	20
	p-xylene	60	16.0	0	1.30	20
Bis(p-bromophenyl) ether	Nujol	20	8.7	0.39		56

Table 5-1 continued:

COMPOUND	SOLVENT	TEMP. (°C)	$\tau_0$ (psec)	$\alpha$	$\mu$ (D)	REF.
4-4'-dibromodiphenyl sulfide	Benzene	20	8.2			57
Bis(p-nitrophenyl) ether	Benzene	20	12.5	0.1	2.22	55
	Benzene	20	13.9	0.10		56
Bis(o-nitrophenyl) ether	Benzene	20	52.0	0.14		56
	Benzene	40	37.4	0.14		56
	Benzene	60	27.8	0.08		56
Bis(diphenylmethyl) ether	Benzene	20	130	0.2	1.23	55
	Benzene	40	120	0.1	1.15	55
Bis(p-nitrophenyl) methane	Benzene	20	22.8	0.11		56

(2) ASYMMETRIC MOLECULES

COMPOUND	SOLVENT	TEMP. (°C)	$\tau_0$ (psec)	$\alpha$	$\mu$ (D)	REF.
2-nitrophenyl phenyl ether	Benzene	20	41			54
	Benzene	40	30			54
	Benzene	60	23			54
4-bromophenyl phenyl ether	Benzene	20	72			54
	Benzene	40	53			54
	Benzene	60	43			54
m-nitrodiphenyl ether	Benzene	20	41.0		4.04	57
2-hydroxydiphenyl ether	Benzene	20	20		1.60	45
2-methyl diphenyl ether	Benzene	20	6.6		1.03	45
4-Biphenyl phenyl ether	Benzene	20	9.4			54
	Benzene	40	9.8			54
	Benzene	60	9.1			54
			20	10.1		1.07
Benzyle phenyl ether	Benzene	20	20			54
	Benzene	40	16			54
	Benzene	40	31		1.13	52
	Benzene	60	12			54
	Benzene	60	17.5		1.14	52
m-Dibenzoyl benzene	p-xylene	25	43.6		2.52	20
	p-xylene	60	27.7		2.50	20
4-Benzoyl pyridine	p-xylene	25	38.0	0.07	2.99	20
	p-xylene	40	30.4	0.07	3.01	20
o-Pyridyl phenyl ether	Benzene	20	17.7		1.96	57
p-Pyridyl phenyl ether	Benzene	20	52.2		2.46	57

Table 5-1 Continued:

<u>COMPOUND</u>	<u>SOLVENT</u>	<u>TEMP. (°C)</u>	<u><math>\tau_0</math> (psec)</u>	<u><math>\alpha</math></u>	<u><math>\mu</math> (D)</u>	<u>REF.</u>
n-Butyl phenyl ether	Benzene	20	25	0.1	1.19	55
	Benzene	20	46	0.1	1.11	55
	Benzene	40	32	0	1.13	55
m-Diphenoxybenzene	Benzene	60	23	0	1.15	55
	Benzene	20	11			54
	Benzene	40	8			54
	Benzene	60	6			54

(3) OTHER MOLECULES

<u>COMPOUND</u>	<u>SOLVENT</u>	<u>TEMP. (C°)</u>	<u><math>\tau_0</math> (psec)</u>	<u><math>\alpha</math></u>	<u><math>\mu</math> (D)</u>	<u>REF.</u>
Fluorenone	Benzene	20	19.9			58
	Benzene	40	14.9			58
	Benzene	60	11.5			58
Thianthrene	Benzene	20	31			54
	Benzene	40	24			54
	Benzene	60	19			54

(i) *Mesomeric Moment Mechanism*<sup>50</sup>.

There are four possible molecular configurations for diphenyl ether as shown in Figure 5-1<sup>50</sup>. Configuration A represents that two benzene rings are coplanar, whereas Configuration B shows that two benzene rings are perpendicular to the plane of the paper. Configurations C and D show that one of the benzene rings lies on the same plane of the paper, while another ring is perpendicular to the plane. Obviously Configuration A is expected to exhibit the greatest steric repulsion from



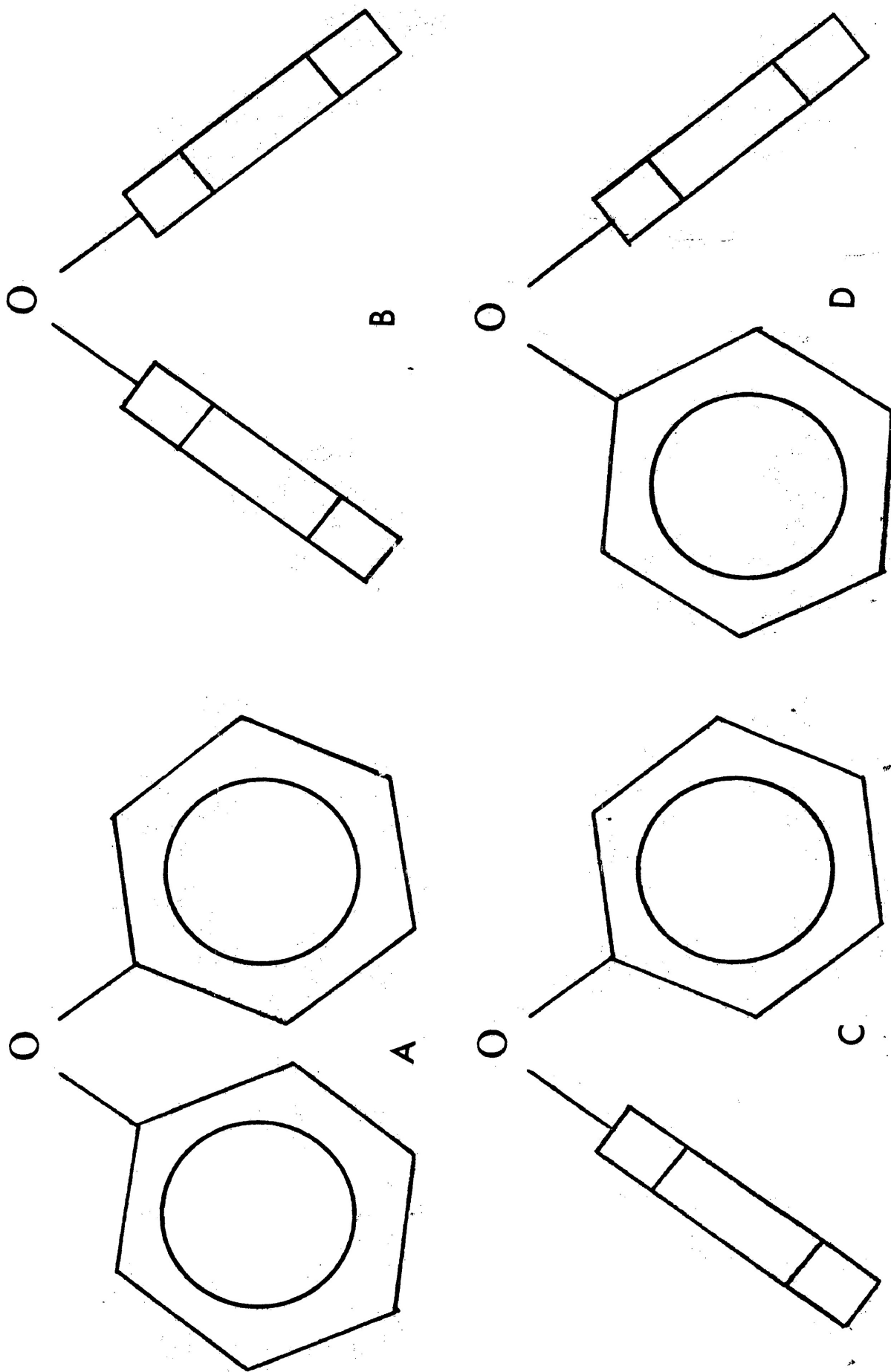


Figure 5-1: Four possible molecular configurations of diphenyl ether

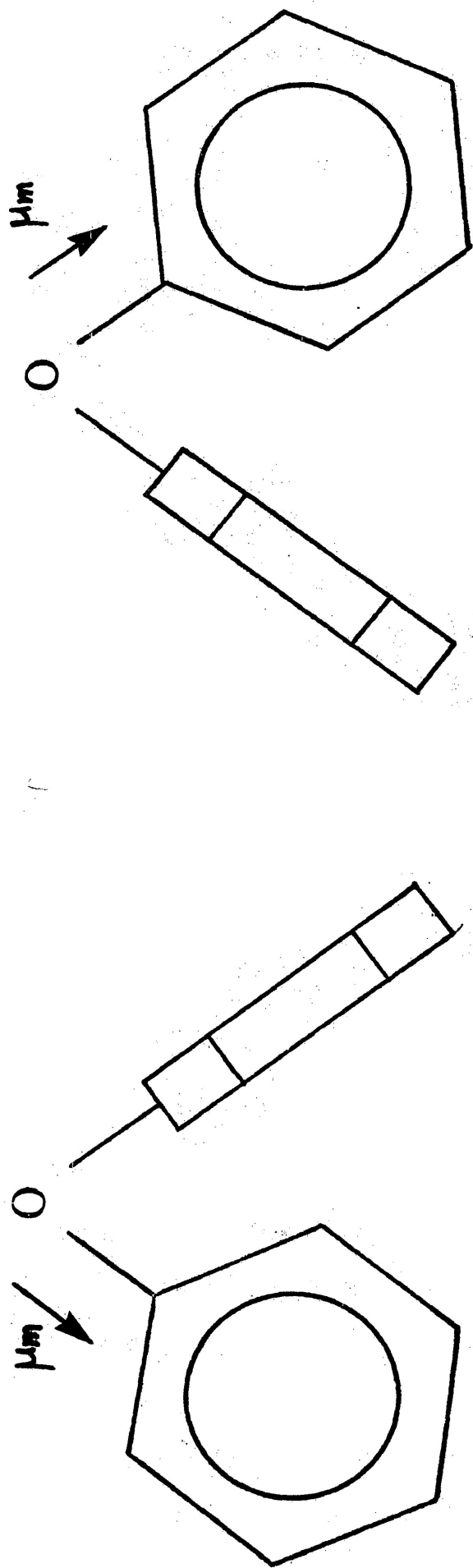


Figure 5-2: Change of the mesomeric moment of diphenyl ether with internal rotation

the hydrogens in other positions, while the repulsion of Configuration B is expected to be very weak. However, we should also take into account delocalization energy arising from <sup>the</sup> overlap of  $\pi$  electrons of the central oxygen atom with the benzene rings. This energy is appeared to increase with the order:  $A > C=D > B$ . Electron diffraction measurements favour Configurations C and D. Now focusing our attention on the mesomeric effect of Configurations C and D, we see that the mesomeric moment changes its direction by internal rotation as shown in Figure 2.

