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Microwave Absorption and Molecular Structure. XXXIII. Change of Mesomeric Moment as a Mechanism of Dielectric Relaxation[1]

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Serious objections have been found to all but one of the mechanisms which have thus far been proposed to account for the abnormally low dielectric relaxation times found for diphenyl ether and several molecules of a somewhat similar nature. A quantitative examination of the shift of electronic charge and consequent change in direction of the π-electron or mesomeric moment accompanying rotation of the rings around their bonds to the rest of the molecule shows that this intramolecular rotation can be the mechanism responsible for these abnormally short relaxation times. Tentative experimental evidence is thus obtained of variation of charge shift with rotation around a bond.

Measurements of dielectric relaxation time by a calorimetric method at meter wave lengths gave an abnormally short relaxation time for phenyl ether[2] in dilute benzene solution and a rather short value for diphenylamine[2] under similar conditions. Although these measurements were at frequencies small in comparison to the critical frequency, which is the reciprocal of the relaxation time, the anomalously small magnitude of the relaxation time for phenyl ether was confirmed by dielectric constant and loss measurements at centimeter wave lengths[3] on the pure liquid and by further measurements on solutions at decimeter wave lengths.[4] Additional measurements have been made on solutions and on other substances whose structures suggested the possibility of similar behavior. Various mechanisms have been proposed to account for this seemingly anomalous behavior and discussed[5] in qualitative fashion. It is the purpose of this paper to examine what seems to be the most probable mechanism in as quantitative a manner as possible.

The anomaly in the size of the relaxation time of diphenyl ether, $(C_6H_5)_2O$, is brought out by comparison with that of benzophenone, $(C_6H_5)_2CO$, which should be similar in molecular shape and which has a molar volume[5] 170 cc. at 60° as compared to 164 for diphenyl ether. The relaxation time found by Fischer[2] for diphenyl ether in dilute benzene solution at 23° was 0.28×10^{-11} sec. as compared to 2.04×10^{-11} for benzophenone. Somewhat higher values were found[4] in decimeter wave length measurements for diphenyl ether at mole fractions between 0.2 and 0.5 in benzene. The reduced relaxation time, τ/η, the ratio of the relaxation time to the measured viscosity η, showed a linear dependence upon concentration, which, by extrapolation, gave reduced relaxation times at 21° of 0.45×10^{-9} for very dilute solutions and 0.20×10^{-9} for pure diphenyl ether. This latter value is slightly lower than those obtained from the actual measurements[3] at centimeter wave lengths on the pure liquid, 0.227×10^{-9} at 40° and 0.250×10^{-9} at 60°. For comparison of the pure liquid values with that for benzophenone, the relaxation times have been corrected approximately for the effect of the internal field to give τ_μ/η values at 60°, 0.23×10^{-9} for diphenyl ether as compared to 1.19×10^{-9} for benzophenone.[5]

A previous paper[5] of this series has shown from experimental data the improbability of a variety of mechanisms previously suggested to account for the low relaxation time of diphenyl ether. These included inversion of the molecule, intramolecular rotation of a phenoxy group and change in the di-

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[1] This research was supported in part by the National Science Foundation. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] E. Fischer, *Z. Elektrochem.*, **53**, 16 (1949).

[3] J. H. Calderwood and C. P. Smyth, THIS JOURNAL, **78**, 1295 (1956).

[4] F. Dieringer, *Z. Physik*, **145**, 184 (1956).

[5] D. M. Roberti, O. F. Kalman and C. P. Smyth, THIS JOURNAL, **82**, 3523 (1960).

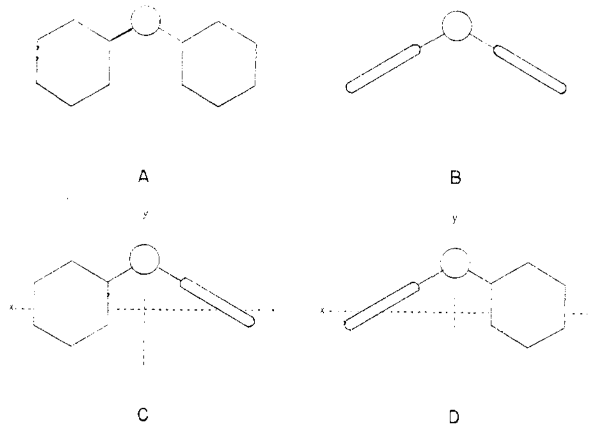

Fig. 1.—Possible structures of the diphenyl ether molecule.

