tetramethylbenzidine have already been cited. There is no evidence of such lowering in the values of the relaxation times found for 2,4,6-trinitroanisole, 2-amino-4-methylpyridine and N,N-dimethyl-p-nitroaniline. This is consistent with the blocking of rotation by steric repulsion in 2,4,6-trinitroanisole and with the hindrance to rotation by double bond character or orbital overlap in N,N-dimethyl-p-nitroaniline. In the case of the latter, however, the small contribution from intramolecular rotation could be obscured by the large absorption associated with the orientation of the very large molecular dipole moment. In the absence of hydrogen bonding in 2-amino-4-methylpyridine, one would expect a small contribution to the relaxation process from the rotation of the amino group, which has a moment component, 1.0×10^{-18}, perpendicular to its axis of possible rotation, but the only evidence of intramolecular rotational motion is the difference between the values of a_∞ and a_D.

Microwave Absorption and Molecular Structure in Liquids. XXXIX. The Relaxation Times of Some Substituted Phenyl Ethers and Analogous Molecules[1,2]

BY WILLIAM P. PURCELL[3] AND CHARLES P. SMYTH

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The dielectric constants and losses at wave lengths of 1.2, 3.2, 10, 25 and 50 cm.. and 575 m. have been measured for bis-(o-nitrophenyl)-ether, bis-(p-nitrophenyl)-ether, bis-(p-nitrophenyl)-methane and cyclohexyl phenyl ether in benzene solution and for bis-(p-bromophenyl)-ether in Nujol solution. The data have been used to calculate the dielectric relaxation times of the molecules and the results have been analyzed in terms of internal and molecular dipole orientation. The dipole moment found for cyclohexyl phenyl ether is 1.55. The values found for the relaxation times seem to support the hypothesis of ring rotation as the mechanism of intramolecular relaxation.

The most reasonable mechanism so far proposed to account for the anomalously low relaxation time of diphenyl ether[4-10] suggests that a shift of charge accompanying rotation of a phenyl ring about its bond to the rest of the molecule is primarily responsible for the dipole orientation, over-all molecular rotation contributing only slightly to the dielectric relaxation.[11] The same mechanism has been suggested[10] for diphenylmethane, which also has an unusually low relaxation time. In the hope of shedding new light on the problem the authors have investigated some substituted diphenyl ethers, cyclohexyl phenyl ether and a substituted diphenylmethane.

Experimental Methods

Apparatus.—The apparatus and the various methods of measurement have been described in previous papers.[12-14]

Purification of Materials.—Bis-(o-nitrophenyl)-ether, obtained from Professor S. Uyeo of Osaka University, was used without further purification.

Bis-(p-nitrophenyl)-ether, obtained from Eastman Kodak Co., was recrystallized twice from benzene and dried under vacuum in an Abderhalden pistol.

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(2) This paper represents part of the work submitted by Mr. W. P. Purcell to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Allied Chemical Corporation Fellow, 1959–1960.

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(12) H. L. Laquer and C. P. Smyth, ibid., 70, 4097 (1948).

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Bis-(p-nitrophenyl)-methane, obtained from Eastman Kodak Co., was recrystallized twice from benzene and dried under vacuum in an Abderhalden pistol.

Cyclohexyl phenyl ether was synthesized[15] by Mr. W. E. Vaughan and Mr. V. Breuninger by the addition of phenol to cyclohexene in benzene solution with boron trifluoride as catalyst at 0°. The vapor phase chromatogram showed less than 1% impurity and the infrared spectrum had no phenolic peaks; $n^{23}D$ 1.5285.

Bis-(p-bromophenyl)-ether, obtained from Eastman Kodak Co., was recrystallized twice from ethanol and once from benzene and was dried under vacuum in an Abderhalden pistol; m.p. 61.0–61.7°.

Experimental Results

The experimental results were treated in the manner previously described.[16] The slopes of the straight lines thus obtained, a', corresponding to ϵ', and a'', corresponding to ϵ'', were plotted in Cole–Cole arcs[17] in the usual fashion[16] for all but cyclohexyl phenyl ether to obtain the critical wave lengths λ_m, the corresponding relaxation times τ, the distribution coefficients α and the arc intercepts at infinite frequency a_∞. The values of these quantities are given in Tables I and II. The concentration range in mole fraction is given in parentheses for bis-(o-nitrophenyl)-ether, bis-(p-nitrophenyl)-ether, bis-(p-nitrophenyl)-methane and cyclohexyl phenyl ether, which were measured in benzene solution. The concentration range in weight fraction of solute is given for bis-(p-bromophenyl)-ether, which was measured in Nujol solution.