Therefore, the change of the moment depends only on internal rotation, which would mainly contribute to the dielectric relaxation. This necessarily means shortening of the observed relaxation time  $\tau_o$  in comparison with the molecular relaxation time. In the case of benzophenone, however, such an internal rotation is highly hindered by the strong overlap of  $\pi$  orbitals of benzene rings with  $sp^2$  orbitals of the central carbon atom so that only the molecular re-orientation would influence on the relaxation processes. This is the difference between the mechanism of dielectric relaxation of diphenyl ether and that of benzophenone.

*(ii) Double Internal Rotation<sup>51</sup>.*

In this model, the effect of mesomeric moment is entirely excluded, instead, the internal rotation around the C-O bonds is inspected mechanically and it is concluded that if the

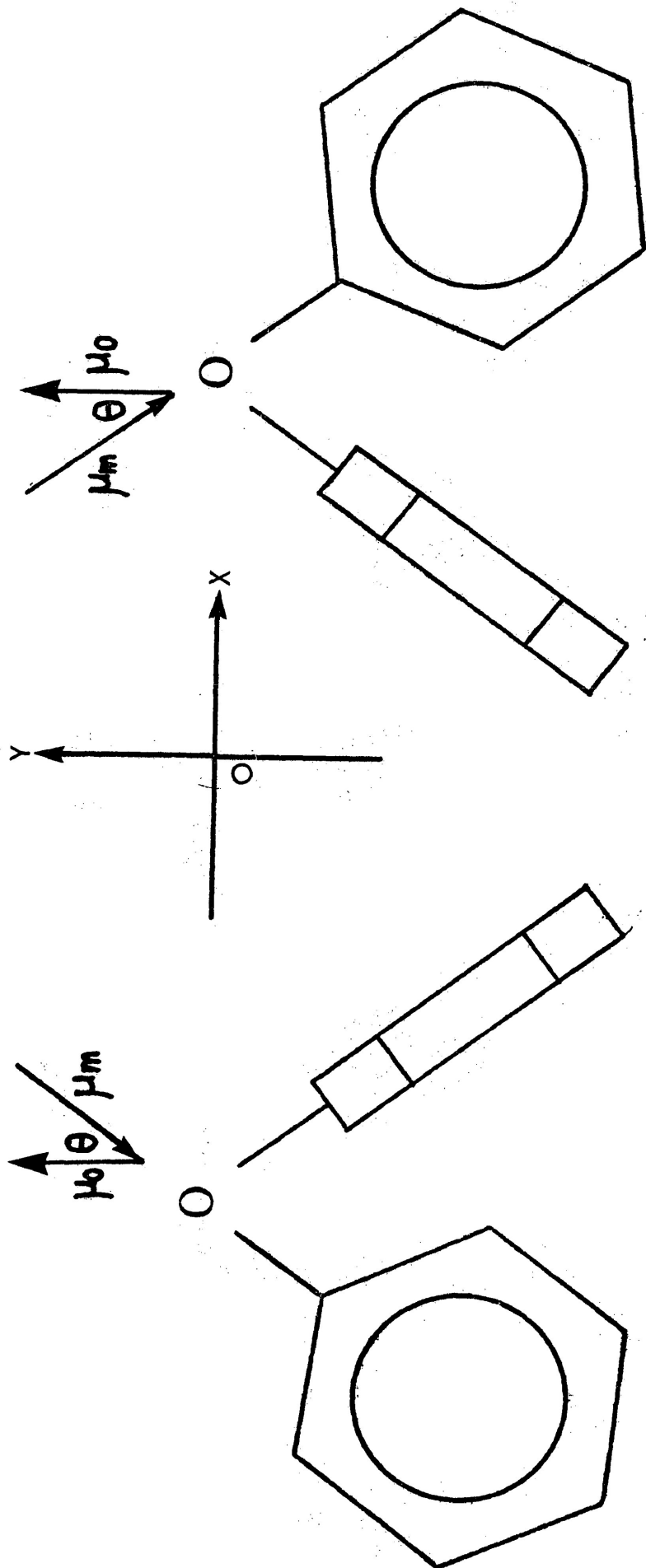


Figure 5-3: Molecular configurations of diphenyl ether and the corresponding dipole moments.  $\mu_o$  and  $\mu_m$  represent molecular and mesomeric moments, respectively, and  $\theta$  is  $1/2 < \text{COC}$

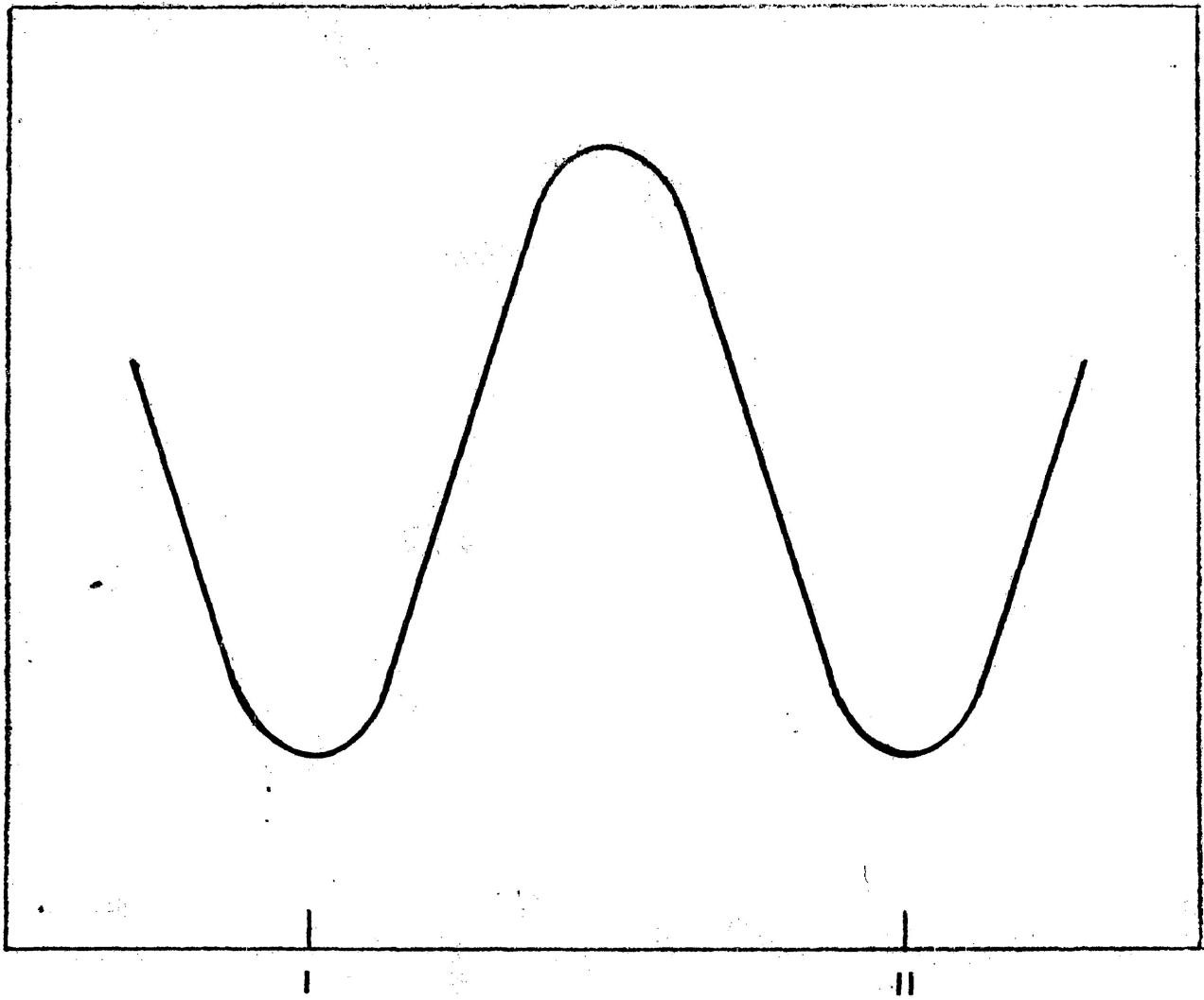


Figure 5-4: Potential energy curve corresponding to 5-3.

internal rotation takes place with minimal potential energy, i.e.,  $\phi_1 = 180^\circ - (90^\circ + \phi_2)$ , where  $\phi_1$  and  $\phi_2$  are the rotational angles of two phenyl rings, the simultaneous variations of  $\phi_1$  and  $\phi_2$  should occur.

In addition, the successive rotations of two phenyl rings lead to overall molecular rotation and approximately <sup>the</sup> same volume swept out by the rotations as that of benzene. Such a coupled rotation would, therefore, explain the anomalous relaxation time of diphenyl ether.

Recently structural problems of diphenyl ether and the related compounds have been investigated by N.M.R.<sup>62,66</sup> and dipole moments<sup>59,61</sup>.

(b) *CORRELATION FUNCTION TREATMENT OF DIELECTRIC RELAXATION OF DIPHENYL ETHER.*

We shall consider two equivalent potential wells for internal rotation of diphenyl ether in accordance with the mesomeric moment mechanism.

The potential energy curve corresponding to Figure 5-3 is shown in Figure 5-4.