rection and size of the "atomic moment" associated with the two unshared pairs of electrons in the oxygen. Although the small relaxation times found[5] for diphenylmethane and bibenzyl showed that unshared electron pairs were not essential for the lowering of relaxation time, it appears probable that a shift of charge accompanying rotation of a phenyl ring about its bond to the rest of the molecule may be primarily responsible for the dipole orientation in the externally applied electric field used in the measurement. A strong argument in favor of ring rotation as the cause of lowering is given by the fact[6,7] that prevention of ring rotation by bonding eliminates the abnormal lowering of relaxation time.

Before examining the details of a possible charge shift brought about by rotation of a ring within the molecule, it is desirable to inquire as to the magnitude to be expected for the relaxation time of ring rotation. The molecules of pyridine and fluorobenzene are rather similar in size and shape to the phenyl group.[8] The reduced relaxation times for pyridine, 0.56×10^{-9} at 20° and 0.62×10^{-9} at 60° and for fluorobenzene 0.84×10^{-9} at 20°, are larger than those given above for diphenyl ether, but not of a different order of magnitude. Possibly, rotation of the ring may occur more easily within the volume occupied by the diphenyl ether molecule than it can when the rings form the fairly closely packed liquid structures of pyridine and fluorobenzene. Evidence of the slightness of the influence of liquid viscosity upon the relaxation process of diphenyl ether is given by the fact that the relaxation time found[5] for it in Nujol at 20°, 0.62×10^{-11} sec., was only slightly larger than that found[4] for it in benzene, although the viscosity of the Nujol, 210 c.p.s., was about 340 times that of benzene. In contrast, the relaxation time of benzophenone was found to be 18 times as large in a paraffin oil of viscosity 197 c.p.s. as it was in benzene.[9] Obviously, the relaxation time observed for diphenyl ether must depend primarily on an intramolecular mechanism and, in view of the approximate nature of the relations between molecular size and shape and liquid viscosity, it is not unreasonable, tentatively, to associate the relaxation time with the rotation of a ring around its C–O bond and try to ascertain whether this ring rotation can cause sufficient shift of electronic charge in the molecule to give rise to a dielectric loss of the magnitude observed.

Three structures have been considered for the diphenyl ether molecule as shown in Fig. 1. In structure A, the two rings are coplanar with each other and with the two carbon–oxygen bonds. The intramolecular dimensions and, in particular, the Stuart–Briegleb models show that steric repulsion makes this structure very improbable. Structure B, in which the two rings are perpendicular to the plane of the two carbon–oxygen bonds shows the least steric repulsion, but the two equivalent structures C and D, in which one ring is coplanar with and the other perpendicular to the plane of the two carbon–oxygen bonds, are sterically possible. These are made more probable by the resonance energy or additional binding resulting from shift of electronic charge from the oxygen into the ring which is coplanar with the two carbon–oxygen bonds. The equivalent structures C and D are most consistent with the results of electron diffraction measurements[10] and with the dipole moments found[11] for 2,2′-disubstituted diphenyl ethers. The most probable structures C and D will be used as the basis for the examination of the low relaxation time. The oxygen valence angle has been concluded[12] to be $\theta = 120°$.

Due to orbital overlap, a certain amount of electronic charge flows from the oxygen into the ring which is coplanar with the two carbon–oxygen bonds. This creates a mesomeric moment with its positive end at the oxygen and its dipole axis in the direction of the O–C bond. Such a shift of electronic charge is at a minimum when the ring is perpendicular to the C–O–C plane and at a maximum when the ring is in the C–O–C plane. That part of the moment which is dependent on the angle between the ring plane and the C–O–C plane is given[13] by

$$m = m_0 \cos^2 \varphi \qquad (1)$$

No accurate estimate is available for the value of m_0. Widely differing values calculated[14,15] for the mesomeric moment of diphenyl ether from alkyl and aryl dipole moment differences on the basis of the planar structure A must be too small for structures C and D. 0.6 has been calculated for phenol[14] and 0.8 for anisole[14] from the dipole moment differences. By a molecular orbital method two values, 1.12 and 1.04, have been calculated[16,17] for phenol from the shift of the ultraviolet absorption band. These values represent averages of the values for different positions of the

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[6] G. W. Nederbragt, private communication.

