# *Molecular Configuration of Diphenyl Ether as Revealed by Dielectric Relaxation Times and Molar Kerr Constants*

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## Mesomeric Moments in Morino's Structure

Professor Morino(1,2) of the University of Tokyo proposed a space model of a diphenyl ether molecule in 1938. It is easy to see that steric conditions prevent two rings in diphenyl ether from being fully coplanar. Indeed, the nearest non-bonding hydrogen atoms are the small distance of 0.5 Å apart in a coplanar structure. After calculating the repulsive energies between these atoms for a variety of configurations, Morino reached the conclusion that the rings in diphenyl ether tend to be on planes perpendicular to each other. Later, this view

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1) Y. Morino, first cited in Ref. 3 and later fully treated in Ref. 2.

2) K. Higasi, "Dielectric Relaxation and Molecular Structure", Research. Inst. Appl. Elec., Hokkaido Univ., (1961).

was found to be in good agreement with experimental results obtained by measurements of the dipole moments of diphenyl ether derivatives[3] and by electron diffraction studies of *p, p′*-dihalogenodiphenyl ethers[4].

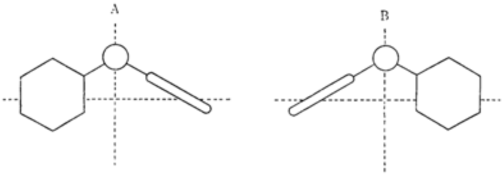

Fig. 1. Two important structures, A and B.

In these earlier studies, however, little attention was paid to the existence of mesomeric moments; Morino's structure in the literature[3] must, therefore, be improved in view of this effect. In order to make this point clearer, two structures, A and B, will be considered, both structures fulfilling Morino's condition: *the two rings are in planes at right angles to each other.* In structure A the ring on the left side of the oxygen atom is taken in the plane of the C–O–C triangle, while the other ring on the right side is perpendicular to the plane of this triangle. In structure B the right ring is in the triangle plane, while the left ring is perpendicular to it.

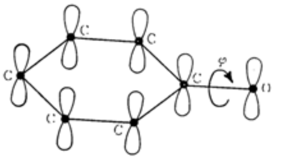

Fig. 2. Overlap of p-orbitals.

Among the atomic orbitals of the oxygen atom, attention will be directed to a pure p orbital which is occupied by two electrons and has its maximum electron density in the direction perpendicular to the C–O–C plane. When the C–O–C triangle is in the plane of a benzene ring, that is, when $\varphi=0$ in Fig. 2, all the p orbitals in the picture are parallel to each other (see Fig. 2). Consequently, in structure A the p orbital of oxygen has a great interaction with the p orbitals of the benzene ring on the left side. On the other hand however, the same orbital has no overlap with the p orbitals belonging to the right ring. It may be said that the oxygen atom is conjugated with the left ring but not with the right ring. According to the molecular orbital theory, $\pi$-electrons move freely in the domain of the conjugated part and a fraction of the electrons migrate from the oxygen to the side of the left ring, while no such electron-migration is possible towards the right ring. The so-called "mesomeric moment" is produced only in one direction, that is, towards the left ring in structure A and towards the right ring in structure B.

If the above mesomeric moment had a small magnitude, it seemed that one could usually ignore its effects. However, this seems to have been erroneous. A search in the literature[5] will reveal that the $OCH_3$ group substituted in benzene is reported to have a mesomeric moment of considerable value, 0.8∼0.96 D. If the $OCH_3$ group lies in the plane of the benzene ring, the mesomeric moment will have a maximum value. Very likely the $OCH_3$ group has some freedom of rotation. Rotation from the coplanar position will always lower the value of the mesomeric moment; for a twist angle $\varphi$ mesomeric moment, $\mu_m$, will be expressed by[6]

$$\mu_m=\mu_{max}\cos^2\varphi \tag{1}$$

The observed values of mesomeric moments show an average value of $\mu_m$ for all possible states of rotation, while the mesomeric moment in structure A or structure B corresponds to $\mu_{max}$. Consequently, the latter magnitude must be larger than the former. One may consider that *the moment* 0.8∼0.96 *D will represent the lowest limit of this kind of mesomeric moment in diphenyl ether.*

By a change from structure A to structure B, the region of conjugation is changed and the direction of the mesomeric moment is altered by 120°. Further, such a structural change can be brought about by internal rotation; Morino[1] noticed that the barrier to this sort of internal rotation has an insignificant height. This point was later verified more fully[2].