The occupational probability  $P_i$  at each site ( $i = 1, 2$ ) is given by

$$\begin{aligned} P_1(t) &= \frac{1}{2} + m\psi(t) \\ P(t) &= \frac{1}{2} - m\psi(t) \end{aligned} \quad (5-1)$$

where  $\psi = \exp(-2kt)$  and  $m$  is a constant determined from the initial conditions. If each site is assumed to be occupied completely, the dipole moment  $\mu_i$  at the site would be;

$$\begin{aligned}\mu_1(0) &= \mu_x x(0) + \mu_y y(0) \\ \mu_2(0) &= -\mu_x x(0) + \mu_y y(0)\end{aligned}\quad (5-2)$$

where  $\mu_x = -\mu_m \sin\phi$ ,  $\mu_y = \mu_0 - \mu_m \cos\phi$ , and  $x(t)$  and  $y(t)$  stand for the unit vectors along the x and y axes, respectively.

The total dipole moment of the system at an arbitrary time is, therefore, given by:

$$\begin{aligned}\mu(t) &= \mu_1(0)P_1(t) + \mu_2(0)P_2(t) \\ &= \mu_x(2m)\psi(t)x(t) + \mu_y y(t)\end{aligned}\quad (5-3)$$

$m$  can be obtained by the assumptions in Eq. (5-2).

$$P_1(0) = 1 \quad \text{and} \quad P_2(0) = 0 \quad \text{give} \quad m = \frac{1}{2}$$

$$P_2(0) = 1 \quad \text{and} \quad P_1(0) = 0 \quad \text{give} \quad m = -\frac{1}{2}$$

(5-4)

Hence Eqs. (5-4) and (5-3) lead to

$$\begin{aligned}\mu_1(t) &= \mu_x \psi(t)x(t) + \mu_y y(t) \\ \mu_2(t) &= -\mu_x \psi(t)x(t) + \mu_y y(t)\end{aligned}\quad (5-5)$$

The correlation function  $\phi(t)$  for this system may be given by

$$\phi(t) = \frac{\sum_i^2 P_i \langle \mu_i(0) \cdot \mu_i(t) \rangle}{\sum_i^2 P_i \langle \mu_i(0) \cdot \mu_i(t) \rangle}\quad (5-6)$$

where  ${}^{\circ}P_i$  is the equilibrium occupational probability (in the present case,  ${}^{\circ}P_1 = {}^{\circ}P_2 = \frac{1}{2}$ ).

Making the scalar-products in Eq.(5-6) from Eqs.(5-2) and (5-5) we finally find:

$$\phi(t) = \frac{\mu_y^2}{\mu_x^2 + \mu_y^2} \langle \chi_y(0) \cdot \chi_y(t) \rangle + \frac{\mu_x^2}{\mu_x^2 + \mu_y^2} \langle \chi_x(0) \cdot \chi_x(t) \rangle$$

This should give the following equation for dielectric relaxation

$$\frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{C_1}{1 + i\omega\tau_m} + \frac{C_2}{1 + i\omega\tau_2} \quad (5-7)$$

where

$$C_1 = \frac{\mu_y^2}{\mu_x^2 + \mu_y^2}, \quad C_2 = \frac{\mu_x^2}{\mu_x^2 + \mu_y^2} \quad (5-8)$$

$$\langle \chi_x(0) \cdot \chi_x(t) \rangle = \langle \chi_y(0) \cdot \chi_y(t) \rangle = \exp\left(-\frac{t}{\tau_m}\right)$$

( $\tau_m$  is the molecular relaxation time)

$$\text{and } \frac{1}{\tau_2} = \frac{1}{\tau_m} + (2k)$$

As the group relaxation time  $\tau_g$  may be defined by  $\tau_g = (2k)^{-1}$ , then

$$\frac{1}{\tau_2} = \frac{1}{\tau_m} + \frac{1}{\tau_g} \quad (5-9)$$



$C_2$  can be rewritten as

$$C = \frac{1}{1 + \left(\frac{\mu_y}{\mu_x}\right)^2} = \frac{1}{1 + \left(\frac{2\mu_{C-O}}{\mu_m} - 1\right)^2 \cot^2 \theta} \quad (5-10)$$

where  $\mu_{C-O}$  is the bond dipole moment at C-O bond.

If  $\mu_x \gg \mu_y$  in Eq. (5-7), the second term on the right hand would be dominant so that Eq. (5-9) may govern the relaxation process, which is essentially the same as Fong's conclusion.

Therefore we have seen that Fong's result can be derived with the help of Higasi's point of view.

### (c) DISCUSSION AND RESULTS

The anomalously short relaxation time can be explained by the present treatment as follows:

Substitutions of  $\mu_{C-O} = 0.95 = \mu_m$  and  $\theta = 60^\circ$  in Eq. (5-10) lead to  $C_2 = 0.75$ , (This is only a tentative estimate, which just states that if  $\mu_m \geq \mu_{CO} = 0.95$  (D), then  $C_2 \geq 0.7$ ) and from Eq. (5-9)  $\tau_m = 19$  (psec)<sup>20</sup> (relaxation time of benzophenone) and  $\tau_g = 7.3$  (psec)(pure pyridine at 20°C)<sup>101</sup> give  $\tau_{obs} = 5.3$  (psec), which can be compared with the experimental results (see Table 5-1).

According to Eq. (5-10), if  $\mu_{C-O}$  has the same direction as the mesomeric moment  $\mu_m$ , and  $|\mu_{C-O}| \leq 1$  (D),  $C_2$  becomes almost unity for  $\mu_m \approx 1$ (D). (Note that for  $(p-X C_6H_5)_2$ ,  $\mu_{C-O}$  in Eq. (5-10) can be readily obtained by [(dipole moment of C-O) - (dipole moment of C-X)]. Therefore molecules which contain  $X = F, Cl, Br,$  and  $I^{12}$  are expected to have  $C_2 \approx 1$ , and apparently short relaxation time, because they have  $\mu_{C-X}$  of  $1$  (D)  $\sim 2$  (D), and the same directions of  $\mu_{C-X}$  as  $\mu_m$ . Molecules of  $X = CH_2F, CF_3, CH_2Cl, CHCl_2, CH_2Br, OCH_3, SCH_3, OH, CH_2OH, SH, COOH, COOCH_3,$  and  $NCCH_3)_2$ , may also satisfy the above conditions, although they are so called "flexible".

For bis-(p-nitrophenyl) ether, the present model fails to explain the short relaxation time of  $\tau_2 = 12.5$  (psec) without assumption of  $\mu_m \approx 3$  (D). But at the same time it should be also pointed out that bis-(p-nitrophenyl)methane has  $\tau_0 = 22.8$  (psec), which may be explained not by Fong's model but by the present treatment.

The short relaxation time of diphenyl methane may be explained in terms of the hyperconjugation of the central  $-CH_2-$  group with the two phenyl rings<sup>50</sup>.

In the case of benzophenone, Eq. (5-10) can be written as

$$C_2 = \frac{1}{1 + \left( \frac{\mu_{C=O} - \mu_m \cos 60^\circ}{\mu_m \sin 60^\circ} \right)^2}$$

where  $\angle \text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}$  is taken as  $120^\circ$ <sup>67,68</sup>. Insertions of  $\mu_m = 1$  (D) and  $\mu_{\text{C}=\text{O}} = 2.83$  in the above equation give  $C_2 = 0.12$ , which indicates that contribution from the molecular relaxation to the mean relaxation time is very large in this molecule. Fong's model requires freezing of internal rotation around the  $\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}$  bond to account for the observed relaxation time of benzophenone in connection with that of fluorenone (obviously internal rotation around the  $\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}$  bond in this molecule is not probable). However as seen from the above estimates, the present model implies that the relaxation time of benzophenone should be similar to that of fluorenone even if the internal rotation in the former compound is possible. Non-planar configuration of the two aromatic rings in benzophenone is recently suggested from N.M.R. measurements by Montaudo, Finocchiaro and Maraviglia. This configuration is also favoured by several workers<sup>67,69</sup>.

We cannot strictly apply the present model to the asymmetrical molecules. However it is of interest to note that o-methylphenyl phenyl ether ( $\mu=1.03$  D) and biphenyl phenyl ether ( $\mu=1.07$  D) have relaxation times of 6.6 (psec) and 10.1 (psec), respectively, and dipole moments of the both compounds are very close to that of diphenyl ether ( $\mu=1.12$  D). (See Table 5-1).

If molecular configurations given in Figure 5-5 are possible, and dipole moments of the phenyl group indicated by " $\text{C}_6\text{H}_5$ " and the methyl group are negligibly small, the same treatment as that employed for diphenyl ether would be possible.

