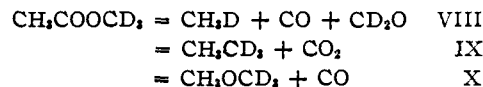


reactions 17-20, whose rate is considerably decreased at these low temperatures.

At -195° , the yield of CH_3CD_3 was lower by a factor of 5 than at 17° , whereas those of C_2H_6 and C_2D_6 underwent little change, clearly showing that intermolecular recombination is almost completely inhibited under these conditions.

In conclusion, it should be pointed out that the evidence for cage recombination presented in this paper and in previous studies is based solely on the following experimental results: (1) the yields of certain products, after correcting for changes in decomposition and intermolecular contributions, are independent of temperature, the presence of scavengers and of solvents, and (2) the negligible yields of these products in the vapor-phase radiolysis performed in the presence of scavengers. Because of (2), it is difficult to accept an intramolecular

rearrangement as an alternative explanation. It remains true, nevertheless, that for such a compound as $\text{CH}_3\text{COOCD}_3$, three intramolecular processes are consistent with (1)



From the mass-spectra cracking-pattern of $\text{CH}_3\text{-COOCD}_3$, it may be deduced¹¹ that the positively ionized methyl acetate molecule does not undergo any of the processes VIII to X. Also, from photochemical studies¹² on the vapor phase, no evidence has been found for the occurrence of any of these processes.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Microwave Absorption and Molecular Structure in Liquids. XXXVIII. The Effect of Structural Factors upon Group Rotation in Some Aromatic Molecules^{1,2}

BY WILLIAM P. PURCELL³ AND CHARLES P. SMYTH

RECEIVED AUGUST 29, 1960

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 4,4'-bis-(dimethylamino)-benzophenone in benzene solution at 20, 40 and 60°, and for 2,4,6-trinitroanisole, 2-amino-4-methylpyridine and N,N-dimethyl-p-nitroaniline in benzene solution at 20°. The data have been used to calculate the dielectric relaxation times of the molecules. The relaxation times give no positive evidence of intramolecular group rotation in these molecules, but the considerable differences indicated between the infinite-frequency dielectric constants and the squares of the refractive indices show high-frequency absorption due to such oscillational or rotational motion. The moment value 4.99×10^{-18} is found for 4,4'-bis-(dimethylamino)-benzophenone.

If a molecule has a rotatable polar group whose moment component does not lie in the axis of group rotation, the molecule can relax by group and overall molecular dipole orientations. The former mechanism has its position of maximum absorption at higher frequencies than the latter mechanism. Experimentally one observes an absorption curve which is resolvable⁴ into two peaks corresponding to the two mechanisms, or else the absorption curves are too close to one another to afford resolution, in which case one simply observes an apparent lowering of the relaxation time to be expected if the molecule were rigid. The contribution of group rotation is evident in the low relaxation times of 1,4-dimethoxybenzene, benzidine and N,N,N',N'-tetramethyl benzidine, which are 6.9,⁵ 1.6⁶ and 2.2×10^{-12} sec.,⁶ respectively, measured in benzene solution at 20°. These values may be compared with the relaxation time of the much smaller molecule, chlorobenzene, for which $\tau = 8.3 \times 10^{-12}$ sec.⁷ measured at 20° in benzene solution. In the present paper the authors have investigated molecules

containing methoxy, amino and dimethylamino groups with the hope of determining what influence, if any, the group has upon the dielectric relaxation and how the rotation of the group may be hindered or prevented by structural factors.

Experimental Methods

Apparatus.—The apparatus and the various methods of measurement have been described in previous papers.⁸⁻¹⁰

Purification of Materials.—4,4'-Bis-(dimethylamino)-benzophenone, obtained from Eastman Kodak Co., was recrystallized twice from ethanol and dried under vacuum in an Abderhalden pistol.

2,4,6-Trinitroanisole, obtained from Eastman Kodak Co., was recrystallized three times from ethanol and dried under vacuum in an Abderhalden pistol, m.p. 67.8-68.5°.

2-Amino-4-methylpyridine, obtained from Eastman Kodak Co., was recrystallized four times from ethanol and dried under vacuum in an Abderhalden pistol, m.p. 99.2-99.3°.

N,N-Dimethyl-p-nitroaniline, obtained from Matheson Coleman and Bell, was recrystallized twice from ethanol and dried under vacuum in an Abderhalden pistol, m.p. 164.5-165.2°.

Benzene, obtained from Allied Chemical Corp., was used without further purification.