The data for cyclohexyl phenyl ether do not fit a Cole–Cole arc plot and, therefore, other means[8,18] were employed to determine the relaxation times. These methods were applied to the other substances also.

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TABLE I

SLOPES FOR THE DEPENDENCE OF THE DIELECTRIC CONSTANT AND LOSS OF SOLUTIONS ON CONCENTRATION OF SOLUTE

Wave length (cm.)	Benzene solution					
	20°		40°		60°	
	a'	a''	a'	a''	a'	a''
Bis-(o-nitrophenyl)-ether (0–0.003)						
1.25	5.7	7.0	8.6	8.7	6.6	10.1
3.22	11.8	16.7	13.6	17.3	15.6	17.9
10	33.3	25.7	38.6	22.1	41.7	18.4
25	59.3	18.9	56.6	13.3	51.4	8.7
50	64.5	11.3	58.4	7.5	52.6	5.0
575 m.	67.5		60.7		52.1	

	20°		20°	
	Bis-(p-nitrophenyl)-ether (0–0.006)		Bis-(p-nitrophenyl)-methane (0–0.004)	
1.2	4.0	2.6	2.5	5.6
3.2	7.7	3.5	14.6	12.6
10	10.5	1.6	24.9	9.3
25	10.7	1.05	29.4	3.1
50	10.85	0.6	31.2	2.1
575 m.	11.0		31.6	

	a' 20°	a''
Cyclohexyl phenyl ether (0–0.07)		
1.27[a]	0.78	0.655
3.23	1.31	.71
10[b]	2.13	.87
25[b]	3.04	.57
50[b]	3.30	.37
575[a] m.	3.31	

Nujol solution
Bis-(p-bromophenyl)-ether (0–0.066)

1.27[b]	0.28	0.028
3.22[b]	.30	0.024
575[b] m.	.343	

[a] Measurements made by Mr. W. E. Vaughan. [b] Measurements made by Mr. E. L. Grubb.

TABLE II

SLOPES FOR THE DEPENDENCE OF THE SQUARE OF THE REFRACTIVE INDEX a_D ON CONCENTRATION, WITH INFINITE FREQUENCY INTERCEPTS a_∞, CRITICAL WAVE LENGTHS λ_m. RELAXATION TIMES τ AND DISTRIBUTION PARAMETERS α

t, °C.	a_D	a_∞	λ_m (cm.)	$\tau(10^{-12}$ sec.$)$	α
Bis-(o-nitrophenyl)-ether[a]					
20	0.84	3.8	9.80	52.0	0.14
40		3.8	7.05	37.4	.14
60		3.8	5.24	27.8	.08
Bis-(p-nitrophenyl)-ether[a]					
20	0.90	2.6	2.62	13.9	0.10
Bis-(p-nitrophenyl)-methane[a]					
20	1.13	1.4	4.30	22.8	0.11
Bis-(p-bromophenyl)-ether[b]					
20	0.23	0.23	1.64	8.7	0.39

[a] Measured in benzene solution. [b] Measured in Nujol solution.

The moment of cyclohexyl phenyl ether in benzene solution was calculated from the data by means of the Debye, Halverstadt–Kumler[19] and

(19) I. J. Halverstadt and W. D. Kumler. THIS JOURNAL, 64, 2988 (1942).

Guggenheim[20] methods as 1.55×10^{-18}. In order to carry out the calculations, solution densities were measured by Mr. W. S. Lovell, giving a slope 0.118 g./cm.[3] for the density–weight fraction curve at 20°.

Discussion of Results

Each of the five molecules measured presumably has at least two relaxation mechanisms with corresponding relaxation times. However, all of the molecules except cyclohexyl phenyl ether gave an apparent most probable relaxation time. The large differences between the values of a_D and a_∞ for the first three compounds in Table II show the absorption due to intramolecular rotation. For some cases[21] of multiple relaxation one can resolve the absorption curve, a'' against log λ, into more than one Debye-type curve. The area under each curve is proportional to the square of the moment associated with the orientation which leads to that particular absorption. For example, the fixed moment of diphenyl ether is smaller than the moment associated with ring rotation[11] and, therefore, the intramolecular process is dominant.