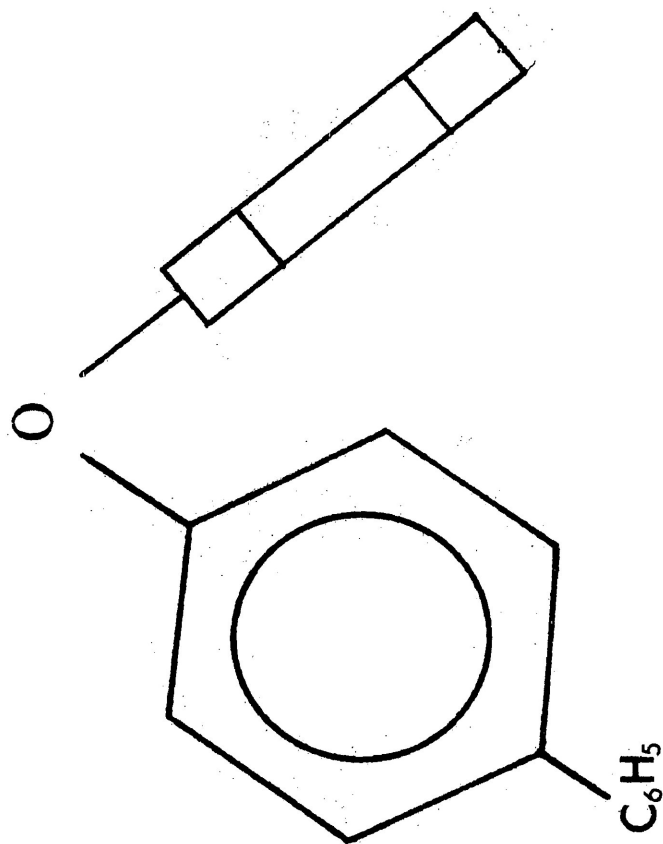
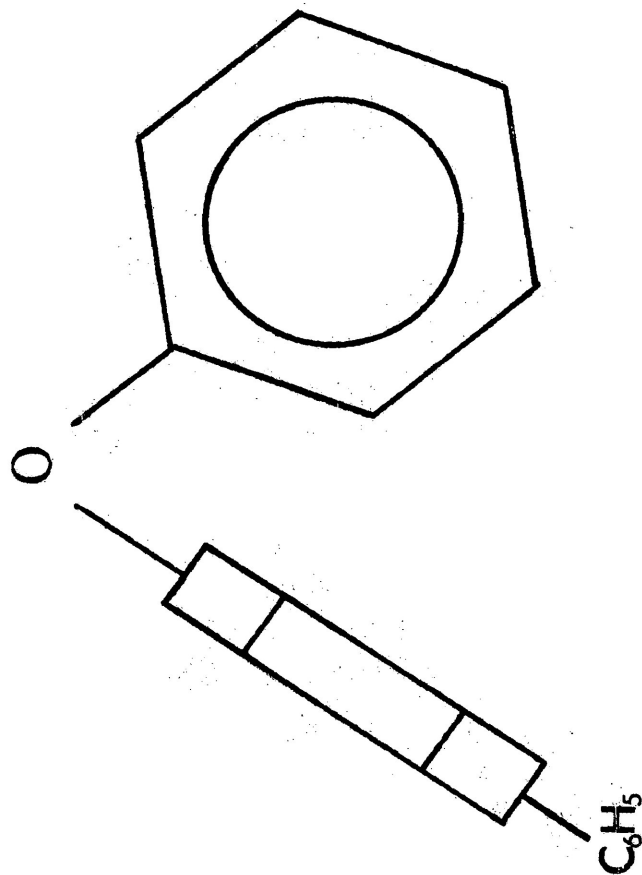


Figure 5-5 (b): Molecular Configurations for binhenyl phenyl ether

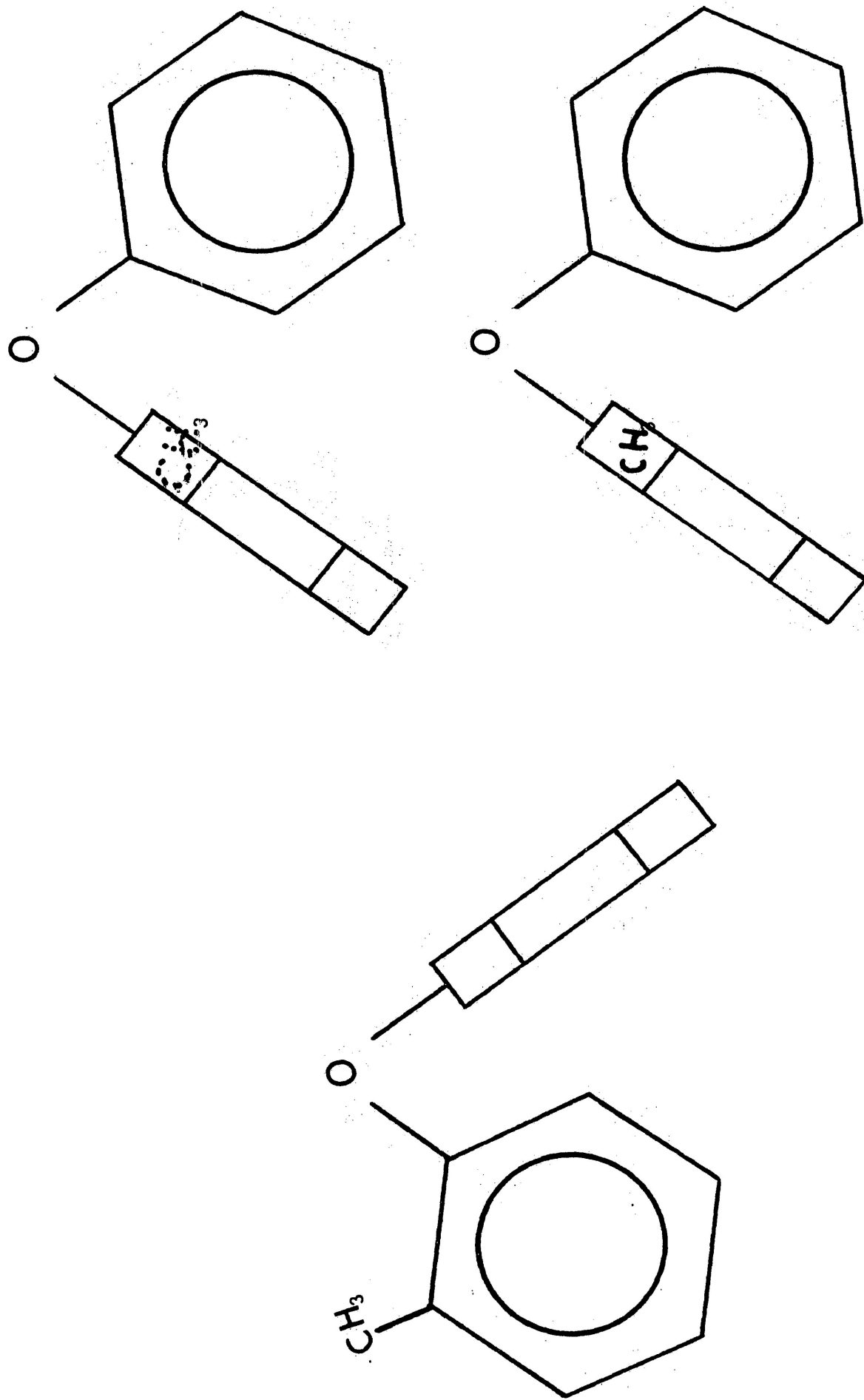


Figure 5-5 (a): Molecular configurations for o-methylphenyl ether.

If  $\tau_m = 18$  (psec) and  $\tau_g = 9$  (psec) are assumed for o-methylphenyl phenyl ether, Eq. (5-9) gives  $\tau_{obs} = 6.0$  (psec). Similarly if  $\tau_m = 3 \times 9 = 27$  (psec) and  $\tau_g = 3 \times 9 / 2 = 13.5$  (psec) are assumed for biphenyl phenyl ether, Eq. (5-9) gives  $\tau_{obs} = 9$  (psec). On the other hand, in the cases of o-hydroxyphenyl phenyl ether and o-nitrophenyl phenyl ether, the group moments of -OH (1.6D) and -NO<sub>2</sub> (4(D)) cannot be neglected so that shortening of relaxation times may not occur<sup>12</sup>.

Bis-(alkyl) ether is not expected to show the shortening of relaxation time, because there is no mesomeric moment, and internal rotation around C-O bonds would be different from those of diphenyl ether.

Allyl ether was measured in p-xylene at 25°C to have  $\tau_o = 5.65$  (psec),  $\alpha = 0$  and  $\mu = 1.22$  (D). The  $\tau_o$  value is well compared with those of di-n-butyl ether<sup>70</sup> ( $\tau_o = 6.5$  (psec) in benzene at 25°C) and di-n-propyl ketone<sup>71</sup> ( $\tau_o = 5.4$  (psec) in benzene at 25°C), which suggests that the shortening of relaxation time does not occur in the compound. Furthermore, the observed dipole moment is in excellent agreement with that of diethyl ether ( $\tau_o = 2.4$  (psec) and  $\mu = 1.22$  (D))<sup>20</sup>, which implies that the  $\pi$  electrons involved in this compound do not shift toward C-O bonds so that the coupling of molecular relaxation time with group one may not be expected.

Anderson and Smyth<sup>54</sup> attempted to calculate dipole moments for substituted phenyl ethers based on "free rotation model" without considering mesomeric moments and obtained "not bad" agreement between calculated and experimental values for most of compounds treated by them. But here dipole moment calculations are made for simple compounds to obtain the mesomeric moments from the experimental values. For 4-4'-dihalodiphenyl ether, molecular models are essentially based on Figure 5-1, and the results are listed in Table 5-2 together with those of Anderson and Smyth. On the other hand, for 4-halophenyl phenyl ethers, the molecular models are given in Figure 5-6, and the results are collected in Table 5-3. It will be seen that for 4-4'-dihalodiphenyl ethers, calculated mesomeric moments in cases A, C. and D are very small, however, for 4-halophenyl phenyl ether, they are in the order of 1 (D), which was assumed in estimates of  $C_2$  previously.