## Dielectric Relaxation Times

According to Debye[7] the dielectric relaxation time of a polar liquid is largely determined both by the size of the polar molecule and by the viscosity of the surrounding medium. Diphenyl ether and benzophenone, both having almost the same molecular size, are expected to have a relaxation time of nearly the same magnitude under the same set of conditions.

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[3] K. Higasi and S. Uyeo, ibid., **14**, 87 (1939); S. Uyeo and K. Higasi, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **60**, 199 (1939); K. Higasi and Uyeo, ibid., **60**, 204 (1939).

[4] K. Higasi, S. Uyeo and S. Yamaguchi, *Bull. Inst. Phys. Chem. Research, Tokyo*, **23**, 788 (1947).

[5] L. E. Sutton, "Dipole Moments", p. 373, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods", Academic Press Inc., New York (1955); A. R. Katritzky, E. W. Randall and L. E. Sutton, *J. Chem. Soc.*, **1957**, 1769.

[6] E. G. McRae and L. Goodman, *J. Chem. Phys.*, **29**, 334 (1958).

[7] P. Debye, "Polar Molecules", The Chemical Catalogue Co., New York (1929).

However, this is not what is actually observed. The relaxation time of diphenyl ether in benzene at 25°C, $4.1\times10^{-12}$ sec., is only 22% of that of benzophenone, $18.7\times10^{-12}$ sec.[8] Since the magnitude of the latter substance has been regarded as normal in the light of the Debye theory, the relaxation time of diphenyl ether must be considered anomalous.

Let it be assumed, for the sake of simplicity, that diphenyl ether consists of a mixture of molecules which have structure A or structure B. By application of the electric field, the proportions of the mixture will be changed according to Maxwell's distribution law; hence dielectric polarization will be produced[9]. If an alternating field is applied, dielectric dispersion will occur in the range of a certain critical frequency; the latter is largely determined by the activation energy necessary for the change from structure A to structure B, or vice versa. This predicts a new mechanism of dielectric absorption. It must be entirely different from that proposed by Debye, in whose conception rigid spherical dipoles rotate in the viscous medium. Further, by reason of the low barrier to internal rotation which makes structural change from A to B or from B to A feasible, one will expect that the relaxation time of this mechanism will be small—perhaps smaller than usual. The unusually short relaxation time of diphenyl ether, $4.1\times10^{-12}$ sec., has been explained thus[2,10].

Recently Dr. Vaughan and Prof. Smyth[11] of Princeton University discovered that diphenyl ether has two absorption peaks of unequal height, the smaller one being located at a frequency very near to that of benzophenone. This observation is extremely interesting, because one can estimate the magnitudes of the two dipole moments associated with the two absorption peaks. If $\mu_1$ and $\mu_2$ represent the effective moments of the two peaks which one may consider as arising from overall rotation and internal rotation respectively, then $\mu_1=0.60$ D and $\mu_2=0.97$ D. The smaller peak was detected only on data at 40°C, while data at 60°C closely fit a Cole-Cole arc. Consequently, some might be skeptical as to the existence of the small absorption. If no such absorption exists at all, the magnitude of $\mu_2$ should become identical with that of the molecular dipole moment itself[12]. For this reason one may estimate

$$0.97\,\mathrm{D}\simeq\mu_2\leqslant1.14\,\mathrm{D} \qquad (2)$$

Further we may assume

$$\mu_2=\mu_{\max}\sin\theta/2 \qquad (3)$$

in which $\theta$ is the oxygen valence angle[2]. If $\theta=120°$, $\mu_{\max}$ will have a magnitude

$$1.12\,\mathrm{D}\simeq\mu_{\max}\leqslant1.32\,\mathrm{D} \qquad (4)$$

The above estimate is considered to be of the right order of magnitude in spite of the fact that it is based on a tentative assumption.