Over-all rotation of the molecule with its dipole moment of 6.64 and rotation of the phenyl rings about the C–O bonds are the two mechanisms by which bis-(o-nitrophenyl)-ether can relax. Ring rotation is associated with the permanent moment component of the ring perpendicular to the C–O axis, which, from simple geometry and the moment of nitrobenzene, is about 3.5. Also this internal rotation is associated with the maximum mesomeric moment, which, in diphenyl ether,[11] is about 1.0. The areas under the absorption curves will, therefore, be in the ratio of $(6.6)^2 : [(3.5)^2 + (1.0)^2] = 44:13$, corresponding to molecular and ring rotation. It is evident, therefore, that the dominating mechanism for bis-(o-nitrophenyl)-ether is that of over-all molecular rotation. Upon examination of the Stuart–Briegleb models and assuming the configuration, suggested by Higasi and Uyeo,[22] of one ring in the plane of the COC angle and the other ring perpendicular to the plane, it is apparent that rotations about any of the three molecular axes will lead to very large relaxation times. The suggested configuration of the molecule is unsymmetrical and the resultant molecular moment does not lie along any of the molecular axes; therefore, three different relaxation times, all of which would be quite large, are predicted[23] for the over-all molecular relaxation process.

A plot of a' against $a''\omega$ gives points which, at 20°, can be most nearly represented by a straight line of slope corresponding to a relaxation time 57.5 $\times 10^{-12}$ sec. At 40° and at 60°, the points can be well represented by two lines at each temperature giving relaxation times $\tau_1 = 46 \times 10^{-12}$ and $\tau_2 = 17 \times 10^{-12}$ sec. at 40°, and $\tau_1 = 36 \times 10^{-12}$ and $\tau_2 = 19 \times 10^{-12}$ sec. at 60°. The longer relaxation times are reasonable values for the rotation of the molecule as a whole and the shorter are reasonable for the rotation of the o-nitrophenyl group, which should be much longer than that attributed to the

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(21) W. P. Purcell and C. P. Smyth. THIS JOURNAL, 82, 6299 (1960).
(22) K. Higasi and S. Uyeo. Bull. Chem. Soc. Japan, 14, 87 (1939).
(23) F. Perrin. J. Phys. radium, 5, 497 (1939).

unsubstituted phenyl group in diphenyl ether. The failure to detect intramolecular rotation at 20° may well be due to its reduction by the considerable steric hindrance caused by the nitro groups. The greater rotational energies at the higher temperatures may make possible the partial overcoming of this hindrance with consequent appearance of the intramolecular relaxation process.

Bis-(p-nitrophenyl)-ether should also relax by molecular orientation and ring rotation. The former mechanism is associated with the observed permanent moment of 2.79 and the internal rotation is associated with the maximum mesomeric moment, which might be somewhat greater than 1.0 because of the contribution from the nitro groups in the *para* positions. The relaxation time corresponding to over-all molecular rotation should be shorter for bis-(p-nitrophenyl)-ether than for bis-(o-nitrophenyl)-ether and slightly larger than that for benzophenone which is 19 × 10⁻¹² sec. in benzene at 20°. It is surprising to find the plot[18] of a′ against a″ω giving a single straight line with a slope corresponding to a relaxation time 17 × 10⁻¹² sec., instead of the two lines corresponding to two relaxation processes, molecular and intramolecular. However, analysis by the method of chords[8] gives two relaxation times, 24×10⁻¹² and 7×10⁻¹² sec., the first value about what would be expected for molecular rotation and the second a little higher than that attributed to the rotation of the ring in diphenyl ether. The p-nitrophenyl group should obviously have a higher relaxation time for rotation than the unsubstituted phenyl. This analysis gives the ratio of the amounts of the two absorption processes as about 1.5:1 instead of 7.8:1, as estimated from the squares of the two dipole moments concerned, but the calculation is very approximate.

Diphenylmethane has a reduced relaxation time very close to that of diphenyl ether,[10] since the predominant mechanism of relaxation in the two molecules is the same. However, the square of the dipole moment of bis-(p-nitrophenyl)-methane is about 300 times that of the unsubstituted molecule, which is approximately the moment associated with internal rotation in both molecules. It is evident, therefore, that the contribution of internal rotation to the relaxation of bis-(p-nitrophenyl)-methane should be negligible. This is borne out by the closeness of its relaxation time 22.8 × 10⁻¹² sec. to the value obtained for the molecular orientation process in bis-(p-nitrophenyl)-ether, 24 × 10⁻¹², which is practically identical in molecular size and shape.