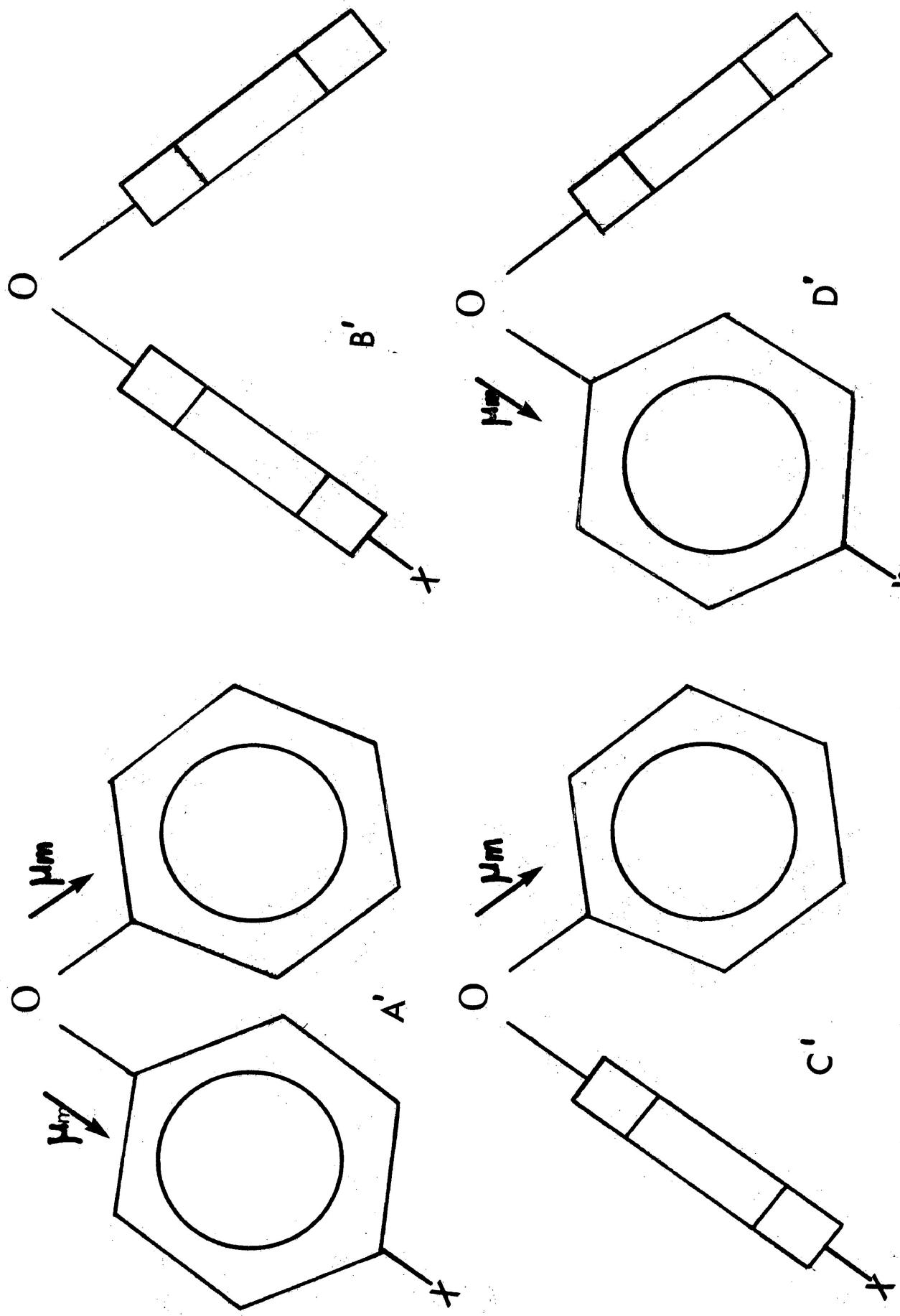


Figure 5-6: Molecular models for calculations of mesomeric moments



Table 5-2: Calculated mesomeric moments  $\mu_m$  for 4-4'-dihalo-diphenyl ethers ( $p\text{-XC}_6\text{H}_5$ )<sub>2</sub>O, and diphenyl ether.

(see Figure 5-1)

	Model	F	Br	H
$\mu_{\text{obs}}$ (D)		0.51 <sup>a)</sup>	0.60 <sup>a)</sup>	1.16 <sup>b)</sup>
$\mu_{\text{XC}_6\text{H}_5}$ (D)		1.46 <sup>b)</sup>	1.54 <sup>b)</sup>	--
$\mu_m$ (D)	A	0.09	0.10	2.20
	C & D	0.15	0.17	1.25
$\mu_{\text{calc}}$	B	0.42	0.50	1.04
$\mu_{\text{calc}}^*$		0.44 <sup>a)</sup>	0.50 <sup>a)</sup>	--

$\mu_{\text{CO}} = 1.04$  (D) was used after ref. (50). a) and b) were obtained from refs. (54) and (12).  $\mu_{\text{calc}}$  based on Model B is expected to be the same as  $\mu_{\text{calc}}^*$ .  $\angle \text{COC}$  was regarded as  $120^\circ$  b).

Table 5-3: Calculated mesomeric moments  $\mu_m$  for 4-halophenyl phenyl ethers  $p\text{-XC}_6\text{H}_5\text{O C}_6\text{H}_5$ .

(see Figure 5-6)

	Model	F	Cl	Br
$\mu_{\text{obs}}$ (D)		1.37 a)	1.55 a)	1.57 a)
$\mu_{\text{C}_6\text{H}_5\text{X}}$ (D)		1.46 b)	1.58 b)	1.54 b)
$\mu_m$ (D)				
	A'	0.84	0.98	1.10
	C'	1.11	1.21	1.26
	D'	0.51	0.74	0.77
$\mu_m$ (av)	C' & D'	0.81	0.98	1.02
$\mu_{\text{calc}}$	B'	1.30	1.39	1.36
$\mu_{\text{calc}}^*$		1.30 a)	1.39 a)	1.32 a)

$\mu_m(\text{av})$  was obtained by  $1/2 (\mu_m(\text{C}') + \mu_m(\text{D}'))$ , where  $\mu_m(\text{C}')$  and  $\mu_m(\text{D}')$  are  $\mu_m$ 's for models C' and D', respectively, and other symbols are the same as those in Table 5-3.

## CHAPTER 6 Some Sulfur Compounds

### (a) *DI- $\beta$ -NAPHTHYL AND DIMETHYL DISULFIDES*

Dialkyl and diaryl disulfides are thought to have skew configurations<sup>72-76</sup>. Bergson<sup>77-78</sup> has shown from molecular orbital considerations that a dihedral angle of  $90^\circ$  is energetically favoured in a sulfide, as this leads to minimal repulsions between the lone-pair electrons of the two sulfur atoms. Furthermore, the stability of this form could be enhanced by  $\pi$ -bonding arising from overlap of the p electron pair of one sulfur atom with 3d orbitals of the other. These considerations are compatible with the observed S-S bond shortening<sup>74</sup>.

The dielectric measurements of dialkyl and diaryl disulfides were made by Aroney, Chio, Le Fevre, and Radford<sup>79</sup>, whose results are collected in Table I.

Di- $\beta$ -naphthyl disulfide is measured in p-xylene at  $25^\circ\text{C}$  to have  $\tau_0 = 16.1$  (psec),  $\alpha = 0$ , and  $\mu = 1.94$  (D), and dimethyl sulfide is also measured at the same conditions to have  $\tau_0 = 4.1$  (psec),  $\alpha = 0$ , and  $\mu = 1.97$  (D). These values are well compared with those of Table 6-1 except the relaxation time of di- $\beta$ -naphthyl sulfide.

Table 6-1: Dipole moments  $\mu$  and relaxation times  $\tau$  of some dialkyl and diaryl disulfides. Reported in Ref. (79).

	$\mu$ (D)	$\tau$ (psec)
(t-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O <sub>2</sub>	0.83	1.9
(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>	1.87	4.3
(t-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> S <sub>2</sub>	1.84	8.5
(p-ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> S <sub>2</sub>	0.45	20
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>2</sub>	1.79	15
( $\beta$ -C <sub>10</sub> H <sub>7</sub> )S <sub>2</sub>	1.97	33

	<u>Temp.</u>	$\tau$	$\alpha$	$\mu$
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>2</sub>	20°C	13	0.3	1.90
	40°C	10	0.3	1.96

Ref. 55

It should be added that Aroney *et al* determined relaxation times in Table I from the dielectric loss measurements at two frequencies, using the Debye equation<sup>79</sup>.

In the disulfide compounds, there is no dipole component along the S-S bond. Therefore if the rotation around the S-S bond is possible, while the rotations around the S-C bonds

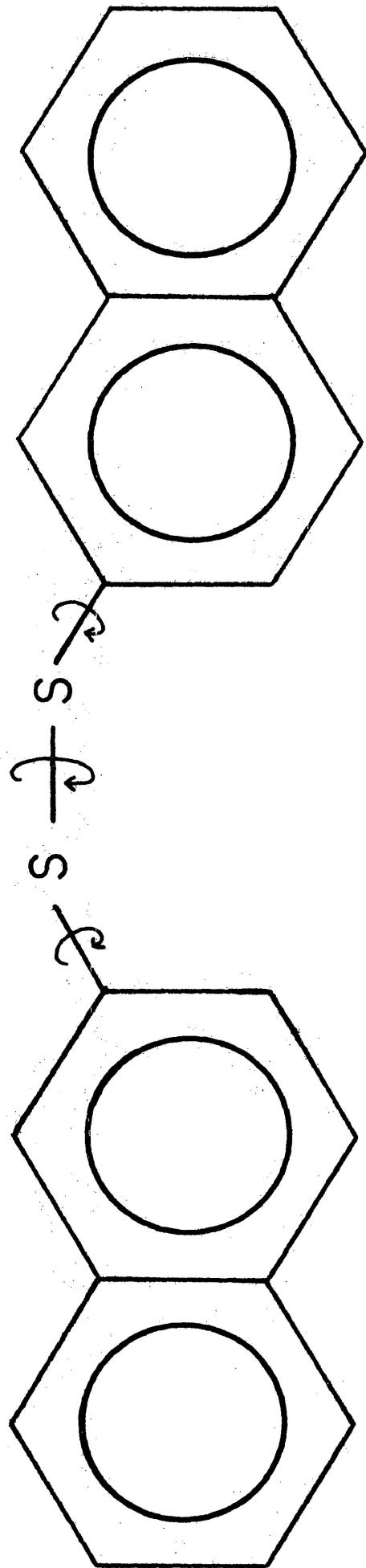


Figure 6-1: Possible rotational axes of di-β-naphthyl disulfide.

are not possible, the shortening of relaxation time similar to that for p-dimethoxybenzene would be expected (see Chap. 1 (c) (ii)) so that the observed relaxation time  $\tau_{\text{obs}}$  could be expressed in the form as

$$\frac{1}{\tau_{\text{obs}}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} \quad (6-1)$$

where  $\tau_1$  is the molecular relaxation time and  $\tau_2$  the group relaxation time associated with the rotation of the S-S bond.