## Molar Kerr Constant

Prof. R. S. W. Le Fèvre and his co-workers[13] at the University of Sydney were the first to determine the molar Kerr constant of diphenyl ether in benzene solution. They reached the conclusion that the space formula of Morino does not represent the molecular configuration of diphenyl ether, because $K_{\mathrm{m}}$ calculated for this structure has a negative value of $-16.6\times10^{-12}$ while the observed value is a positive $K_{\mathrm{m}}=+22.4\times10^{-12}$. However, there is a point here which is worthy of discussion: they assumed the molecular dipole moment to be acting along the bisector of the C–O–C angle.

We shall define three components of the molecular dipole as follows: the direction of $\mu_1$ bisects the angle $C_1$–O–$C_1$, that for $\mu_2$ is parallel to the $C_1\cdots\cdots C_1$ line, and that for $\mu_3$ is perpendicular to the $C_1$–O–$C_1$ triangle. The assumption employed by Le Fèvre et al.[13] is:

$$\mu_1=1.105\,\mathrm{D} \qquad \mu_2=\mu_3=0.0\,\mathrm{D} \qquad (5)$$

Indeed, this is essentially the same assumption as that used in 1939 by Higasi and Uyeo[3]. However, this assumption will be valid only for certain configurations if a mesomeric moment of an appreciable magnitude exists on account of the conjugation of the oxygen and some ring or rings.

From the analysis of relaxation times two effective moments $\mu_1$ and $\mu_2$ have been obtained in the previous section. One can use these values here with a certain amount of justification[2,10].

$$\mu_1=0.60\,\mathrm{D},\quad \mu_2=0.97\,\mathrm{D} \quad\text{and}\quad \mu_3=0.0\,\mathrm{D} \qquad (6)$$

The molar Kerr constant can be calculated with the use of the above values, resulting in $K_{\mathrm{m}}=45\times10^{-12}$. It is to be noted that the calculated value is no longer a negative quantity. In this calculation three principal polarizabilities, $b_1$, $b_2$ and $b_3$, are taken from Le Fèvre's above-mentioned article[13] as 1.8365, 2.2435 and $1.805\times10^{-23}$ respectively*.

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[8] J. Schneider, *J. Chem. Phys.*, **32**, 665 (1960).

[9] H. Fröhlich, "Theory of Dielectrics", Oxford University Press (1949), pp. 15—21.

[10] K. Higasi and C. P. Smyth, *J. Am. Chem. Soc.*, **82**, 4759 (1960).

[11] W. E. Vaughan and C. P. Smyth, *J. Phys. Chem.*, **65**, 98 (1961).

[12] L. G. Wesson, "Tables of Electrical Dipole Moments", Massachusetts Institute of Technology Press (1948).

[13] R. J. W. Le Fèvre, (Mrs.) A. Sundaram and K. M. S. Sundaram, This Bulletin, **35**, 690 (1962).

* This is a crude assumption because, as Prof. Le Fèvre remarked, the "longitudinal" polarizability of a partially quinoid phenyl would be greater than the value for ordinary phenyl.

Alternatively we may employ the values of $\mu_1$ and $\mu_2$ given by Higasi and Smyth[10] from an analysis of mesomeric moments,

$$\mu_1=0.54\,\mathrm{D},\quad \mu_2=0.87\,\mathrm{D}\quad \text{and}\quad \mu_3=0.0\,\mathrm{D} \qquad (7)$$

As a result of the use of these values, the molar Kerr constant will become slightly smaller for the above—$K_m=38\times10^{-12}$.

As can be seen from the two examples, one can approach the observed value $K_m=22.4\times10^{-12}$ indefinitely by choosing a larger value for $\mu_1$ and a smaller value for $\mu_2$. However, the writer believes that one might better consider this problem in the following way:

So far the argument has been stated as if a diphenyl ether molecule had a rigid structure shown by structure A or B. On the contrary, the molecule must be non-rigid, with a restricted freedom of rotation around the C–O bonds.

For the purpose of making a little better approximation, a particular type of rotation will be considered, such as satisfying the condition that the two rings are always in planes at right angles to each other. This condition implies that when the left ring in structure A rotates by an angle $\varphi$, the right ring must rotate in the same direction by the same amount of angle.