[7] W. Maier, *Arch. sci.* (*Geneva*), **12**, 20 (1959).

[8] C. P. Smyth, *Proc. Natl. Acad. Sci. U. S.*, **42**, 234 (1956).

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[11] K. Higasi and S. Uyeo, *Bull. Chem. Soc. Japan*, **14**, 87 (1939).

[12] L. E. Sutton, "Determination of Organic Structures by Physical Methods," (E. A. Braude and F. C. Nachod, Editors), Academic Press, Inc., New York, N. Y., 1955, p. 402.

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

[14] Ref. 12, p. 395.

[15] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1992 (1937).

[16] S. Nagakura and H. Baba, THIS JOURNAL, **72**, 5693 (1952).

[17] K. Nishimoto and R. Fujishiro, *Bull. Chem. Soc. Japan*, **9**, 1036 (1956).

rings, that is, for different values of φ in eq. 1. Consequently, the value of m_0, which is the largest value that m can have, should be larger. It appears reasonable to assign a value not far from 1.0×10^{-18} to m_0.

The resonance energies of phenol and anisole exceed that of benzene by 9 and 11 kcal. per mole, respectively, and the energy of diphenylmethane exceeds that of two moles of benzene by 12 kcal. per mole according to Aston,[18] while, according to the values given by Wheland,[19] these molecules show no excess of resonance energy over those attributable to the rings. Pauling[20] gives 7 kcal. excess resonance energy for phenol. It would thus appear that any barrier to rotation of the rings in these molecules relative to the attached groups, or *vice versa*, due to resonance energy must be small. By analogy, one would expect any resonance barrier to ring rotation in diphenyl ether to be small. This extra resonance energy which is dependent upon the angle φ between the ring plane and the C–O–C plane is given[21] by

$$E = E_0 \cos^2 \varphi \qquad (2)$$

where E_0 is the value for coplanarity. The total extra energy associated with rings 1 and 2 is then

$$E \sim E_0 \cos^2 \varphi_1 + E_0 \cos^2 \varphi_2 \qquad (3)$$

If the two rings rotate simultaneously in such a way that φ_2 is kept equal to $180° - (90° + \varphi_1)$

$$E \sim E_0 (\cos^2 \varphi_1 + \sin^2 \varphi_1) = E_0 \qquad (4)$$

Under these conditions, E would not change with rotation, and resonance energy would not hinder rotation. An approximation to such coupled rotation could occur with sufficient frequency to permit orientation of the π-electron or mesomeric moment as a relaxation mechanism even if E_0 were considerable in size, which it appears not to be.

The components of the total mesomeric moment along the x and y axes in Fig. 1 are

$$m_x = -m_0 \cos^2 \varphi_1 \sin(\theta/2) + m_0 \cos^2 \varphi_2 \sin(\theta/2) \qquad (5)$$
$$m_y = -m_0 \cos^2 \varphi_1 \cos(\theta/2) - m_0 \cos^2 \varphi_2 \cos(\theta/2) \qquad (6)$$

For the case of coupled rotation

$$\varphi_2 = 90° - \varphi_1 \text{ and } \cos \varphi_2 = \sin \varphi_1\text{, therefore}$$
$$m_x = -m_0 \sin(\theta/2)(\cos^2 \varphi_1 - \sin^2 \varphi_1) = -m_0 \sin(\theta/2)(2 \cos^2 \varphi_1 - 1) \qquad (7)$$
$$m_y = -m_0 \cos(\theta/2) \qquad (8)$$

As is customary in such cases, we shall assume that, in addition to the mesomeric moment, the molecule possesses a moment $m_{\mathrm{C-O}}$ in the direction of each C–O bond and equal to the similar $m_{\mathrm{C-O}}$ in aliphatic ethers. The value of $m_{\mathrm{C-O}}$ may be calculated from the moment value 1.18 found[22] for *n*-propyl and *n*-butyl ether, in which the oxygen valence angle is taken as 111°. We obtain $2m_{\mathrm{C-O}} \cos(111°/2) = 1.18$, or $m_{\mathrm{C-O}} = 1.04$. The use of this value may be described as a plausible approximation. The components of the two $m_{\mathrm{C-O}}$ moments in the x-axis obviously cancel each other leaving