On the other hand, in the case when the rotations around the two C-S bonds are possible, while the rotation of the S-S is not possible, the dielectric behaviour somewhat similar to that for diphenyl ether would be expected (see Chap. 5), and the observed relaxation time may be characterized by the equation

$$\frac{1}{\tau_{\text{obs}}} = \frac{1}{\tau_1} + \frac{1}{\tau_d} \quad (6-2)$$

where  $\tau_d$  is the relaxation time connected with the rotations about the two C-S bonds.

As the third case, if it is assumed that the rotations of the three rotational axes in Figure 6-1 simultaneously occur, the following equation would be satisfied

$$\frac{1}{\tau_{\text{obs}}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_d} \quad (6-3)$$

Substitutions of  $\tau_1 = 40$ ,  $\tau_2 = 30$  and  $\tau_d = 20$  in Eqs. (6-1), (6-2) and (6-3) give  $\tau_{\text{obs}} = 17.1$ , 13.3, and 9.2, respectively.

( $\tau_0$  of 2-bromonaphthalene in cyclohexane at 25°C is 25.5 (psec))<sup>25</sup>. It is interesting to note that dinaphthyl ether, which may be responsible for possibility (2), has  $\tau_0 = 15.4$  (psec) in benzene at 25°C<sup>57</sup>. The observed relaxation time of di- $\beta$ -naphthyl disulfide of 16.1 (psec) would, therefore, exclude the possibility of the third case. But because of uncertainty of the above substitutions, we cannot say that possibility (1) is more possible than possibility (2).

From the  $\tau_0$  value of dimethyl disulfide, it can be said that the rotation around the S-S bond is unlikely to occur. (For example, compare it with <sup>the</sup> $\tau_0$  value of dimethoxymethane (3.52 (psec)), which is regarded as <sup>a</sup>rigid molecule). (Chap. 4). This suggests that the possibility (1) may not be valid. Therefore, the possibility (2) is most likely for the disulfide compounds. For dimethyl disulfide, as there is no appreciable mesomeric moment contribution to the shortening of the observed relaxation time, the rotations around the C-S bonds do not apparently contribute to the observed relaxation time.

The possibility (2) is also supported by the measurements of Kerr constant<sup>80</sup>, and dipole moment<sup>79-81</sup>. From the standpoint, the dihedral angles of dialkyl and diaryl disulfides are evaluated.

(b) *THIOPHENOL AND 4-CHLORO-M-BENZENEDITHIOL*

O-chlorophenol is known to make intramolecular hydrogen bond, which is supported by measurements of infra-red spectra<sup>38, 85</sup> and dipole moments<sup>13, 82-84</sup>. Similar hydrogen bonds have been reported for o-halothiophenols by Josien, Castinal and Saumagne<sup>86</sup>, and Lumbroso and Passerini<sup>14</sup>.

Thiophenol is measured in p-xylene at 25°C to have  $\tau_0 = 10.9$  (psec),  $\alpha = 0$ ,  $\tau_1 = 12.8$  (psec),  $\tau_2 = 3.2$  (psec),  $C_1 = 0.84$  and  $\mu = 1.03$  (D). Lumbroso and Dumas<sup>15</sup> determined a group moment angle of 46° and a dipole moment of 1.19 (D) for the compound. Using these values, we obtain  $C_1 = 0.48$ , which is very small in comparison with the observed value. It is interesting to note that the above observed values are well compared with those of anisole. (Farmer and Walker<sup>29</sup>;  $\tau_0 = 9.0$  (psec),  $\alpha = 0.03$ ,  $\tau_1 = 13.3$  (psec),  $\tau_2 = 7.0$  (psec),  $C_1 = 0.33$ , and  $\mu = 1.19$  (D) in p-xylene at 25°C, and Kranbuehl, Klug, and Vaughan<sup>35</sup>;  $\tau_1 = 12.4$  (psec),  $\tau_2 = 2.28$  (psec), and  $C_1 = 0.75$  in benzene at 20°C, for instance, mole fraction = 0.721). Therefore, the observed  $\tau_1$  and  $\tau_2$  of thiophenol may be attributed to molecular and group relaxation times, respectively.

4-Chloro-m-benzenedithiol has  $\tau_0 = 12.6$  (psec),  $\alpha = 0.12$ ,  $\tau_1 = 15.5$  (psec),  $\tau_2 = 2.5$  (psec),  $C_1 = 0.84$ , and  $\mu = 1.45$  (D) in p-xylene at 25°C.



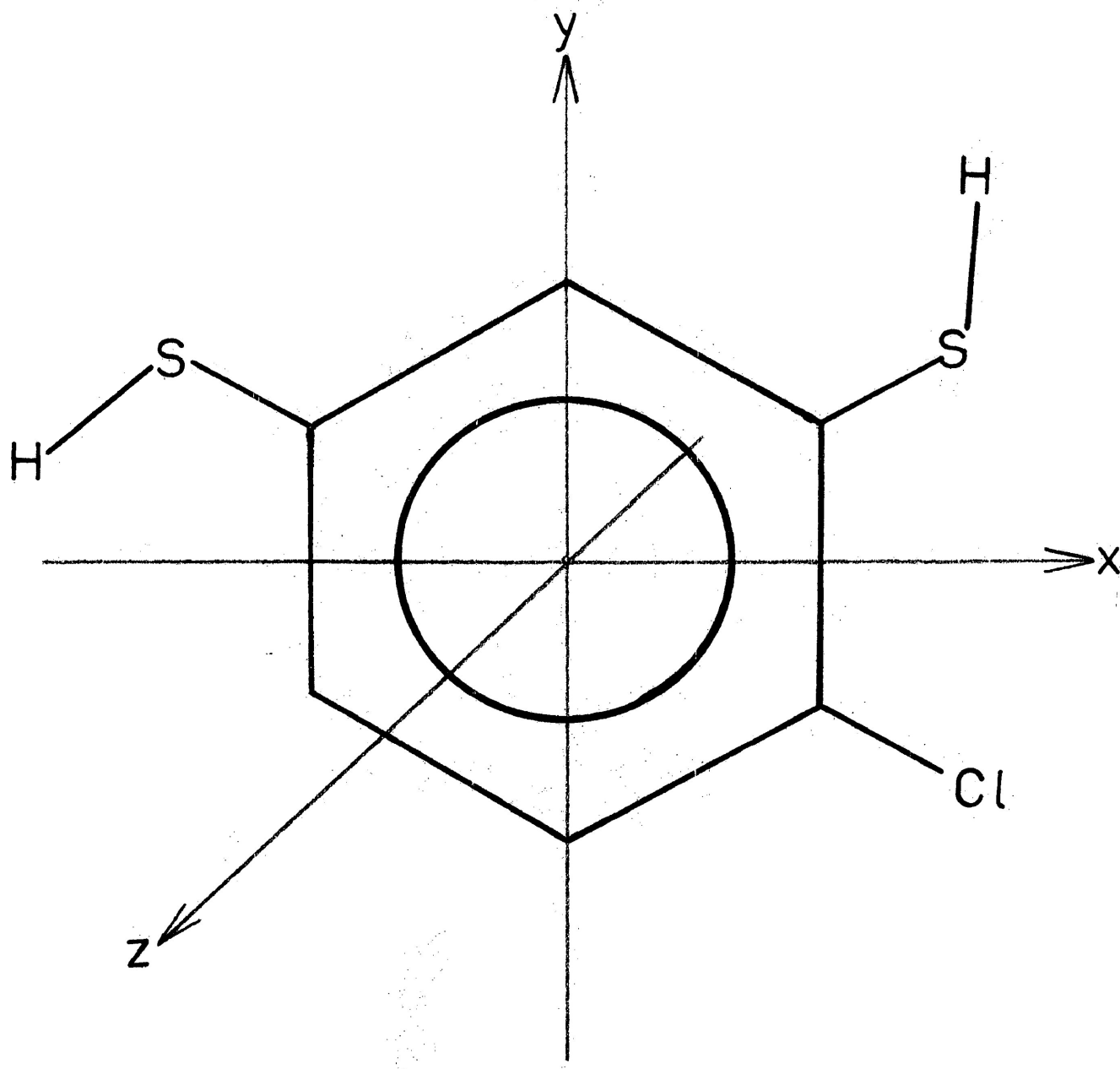


Figure 6-2: Coordinate system for 4-chloro-m-benzenedithiol.

The dipole moment for free rotation is calculated as 1.83 (D), which is too large to account for the observed value. Conformational analysis gives 1.49 (D) for  $(\phi_1, \phi_2) = (0^\circ, 90^\circ) = (0^\circ, 270^\circ)$ , 1.45 (D) for  $(\phi_1, \phi_2) = (90^\circ, 0^\circ) = (270^\circ, 0^\circ)$ , and 1.37 (D) for  $(\phi_1, \phi_2) = (90^\circ, 270^\circ) = (270^\circ, 90^\circ)$ . If this molecule makes <sup>an</sup> intra-molecular hydrogen bond between <sup>the</sup> the chlorine atom and the -SH group at <sup>the</sup> the 2 position, then  $\phi_1 = 180^\circ$  may be expected. However, this angle gives 1.99(D), 2.11 (D), 2.23 (D) and 2.11 (D) for  $\phi_2 = 0^\circ, 90^\circ, 180^\circ$  and  $270^\circ$ , respectively, all of which do not agree with the observed moment.

Now if the SH group at <sup>the</sup> the 4 position is assumed to exhibit free rotation, while that of <sup>the</sup> the 2 position is assumed to be fixed at an angle of  $\phi_1$ , then the average square dipole moment is given by

$$\langle \mu^2 \rangle = \frac{\int_0^{2\pi} \mu^2 d\phi_2}{\int_0^{2\pi} d\phi_2}$$

$$= m_x^2 + \mu^2 + 2Q^2 \sin^2 B + 2Q \sin B (\mu \sin A - m_x \cos A) \cos \phi_1$$

where  $m_x = x \sin C$ ,  $\mu = 2(P + Q \cos B) \cos A + X \cos C$ , and notations are found in  $X = 1.58(D)$ ,  $C = 120^\circ$ ,  $P = 0$ ,  $Q = 1.19 (D)$ ,  $B = 46^\circ$  and  $A = 60^\circ$  give moments of 1.49 (D), 1.83 (D), and 2.11 (D) for  $\phi_1 = 0^\circ, 90^\circ$  and  $180^\circ$ , respectively. The above assumptions

may be supported by agreements between the observed dipole moments and the calculated ones for free rotation of m-dimethoxybenzene, and m-halothiophenols (see Tables 2-5 & 2-6). However,  $\phi_1 = 180^\circ$  gives a moment of 2.11 (D), which does not agree with the observed one, whereas  $\phi_1 = 0^\circ$  gives a moment, which is very close to the observed one. Therefore it will be seen that the formation of <sup>an</sup> intramolecular hydrogen bond in this compound is unlikely. This may be also indicated by comparison of  $\tau_2 = 2.48$  (psec) with  $\tau_2 = 3.15$  (psec) of thiophenol. Because such an intramolecular hydrogen bond is expected to lengthen the SH group relaxation time.