Experimental Results

The experimental results were treated in the manner previously described.¹¹ The slopes of the

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 (10) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).
 (11) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *THIS JOURNAL*, **72**, 3447 (1950).

(1) This research was supported by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents part of the work submitted by 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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straight lines thus obtained for the plots of ϵ' and ϵ'' against concentration, a' , corresponding to ϵ' , and a'' , corresponding to ϵ'' , were plotted in Cole-Cole arcs¹² in the usual fashion¹¹ 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 concentration range in mole fraction is given in parentheses for each set of solutions in Table I.

TABLE I
SLOPES FOR THE DEPENDENCE OF THE DIELECTRIC CONSTANT AND LOSS OF BENZENE SOLUTIONS UPON MOLE FRACTION OF SOLUTE

Wave length (cm.)	4,4'-Bis-(dimethylamino)- 20°		a' (dimethylamino)- 40°		a'' (0-0.009)- 60°	
	a'	a''	a'	a''	a'	a''
1.25	5.1	3.6	5.9	4.3	6.2	4.6
3.22	5.4	8.3	7.5	9.7	13.2	10.5
10	23.6	14.7	30.3	11.6	26.6	9.2
25	36.8	11.3	35.8	7.7	33.4	5.45
50	41.2	6.25	36.5	4.0	33.8	2.75
575 m.	41.5		36.9		33.0	

	2,4,6-Trinitro- anisole (0-0.006) 20°		2-Amino- 4-methyl- pyridine (0-0.009) 20°		N,N-Di- methyl- <i>p</i> - nitro- aniline (0-0.002) 20°	
	R _D	P _∞	R _D	P _∞	R _D	P _∞
1.2	1.4	0.7	2.58	2.1	4.7	7.6
3.2	2.7	1.8	5.1	2.8	13	22
10	4.0	2.0	6.95	2.25	42.5	33.0
25	5.5	1.0	7.85	0.55	66.9	19.2
50	6.1	0.7	7.8	0.35	72	12
575 m.	6.2		7.80		71.8	

The moment of 4,4'-bis-(dimethylamino)-benzophenone measured in benzene solution at 20° is reported in Table III. The Halverstadt-Kumler,¹³ Guggenheim¹⁴ and Debye methods of calculation were used. To make possible the moment calculation, solution densities were measured to obtain a slope 0.221 g./cm.³ for the density-weight fraction curve at 20°. The moment of 4,4'-bis-(dimethylamino)-benzophenone was calculated by several methods (Table III) and may be compared with the previously reported¹⁵ value of 5.16. Calculation of the dipole moment involves the problem of determining the sum of the electronic, P_E, and atomic, P_A, polarizations. Table III, column four gives values for the moment calculated from an induced polarization estimated from a_∞ (Table II) where

$$a_\infty = \frac{\epsilon_\infty - \epsilon_1}{X}$$

ϵ_1 is the dielectric constant of the solvent and X is the mole fraction of solute. It must be born in mind that the induced polarization, calculated in this manner, is very approximate because the value for a_∞ estimated from the Cole-Cole arc plot contains a considerable error.

Discussion of Results

There are at least three mechanisms by which 4,4'-bis-(dimethylamino)-benzophenone might relax—over-all molecular rotation, dimethylamino

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TABLE II

SLOPES a_D FOR THE DEPENDENCE OF SQUARE OF REFRACTIVE INDEX UPON MOLE FRACTION, WITH INFINITE FREQUENCY INTERCEPTS a_∞ , CRITICAL WAVE LENGTHS λ_m , RELAXATION TIMES τ AND DISTRIBUTION PARAMETERS α IN BENZENE SOLUTION

Temp., °C.	a_D	a_∞	λ_m (cm.)	τ (10 ⁻¹² sec.)	α
4,4'-Bis-(dimethylamino)-benzophenone					
20	2.12	4.5	10	53	0.1
40		4.6	6.9	37	.1
60		4.6	5.6	30	.1
2,4,6-Trinitroanisole					
20	0.50	1.15	7.1	38	0.14
2-Amino-4-methylpyridine					
20	0.20	1.53	2.9	15.4	0.05
N,N-Dimethyl- <i>p</i> -nitroaniline					
20	1.46	3.5	8.8	47	0.03

TABLE III

MOMENT VALUES ($\times 10^{18}$) FOR 4,4'-BIS-(DIMETHYLAMINO)-BENZOPHENONE

R _D	P _∞	(P _∞ - R _D)	Calcd. from: (P _∞ - P _{E+A})
84.31	677.4 ^a	5.34 ^a	4.99 ^a
		5.31 ^b	
P _{E+A}			
160	664 ^a	5.29 ^c	4.92 ^c