Because of the small moment value[24] 0.60 × 10⁻¹⁸ of bis-(p-bromophenyl)-ether, the loss values obtained for dilute solutions in benzene were so small that their large relative errors rendered them useless. It is planned to repeat these measurements using somewhat less dilute solutions. In the meantime, the measurements by Mr. E. L. Grubb in Nujol solution will be used for comparison with the other molecules under discussion. The absence of any difference between the values of a_D and a_∞ shows the absence of any considerable absorption in the millimeter wave or infrared region. The

very large value of α, which is typical of solutions in Nujol,[25] makes impossible a significant quantitative analysis in terms of two relaxation times. However, the most probable relaxation time 8.7 × 10⁻¹² in Table III, in spite of the high viscosity of the solvent, is much smaller than the values found for the similarly shaped bis-(p-nitrophenyl) ether and bis-(p-nitrophenyl)-methane. It is close to the value 7×10⁻¹² attributed to rotation of the nitrophenyl group in the former molecule and slightly higher than the value 6.2 × 10⁻¹² for diphenyl ether in Nujol solution[10] at 20°, which was attributed to rotation of the phenyl group. The relaxation time for the p-bromophenyl group in Nujol should be higher than that of the phenyl group in Nujol and of the p-nitrophenyl group in benzene. It appears, therefore, that the predominant relaxation process for bis-(p-bromophenyl) ether is the rotation of the rings rather than of the molecule as a whole, although a contribution from molecular relaxation, presumably, raises the value in Table III a little above the value for the group.

TABLE III

RELAXATION TIMES OF ROTATING GROUPS IN PHENYL ETHERS AT 20°

Ether	Solvents: B, Benzene: N. Nujol Solvent	Rotating group	$\tau(10^{-12}$ sec.)
Diphenyl	B	C_6H_5	4
	N	C_6H_5	6.2
Bis-(p-nitrophenyl)	B	$p\text{-}C_6H_4NO_2$	7
Bis-(o-nitrophenyl)	B	$o\text{-}C_6H_4NO_2$	19
Bis-(p-bromophenyl)	N	$p\text{-}C_6H_4Br$	8.7
Cyclohexyl phenyl	B	C_6H_5	8

Since the data for cyclohexyl phenyl ether in benzene solution did not fit a Cole–Cole arc plot, the results were analyzed in terms of two relaxation times. A plot[18] of a′ against a″ω gave two slopes corresponding to $\tau_1 = 73$ and $\tau_2 = 9.5$. The chord method[8] for calculating two relaxation times gave $\tau_1 = 66$ and $\tau_2 = 6.6$. Fair agreement between calculated and experimental points was obtained by using the mean values, $\tau_1 = 70$ and $\tau_2 = 8.1$, and calculating two Debye-type absorption curves. The large relaxation time 70 × 10⁻¹² sec., presumably associated with the over-all rotation of the molecule, is much higher than would be expected for a molecule of this size. Its explanation must wait upon further measurements on compounds containing the cyclohexyl group. The small relaxation time 8 × 10⁻¹² sec. is sufficiently close to that attributed to ring rotation in the diphenyl ethers and diphenylmethane to warrant its attribution to the rotation of the phenyl ring in the molecule. The moment value 1.55 × 10⁻¹⁸ found for cyclohexyl phenyl ether is larger than the moments of the aliphatic ethers[26] and diphenyl ether but lower than those of the cyclic ethers: ethylene oxide, 1.88; tetrahydrofuran, 1.70; and tetrahydropyran, 1.9.

The considerable uncertainties in the values calculated for intramolecular relaxation times from measurements on dilute solutions make difficult any exact quantitative treatment. In previous

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(26) C. P. Smyth. "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 298-299.

papers[10,11] of this series the low relaxation times found for diphenyl ether and several structurally analogous compounds were attributed to dipole orientation through a mesomeric shift of charge accompanying rotation of the phenyl ring within the molecule. An alternative explanation in terms of dipole orientation through molecular inversion, perhaps, accompanied by twisting seemed less probable, though not definitely excluded by the information available. Table III summarizes the values of the relaxation times which have been attributed to ring rotation in diphenyl ether and closely related ethers.