It can be shown by a little calculation[2] that the two components of the molecular dipole, $\mu_1$ and $\mu_2$, will be changed by the above-mentioned rotation in the followlng way:

$$\mu_1=m_0-\frac{1}{2}\mu_{\max}$$

$$\mu_2=0.866\,\mu_{\max}(\cos^2\varphi-\sin^2\varphi) \qquad (8)$$

in which the valence angle of oxygen is taken as 120°. An estimate of $\mu_{\max}$ has been given above in Eq. 4. It will be seen that $\mu_2$ is zero only when $\varphi=\pm45°, \pm135°$, etc. Consequently, as far as the Morino structure is concerned, one might better consider that the molecular dipole moment is *not* acting along the bisector of the C–O–C angle.

Suppose $\mu_{\max}$ has quite a large value, 1.4 D, and a magnitude, 0.92 D, for $m_0$, which represents a dipole arising from two C–O links; we shall obtain for $\varphi=0$

$$\mu_1=0.22\,\mathrm{D} \qquad \mu_2=1.21\,\mathrm{D} \qquad (9)$$

Since $\mu_2$ has a large value while $\mu_1$ is extremely small, $K_m$ for Eq. 9 must have a large magnitude —in fact $K_m=76\times10^{-12}$. This would be the highest possible value for $K_m$. By use of Eq. 8 one can estimate the variation of $K_m$ with a change in the twist angle $\varphi$ (see the upper curve* in Fig. 3). It will be seen that if the contribution of rotation to $K_m$ is taken into consideration, the average value of $K_m$ will decrease. The observed value $K_m+22.4\times10^{-12}$ may possibly be accounted for in this manner. The variation of $K_m$ with the twist angle $\varphi$ when using Eqs. 7 and 8 is shown in the lower curve* of Fig. 3.

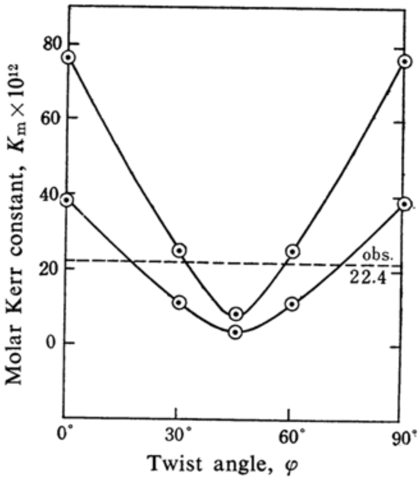

Fig. 3. Variation of the molar Kerr constant of diphenyl ether (Morino) with the twist angle.

It was once suggested by the present writer[2] that the study of the Kerr constant of diphenyl ether might eventually play a decisive role in determining the structure of this molecule. Grateful acknowledgement must be made to Professor Le Fèvre and his group for satisfying this request by carrying out valuable measurements. The analysis of their results has contributed greatly to making many points clearer. However, the magnitude of the molar Kerr constant alone does not appear to be unequivocal evidence *for* or *against* the Morino structure.

Lastly, a few words must be added regarding the dipole moment of diphenyl ether. The dipole moment $\mu$ at a twist angle $\varphi$ is determined by

$$\mu^2=\mu_1{}^2+\mu_2{}^2 \qquad (10)$$

in which $\mu_1$ and $\mu_2$ are given by Eqs. 8. Again we shall assume that $\mu_{\max}=1.4\,\mathrm{D}$; then $\mu=1.23\,\mathrm{D}$, for $\varphi=0$. If free rotation occurs, $\mu=0.88\,\mathrm{D}$. The observed value, 1.14 D[12], is between the two calculated values.

The above example will suggest that the observed dipole moment and the molar Kerr constant of a non-rigid molecule, diphenyl ether being included, represent average values of various magnitudes corresponding to a great number of possible configurations. The dielectric relaxation time provides two effective dipole moments which are other sorts of

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* The estimated values are of only qualitative significance because the three principal polarizabilities are tentatively assumed to be independent of rotation.

average quantities. Possibly the latter is closely associated with the former. However, there is an essential difference: a dipole moment determined from dielectric constant measurements represents a static property of the molecule, while effective moments from dielectric relaxation time analysis are associated with the dynamic nature of the molecule.

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