$$\mu_x = m_x$$
$$\mu_y = 2m_{\mathrm{C-O}} \cos(\theta/2) + m_y$$

For structure C (Fig. 1), $\varphi_1 = 0°$, $\varphi_2 = 90°$, $m_x = -m_0 \sin 60°$, $m_y = -m_0 \cos 60°$; for structure D, $\varphi_1 = 90°$, $\varphi_2 = 0°$, $m_x = m_0 \sin 60°$, $m_y = -m_0 \cos 60°$. Therefore, since $m_0 = 1.0$, for structure C, $\mu_x = -1.0 \times 0.87 = -0.87$; $\mu_y = 2 \times 1.04 \times 0.5 - 1.0 \times 0.5 = -0.54$; for structure D, $\mu_x = 0.87$, $\mu_y = 0.54$. The resultant molecular moment for either C or D is $\mu = (\mu_x{}^2 + \mu_y{}^2)^{1/2} = 1.02$, as compared to the observed values, 1.14 in the vapor, 1.16 in benzene solution,[23] 1.05 calculated by means of the Onsager equation from the data on the pure liquid[3] and 0.96 calculated from measurements in Nujol solution.[5] A change from configuration C to configuration D by internal rotation without any rotation of the diphenyl ether molecule as a whole produces the rotation of a dipole of moment $\mu_x = 0.87$ through an angle of 180°, or if the mesomeric moment m_0 were taken as 1.2, μ_x would come out 1.04 and μ 1.13 in excellent agreement with the values observed for the molecular moment. It is evident that, if these assumptions are correct, the fixed moment in the molecule is $\mu_y = 0.54$ or 0.44 and the moment associated with ring rotation within the molecule is $\mu_x = 0.87$ or 1.04. Since the maximum dielectric loss associated with a relaxation process is proportional to the square of the dipole moment involved, the relative importance of the intramolecular and the molecular relaxation processes is given by $(\mu_x/\mu_y)^2 = 2.6$ or 5.6 according to which set of values is used. In either case, the intramolecular process is dominant. A new analysis[24] of the data by an approximate method gives a predominant short relaxation time, presumably for an intramolecular process, and a long relaxation time, presumably molecular, which disappears entirely as the temperature is raised. Actually, all of the experimental points, including a recent measurement in this Laboratory by Mr. W. E. Vaughan at 0.435 cm. wave length, fit well on a Cole–Cole arc plot corresponding to a single short relaxation time. An essentially equivalent result is obtained by using the Debye equation[25] $\epsilon'' = (\epsilon_0 - \epsilon_\infty)\omega\tau/(1+\omega^2\tau^2)$, to calculate a value of the static dielectric constant ϵ_0 and substituting this value in the Onsager equation[25] to calculate the value of the molecular dipole moment. The apparent moment values thus obtained from the values of ϵ'' at 0.435, 1.24, 3.22 and 10.4 cm. wave length are 1.04, 0.97, 1.04 and 1.12×10^{-18}, respectively. Any small trend in these moment values is obscured by the experimental error in ϵ''. It is evident, however, that the results are consistent with the assumption of a mesomeric moment, the orientation of which is determined by rotation of the phenyl rings within the molecule.

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[18] J. G. Aston, "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, editors, Academic Press, Inc., New York, N. Y., 1955, p. 560.

[19] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 98.

[20] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 197.

[21] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 481.

[22] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 298.

[23] Ref. 22, p. 314.

[24] K. Bergmann, D. M. Roberti and C. P. Smyth, *J. Phys. Chem.*, **64**, 665 (1960).

[25] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 56, 26.

In the case of benzophenone, the mesomeric moment has been given[14] as 0.3×10^{-18}, while the molecular dipole moment is 2.97. As in the case of diphenyl ether, m_0 should be larger than the estimated mesomeric moment. Possibly 0.6 would be an upper limit. In view of the proportionality of the loss to the square of the moment involved, it is evident that the loss due to any orientation of mesomeric moment would be of the order of 0.04 of that associated with orientation of the molecular moment and would thus have escaped detection in the centimeter wave length measurements. The reason for the normal behavior of benzophenone in contrast to the abnormal behavior of diphenyl ether is thus evident.