It was the extremely low value found for the relaxation time of diphenyl ether that indicated the relaxation mechanism to be predominantly an intramolecular process, and this indication was strengthened by the smallness of the effect of the great increase in viscosity accompanying change of the solvent from benzene to Nujol.[10] A simple elastic bending of the molecule would be expected to give rise to absorption at much higher frequencies, while a molecular inversion would be expected to absorb at lower frequencies. Rotation of the phenyl group in the molecule accompanied by shift in mesomeric moment seemed to offer a reasonable explanation of the observed absorption. The substitution of a nitro group in the *para* position of the ring should increase the relaxation for rotation by much less than it would for inversion, while the

protusion of a nitro group in the *ortho* position should hinder rotation much more than it would in the *para* position and hinder inversion less than it would in the *para* position. The much higher relaxation time for the intramolecular relaxation of bis-(o-nitrophenyl)-ether as compared to that of the *para* compound in Table III points to ring rotation rather than inversion as the intramolecular relaxation process. The low relaxation time for bis-(p-bromophenyl)-ether in Nujol and the smallness of the difference between it and the value for the unsubstituted compound in Nujol similarly point to ring rotation as the relaxation mechanism. The shorter of the two relaxation times obtained for cyclohexyl phenyl ether, although longer than the value for diphenyl ether, is significant in showing the presence of an intramolecular relaxation mechanism when only one aromatic ring is present in a molecule of this general type. Further measurements on related compounds are necessary for a fuller understanding of the unexpectedly high values for these two relaxation times.

Infrared Spectra of Metal Chelate Compounds. II. Infrared Spectra of Acetylacetonates of Trivalent Metals[1]

BY KAZUO NAKAMOTO, PAUL J. McCARTHY, ARMAND RUBY AND ARTHUR E. MARTELL

The infrared spectra of acetylacetonates of four trivalent metals have been measured in the range between 4000 and 400 cm.$^{-1}$. With the application of perturbation theory to a previously worked out normal coördinate treatment of the Cu(II) complex, the vibrational frequencies have been calculated for each metal. From the calculated force constants, it has been concluded that the metal–oxygen bonds in the Co(III) and Cr(III) complexes are fairly strong and those of the Fe(III) complex are somewhat weaker. The band at 490 cm.$^{-1}$ in the Al(III) complex has been assigned to the Al–O stretching mode, based on a study of four Al(III) complexes of various β-diketones. A relatively large force constant of the Al–O stretching mode in these complexes suggests that the bond is strongly covalent.

Introduction

Studies of the effects of changing the metal on the infrared spectra of metal chelate compounds have been reported on various types of ligands such as β-diketones,[2] acetylacetone–ethylenediimine and related compounds,[3] 8-hydroxyquinoline,[4] oxalic acid[5] and imidazole derivatives.[6] In these previous investigations, the effect of changing the

(1) This work was supported by the Office of Ordnance Research under Contracts No.'s DA-19-020-ORD-3243 and DA-19-020-ORD-5119.

(2) J. Lecomte, *Discussions Farad. Soc.*, **9**, 125 (1950); C. Duval, R. Freymann and J. Lecomte, *Bull. soc. chim. France*, **19**, 106 (1952).

(3) K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955); **60**, 934 and 1270 (1956).

(4) R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard and W. D. Johnston, *Spectrochim. Acta*, **8**, 1 (1956).

(5) J. Fujita, K. Nakamoto and M. Kobayashi, *J. Phys. Chem.*, **61**, 1014 (1957).

(6) T. R. Harkins, J. L. Walter, O. E. Harris and H. Freiser, THIS JOURNAL, **78**, 260 (1956).

metal was deduced in most cases from shifts of the carbonyl bands which frequently can be identified empirically without much ambiguity.

It should be mentioned, however, that such an empirical approach encounters serious difficulties in some cases. For example, it is almost impossible to assign the bands between 1600 and 1400 cm.$^{-1}$ in the metal chelate compounds of β-diketones since: (1) the bond orders of the C=O and the C=C bonds are similar and both absorb in this region and (2) their relative positions are sensitive to a change in the metal. Furthermore, in such a chelate ring system, coupling between various vibrational modes is serious and the concept of "group frequency" is not generally applicable. For example, Bellamy *et al.*,[7] empirically adopted the strongest band in

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