## CHAPTER 7 Difuryl Mercuries

There are two opinions in connection with the valence angle of mercury when it is bonded to carbon or to carbon and halogen, i.e., (i) the valence angle is  $180^\circ$ <sup>87~92</sup>, and (ii) it is not  $180^\circ$ <sup>93~97</sup>. Measurements of Raman spectra<sup>89,90</sup>, electron diffraction<sup>91</sup>, and X-ray diffraction<sup>92</sup> in <sup>the</sup> vapour state support (i). In addition, Smyth and Oesper<sup>88</sup> assumed (i) in calculation of the dipole moment of benzylmercuric chloride. The valence electrons of Hg(II) which occupies  $6s^2$  orbitals might be expected in compound formation to assume  $sp$  orbitals, which implies (i).

However, Hampson<sup>94</sup> reported dipole moments listed in Table I for diphenyl mercury and mercuri-bis-p-substituted benzene. These non-zero moments suggested (ii).

Coop and Sutton<sup>99</sup> attempted to explain that the non-zero apparent orientation polarization of mercuri-bis-chlorobenzene was due to the atomic polarization, but their calculations showed too low <sup>an</sup> atomic polarization for this compound to account for the apparent orientation polarization.

Sipos, Sawatzky and Wright<sup>95</sup> measured the distortion polarization of diphenyl mercury, and reported <sup>a</sup> dipole moment of 0.79 (D) for the compound. Later it was shown by Sawatzky and Wright<sup>96</sup> that aliphatic bis-mercurials also had non-zero dipole moment. (See Table 7-1).

Table 7-1: Dipole moments of bis-mercurials<sup>96</sup>.

COMPOUND	TEMP. (°C)	SOLVENT	$\mu_{\text{obs}}$ (D)
$(\text{C}_6\text{H}_5)_2\text{Hg}$	40	Benzene	1.08
$(\text{C}_6\text{H}_5)_2\text{Hg}$	30	Benzene	0.92
$(\text{C}_6\text{H}_5)_2\text{Hg}$	20	Benzene	0.72
$(\text{C}_6\text{H}_5)_2\text{Hg}$	40	Dioxane	0.80
$(\text{C}_6\text{H}_5)_2\text{Hg}$	25	Dioxane	0.85
$(\text{C}_6\text{H}_5)_2\text{Hg}$	20	Dioxane	0.89
$(\text{C}_6\text{H}_5)_2\text{Hg}$	40	Dioxane	0.88
$(\text{C}_6\text{H}_5)_2\text{Hg}$	25	Dioxane	0.85
$(\text{C}_6\text{H}_5)_2\text{Hg}$	20	Dioxane	0.93
$(\text{CH}_3)_2\text{Hg}$	20	Dioxane	0.71
$(\text{CH}_3)_2\text{Hg}$	20	Benzene	0.69
$(\text{CH}_3)_2\text{Hg}$	20	Benzene	0.74
$(\text{CF}_3)_2\text{Hg}$	20	Benzene	0.97
$(\text{CF}_3)_2\text{Hg}$	20	$\text{CCl}_4$	0.29
$(\text{C}_2\text{H}_5)\text{Hg}$	20	Benzene	0.55
$(\text{N-C}_3\text{H}_7)\text{Hg}$	20	Benzene	0.54
Mercuracyclohexane	20	Benzene	0.86
Mercuracycloheptane	20	$\text{CS}_2$	0.90

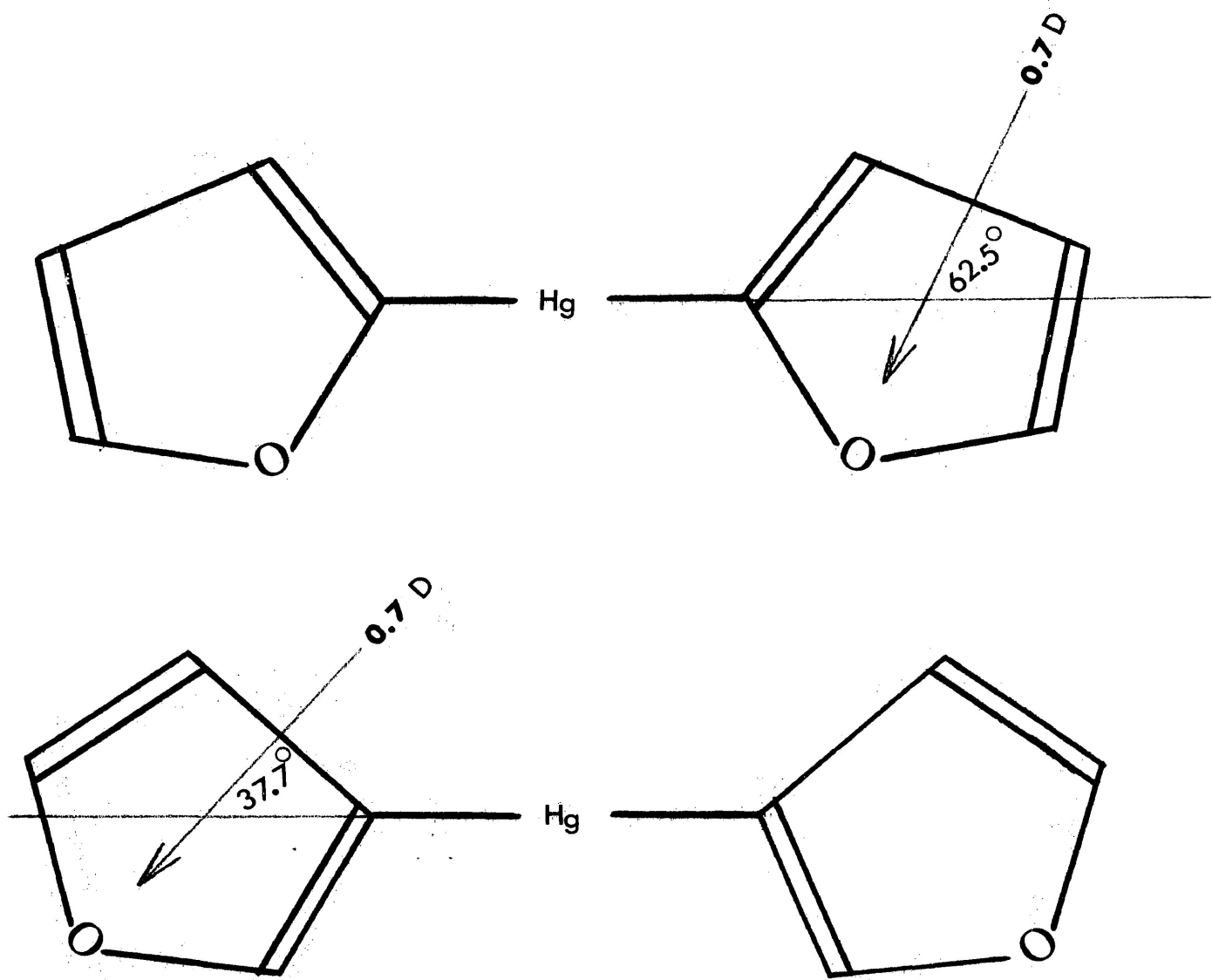


Figure 7-1: Parameters for calculations of dipole moments of 2-2'- and 3-3'-difuryl mercuries<sup>100</sup>

Measurements of dielectric relaxation of 2-2'- and 3-3'-difuryl mercuries would provide some information to this problem. The former compound has  $\tau_0 = 14.4$  (psec),  $\alpha = 0$ , and  $\mu = 1.16$  (D), and the latter one has  $\tau_0 = 15.8$  (psec),  $\alpha = 0$ , and  $\mu = 1.08$  (D).

If  $\angle \text{CHgC}$  is assumed to be  $180^\circ$ , the dipole moments for free rotation are calculated to become 0.46 (D), and 0.61 (D) for the 2-2'-, and 3-3'-compounds, respectively. (see Figure 7-1). Under the same assumption, the dipole moments of the cis configurations are 0.65 (D) for the 2-2'-compound, and 0.86 (D) for the 3-3'-compound. It is, therefore, seen that the assumption of  $\angle \text{CHgC} = 180^\circ$  does not appear to explain the observed dipole moments. Moreover, if this angle is assumed, the most probable relaxation time  $\tau_0$  may be mainly due to re-orientation of the fury rings.

Therefore the shortening of the relaxation time in comparison with the molecular one may be expected as in the case of p-dimethoxybenzene. Supposing the relaxation time of furyl ring is 10 (psec) as a maximum value, then that of the observed value should be 6.6 (psec) which does not agree with the observed relaxation times. On the other hand, if C-Hg-C bond is assumed to be non-linear, there would exist two cases (1) the shortening of relaxation time as seen in diphenyl ether, and (2) normal behaviour of relaxation time as seen in anisole, acetophenone,

chlorobenzene, etc. As discussed in Chapter 5, for the case (1) the observed relaxation time would change, depending on <sup>the</sup>  $C_2$  value, i.e., (6.6~20 (psec)), where  $\tau_m$  is assumed to be  $2 \times 10$  (psec)), whereas Fong's model implies  $\tau_{obs} = 6.6$  (psec). On the other hand, the case (2) would give  $10 \leq \tau_{obs} \leq 20$ . Therefore both cases would explain the observed relaxation times of the difuryl mercuries except Fong's model. Of course, it is very difficult to attribute the relaxation mechanism of the compounds to one of the two cases from the relaxation time alone. However, it may be concluded from the above considerations that  $\angle CHgC$  of 2-2'- and 3-3'-difuryl mercuries appears not to be  $180^\circ$ .