Since Sutton[14] has obtained mesomeric moments of 1.02 for aniline and 1.66 for N,N-dimethylaniline, which have molecular moments of 1.52 and 1.61, respectively, abnormally low relaxation times found for diphenylamine[2] and triphenylamine[26] can be attributed to relaxation mechanisms involving ring rotation as proposed for diphenyl ether.

The molecule of diphenylmethane is very similar in size and shape to that of diphenyl ether, the respective molar volumes being 174 and 164 cc. at 60°. The reduced relaxation times at 60° are[5] 0.23×10^{-9} for diphenyl ether and 0.25×10^{-9} for diphenylmethane. The small dipole moment 0.26×10^{-18} found[5] for diphenylmethane is due to a small shift of electronic charge from the methylene group into the rings, similar to that occurring from the methyl group into the ring in toluene. This may be described[27,28] in terms of hyperconjugation or orbital overlap, which will vary as a ring rotates out of the plane of the two methylene-to-ring bonds. The variation should provide an intramolecular relaxation mechanism similar to that which has been shown to be plausible for diphenyl ether. The relaxation time should obviously be close to that of diphenyl ether, but the smaller charge shift involved should give rise to a smaller dielectric loss, as observed.

It would appear that change in the direction of a mesomeric moment accompanying rotation of a benzene ring in a molecule provides a quantitatively acceptable mechanism for the abnormally low relaxation times observed for several molecules containing two or three phenyl groups attached to a small central atom or group. The fact that molecules containing similar central groups with alkyl instead of aryl groups attached do not show the anomaly in relaxation time increases the probability of the correctness of the hypothesis. The intramolecular orientation process is facilitated by the steric repulsion which makes coplanarity of the rings highly improbable. Although, as has been shown, rotation of one ring can occur most readily when another ring rotates synchronously so as to maintain a 90° angle between the planes of the two rings, less favorable orientation of the ring planes relative to each other need not prevent the dipole orientation to which the loss is ascribed. Differences in dipole moment, in bond length, and in chemical reactivity often may be attributed to differences in orbital character or orbital overlap, perhaps described in terms of "mesomerism." The dynamic behavior of this phenomenon is evidenced or, perhaps, given a certain plausible reality by the apparent relaxation mechanisms of these molecules which have been discussed.

(26) B. B. Howard, unpublished measurements carried out in this Laboratory.

(27) C. A. Coulson, "Valence," Oxford University Press, Oxford, 1952, Chap. XII.

(28) Ref. 22, p. 315.

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

Nuclear Magnetic Resonance Spectra of Resin Acids

BY JAMES C. W. CHIEN

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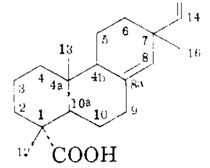
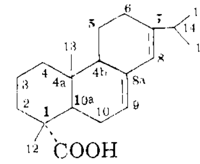
The nuclear magnetic resonance spectra of 17 resin acids were obtained. Most of the peaks were accounted for to give structural information. By consideration of the numbers of olefinic and allylic protons and of the shifts of various methyl groups, the positions of double bonds in several resin acids have been determined.

Introduction

The stereochemistry of pimaric and isopimaric acids has been the subject of many investigations.[1-3] Edwards and Howe[4] pointed out that while the pimaric and isopimaric acids are definitely epimeric at C_7,[5] the actual stereochemistry at this position as concluded by Wenkert and Chamberlin[2] has to be considered as not definitive in view of the very small observed percentages of the γ- and δ-lactones in the equilibrium mixtures derived from dihydropimaric and dihydroisopimaric acids.



Pimaric acid



Abietic acid

Subsequent to the completion of this work, Edwards and Howe[6] reported unequivocal proof

(1) G. C. Harris and T. F. Sanderson, THIS JOURNAL, **70**, 334, 2079, 2081 (1948).

(2) W. Wenkert and J. W. Chamberlin, *ibid.*, **80**, 2912 (1958); **81**, 688 (1959).

(3) B. Green, A. Harris and W. B. Whalley, (a) *Chem. & Ind.* (*London*), 1084 (1958); (b) *J. Chem. Soc.*, 4715 (1958).

(4) O. E. Edwards and R. Howe, *Can. J. Chem.*, **37**, 760 (1959).

(5) The numbering system used in this paper is that of G. C. Harris, "Rosin and Rosin Derivatives," *Encyclopedia Chem. Technol.*, Vol. XI, Interscience Publishing Co., New York, N. Y., 1953, p. 779.