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## A P P E N D I X

### *Tables of Dielectric Constants and Losses*

The calculated dielectric constant  $\epsilon'$ calc and loss  $\epsilon''$ calc were obtained from the Cole-Cole equations, i.e., Eq. (3-1).



1,2-Dimethoxyethane in p-xylene at 25°C

$$\omega = 0.04617$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.311	2.414	2.414	0.0280	0.0220
16.202	2.406	2.407	0.0541	0.0362
24.001	2.396	2.396	0.0569	0.0487
35.11	2.379	2.378	0.0653	0.0597
70.354	2.352	2.335	0.0614	0.0624

$$\epsilon_0 = 2.4176$$

$$\epsilon_\infty = 2.288$$

Dimethoxymethane in p-xylene at 25°C

$$\omega = 0.1070$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.311	2.313	2.317	0.0190	0.0097
16.202	2.312	2.314	0.0205	0.0156
24.001	2.310	2.309	0.0275	0.0204
35.11	2.308	2.301	0.0235	0.0238
70.354	2.282	2.285	0.0179	0.0224

$$\epsilon_0 = 2.3194$$

$$\epsilon_\infty = 2.270$$

4-4'Dimethoxybiphenyl in p-xylene at 25°C

$$\omega = 0.00735$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.312	2.2764	2.275	0.0038	0.0035
16.202	2.2724	2.273	0.0049	0.0052
24.001	2.2712	2.271	0.0071	0.0061
35.11	2.2694	2.269	0.0066	0.0063
70.354	2.2661	2.265	0.0040	0.0046

$$\epsilon_0 = 2.2758$$

$$\epsilon_\infty = 2.2632$$

m-Dimethoxybenzene in p-xylene at 40°C

$$\omega = 0.06752$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
0.95	2.364	2.363	0.0110	0.0083
9.311	2.333	2.331	0.0480	0.0466
24.001	2.277	2.288	0.0470	0.0484
35.11	2.274	2.274	0.0410	0.0411
70.39	2.269	2.259	0.0322	0.0257
140.8	2.258	2.253	0.0151	0.0144

$$\epsilon_0 = 2.365$$

$$\epsilon_\infty = 2.249$$

6-Chloro-1,4-dimethoxybenzene in p-xylene at 40°C

$$\omega = 0.06658$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
1.80	2.442	2.452	0.0417	0.0358
9.311	2.364	2.378	0.0837	0.0844
16.202	2.348	2.337	0.0902	0.0820
24.001	2.307	2.311	0.0701	0.0717
35.11	2.303	2.293	0.0567	0.0587
70.39	2.285	2.275	0.0447	0.0374
140.8	2.80	2.267	0.0262	0.0208

$$\epsilon_0 = 2.466$$

$$\epsilon_\infty = 2.260$$

2,5-Dimethoxy-2,5-dihydrofuran in p-xylene at 25°C

$$\omega = 0.07401$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.312	2.399	2.391	0.0746	0.0732
16.202	2.344	2.349	0.0821	0.0798
24.001	2.322	2.321	0.0708	0.0709
35.11	2.310	2.301	0.0562	0.0565
70.36	2.306	2.285	0.0287	0.0316

$$\epsilon_0 = 2.4386$$

$$\epsilon_\infty = 2.278$$

2,5-Dimethoxytetrahydrofuran in p-xylene at 40°C

$$\omega = 0.07683$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
0.95	2.308	2.309	0.008	0.0039
1.80	2.294	2.308	0.028	0.0074
24.001	2.262	2.263	0.030	0.0317
35.11	2.256	2.253	0.026	0.0260
70.39	2.253	2.244	0.022	0.0150
140.8	2.249	2.242	0.017	0.0078

$$\epsilon_0 = 2.241$$

$$\epsilon_\infty = 2.309$$

2,6-Dimethoxypyridine in p-xylene at 25°C

$$\omega = 0.08041$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.31	2.319	2.318	0.0234	0.0214
16.20	2.305	2.306	0.0235	0.0252
24.00	2.298	2.297	0.0243	0.0243
35.11	2.289	2.289	0.0204	0.0209
70.04	2.281	2.281	0.0138	0.0130

$$\epsilon_0 = 2.3311$$

$$\epsilon_\infty = 2.277$$

4-4'Dimethoxythiobenzophenone in p-xylene at 25°C

$$\omega = 0.01336$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
0.90	2.362	2.343	0.0251	0.0198
1.20	2.350	2.340	0.0300	0.0252
1.50	2.346	2.336	0.0326	0.0297
1.80	2.334	2.331	0.0364	0.0332
2.48	2.308	2.321	0.0386	0.0383
9.31	2.283	2.278	0.0251	0.0260
16.2	2.2725	2.272	0.0179	0.0162
24.0	2.271	2.270	0.0143	0.0112
35.1	2.270	2.269	0.0105	0.0078
70.4	2.2665	2.268	0.0090	0.0039

$$\epsilon_0 = 2.3486$$

$$\epsilon_\infty = 2.268$$

5,6-Dimethoxy-1-indanone in p-xylene at 25°C

$$\omega = 0.02508$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon''</math>obs</u>
0.95	2.440	0.0479
1.20	2.437	0.0615
1.50	2.430	0.0700
1.80	2.425	0.0758
2.36	2.413	0.0529
9.312	2.313	0.0348
16.202	2.302	0.0293
24.001	2.286	0.0293

5,6-Dimethoxy-1-indanone in p-xylene at 25°C ...continued

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon''</math>obs</u>
35.11	2.282	0.0227
70.355	2.274	0.0175

$$\epsilon_0 = 2.4413$$

$$\epsilon_\infty = 2.278 *$$

Allyl ether in p-xylene at 25°C

$$\omega = 0.04416$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.31	2.333	2.334	0.0215	0.0210
16.202	2.325	2.324	0.0288	0.0305
24.001	2.311	2.311	0.0380	0.0348
35.11	2.2955	2.298	0.0354	0.0344
70.39	2.284	2.280	0.0248	0.0243

$$\epsilon_0 = 2.3410$$

$$\epsilon_\infty = 2.271$$

$\beta$ -Dinaphthyl disulfide in p-xylene at 25°C

$$\omega = 0.01390$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.311	2.2767	2.275	0.0046	0.0071
16.202	2.2748	2.271	0.0052	0.0055
24.001	2.2693	2.270	0.0038	0.0041
35.11	2.2659	2.270	0.0029	0.0029
70.354	2.2640	2.269	0.0023	0.0015

$$\epsilon_0 = 2.2935$$

$$\epsilon_\infty = 2.269$$

Thiophenol in p-xylene at 25°C

$$\omega = 0.09752$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
0.95	2.417	2.420	0.0092	0.0065
1.80	2.417	2.419	0.0136	0.0121
9.31	2.416	2.407	0.0375	0.0345
16.202	2.389	2.388	0.0500	0.0469
24.0	2.373	2.369	0.0468	0.0499
35.11	2.356	2.351	0.0412	0.0460
70.39	2.340	2.325	0.0312	0.0199

$$\epsilon_0 = 2.4206$$

$$\epsilon_\infty = 2.321$$

Methyl disulfide in p-xylene at 25°C

$$\omega = 0.09162$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
0.95	2.660	2.675	0.0131	0.0085
1.8	2.657	2.674	0.0191	0.0161
9.311	2.675	2.656	0.0859	0.0790
16.202	2.639	2.624	0.1426	0.1241
24.001	2.5865	2.579	0.1637	0.1565
35.11	2.543	2.519	0.1845	0.1748
70.4	2.458	2.407	0.1434	0.1496

$$\epsilon_0 = 2.6752$$

$$\epsilon_\infty = 2.324$$

4-Chloro-m-benzenedithiol in p-xylene at 25°C

$$\omega = 0.08782$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.311	2.394	2.388	0.0395	0.0446
16.202	2.355	2.365	0.0469	0.0451
24.001	2.346	2.351	0.0411	0.0404
35.11	2.344	2.340	0.0334	0.0338
70.389	2.328	2.328	0.0215	0.0213

$$\epsilon_0 = 2.4307$$

$$\epsilon_\infty = 2.320$$



2-2'Difuryl mercury in p-xylene at 25°C

$$\omega = 0.03194$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.311	2.274	2.271	0.0033	0.0054
16.202	2.267	2.268	0.0056	0.0051
24.001	2.265	2.267	0.0042	0.0042
35.108	2.264	2.266	0.0020	0.0031
70.389	2.263	2.265	0.0017	0.0017

$$\epsilon_0 = 2.2757$$

$$\epsilon_\infty = 2.265$$

3-3'Difuryl mercury in p-xylene at 25°C

$$\omega = 0.03289$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
8.881	2.273	2.270	0.0038	0.0048
16.202	2.267	2.267	0.0045	0.0043
24.001	2.265	2.266	0.0037	0.0034
35.108	2.264	2.265	0.0012	0.0026
70.389	2.263	2.265	0.0010	0.0014

$$\epsilon_0 = 2.2743$$

$$\epsilon_\infty = 2.265$$

o-Dimethoxybenzene in p-xylene at 40°C

$$\omega = 0.06073$$

<u>Freq. (GHz)</u>	<u><math>\epsilon'</math>obs</u>	<u><math>\epsilon'</math>calc</u>	<u><math>\epsilon''</math>obs</u>	<u><math>\epsilon''</math>calc</u>
9.311	2.336	2.335	0.0175	0.0158
16.202	2.327	2.328	0.0224	0.0223
24.001	2.318	2.320	0.0263	0.0265
35.11	2.312	2.311	0.0306	0.0289
67.518	2.296	2.295	0.0258	0.0271
140.8	2.284	2.282	0.0203	0.0190

$$\epsilon_0 = 2.3420$$

$$\epsilon_\infty = 2.272$$