^a Halverstadt-Kumler. ^b Guggenheim. ^c Debye.

group rotation about its bond to the rest of the molecule and a charge shift, as observed in diphenyl ether,¹⁶ resulting from ring rotation. The area under the absorption curve corresponding to over-all molecular rotation will be approximately proportional to the observed moment squared (4.99)², since the contributions to this moment from the small moments associated with intramolecular rotations must be relatively small. Similarly, the other two absorption curve areas will be proportional to the squares of the corresponding moments. The three absorption curve areas thus will have the approximate ratio 25:2:1, corresponding to molecular, dimethylamino group and ring rotations respectively. It is, therefore, obvious that the experimentally observed absorption curve will result primarily from the absorption associated with molecular orientation. Due to the large amount of overlap among the absorption regions, the usual methods^{17,18} for determining multiple relaxation times failed. Indeed, reasonable fits were obtained for the data using Cole-Cole plots and the resulting τ values were used to calculate Debye-type absorption curves which satisfactorily represented the experimental points in terms of a single relaxation time. The large value of the relaxation time shows that there can be little or no contribution to the relaxation process by intramolecular rotation. Mesomeric shift of charge, as evidenced by the large dipole moment value,¹⁹ and consequent double

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bond character may be sufficient to prevent internal rotation. That some rotational oscillation exists is indicated by the considerable difference between a_∞ and a_D in Table II. The relaxation time is much longer than that of benzophenone because of the lengthening of the molecule by the dimethylamino groups.

Anisole has been measured in the pure liquid^{20,21} and in Nujol solution.⁶ The results indicate two absorption regions corresponding to over-all molecular and group rotation. The relaxation times reported for anisole at 20° are $\tau_1 = 13.3$, $\tau_2 = 3.7$ ²¹ and $\tau_1 = 14.6 \times 10^{-12}$ sec., $\tau_2 = 2.0 \times 10^{-12}$ sec.²² Trinitroanisole has been measured in benzene solution in order to study the influence of steric blocking on methoxy group rotation. The data can be interpreted in terms of a most probable relaxation time with a distribution parameter, α , of 0.14. A plot¹⁸ of a' against $a''\omega^{19}$ is linear indicating one dispersion region. The relaxation time (Table II) is much larger than τ_1 for anisole as would be expected in view of the much greater molecular size due to the three added nitro groups. One may conclude, therefore, that the mechanism of dielectric relaxation is that of over-all molecular rotation. Upon examination of the Stuart-Briegleb models, it is clear that one very probable configuration has the methoxy group in a plane perpendicular to the plane of the benzene ring and the nitro groups in the plane of the ring. The resultant moment in this case would not lie along any of the three molecular axes and, therefore, according to the Peirin theory,²³ one would expect at least three different relaxation times corresponding to rotations about different axes. These relaxation time values would be too close to each other to afford resolution of the experimentally observed absorption curve, but the presence of different relaxation times with slight separation makes itself apparent in the large value of the distribution parameter α . In this configuration any considerable rotation of the methoxy group about its bond to the rest of the molecule is prevented by the adjacent nitro groups. However, oscillations of the methoxy group in its potential energy well would be quite probable and these oscillations would contribute to the atomic polarization, thus increasing the normal difference between a_D and a_∞ (Table II).

Measurements of 2-amino-4-methylpyridine were originally undertaken in order to study the influence upon amino group rotation of possible hydrogen bonding to the ring nitrogen. Recent infrared studies,²⁴ however, show quite conclusively that there is little or no hydrogen bond formation between the ring nitrogen and an amino hydrogen. The symmetric stretching vibrations of the amino group of 2-aminopyridine, 3-aminopyridine and 4-aminopyridine measured²⁴ in carbon tetrachloride solution are 3509, 3481 and 3505 cm.⁻¹, respectively. The antisymmetric vibrations are 3410, 3396 and

3413 cm.⁻¹, respectively. The similarity of the vibrational frequencies between a molecule for which intramolecular hydrogen bonding is impossible, e.g., 4-aminopyridine, and a molecule for which there is some possibility of intramolecular hydrogen bonding, 2-aminopyridine, indicates the absence of hydrogen bonding in the latter.

The results for 2-amino-4-methylpyridine indicate a small distribution, $\alpha = 0.05$, of relaxation times about one most probable value. However, the large difference between a_D and a_∞ (Table II) might result from the presence of a high frequency absorption region corresponding to rotatory motion of the amino group. A plot of a' against $a''\omega$ gave a straight line indicating one absorption region. Some substituted pyridines have been measured²⁵ at 20° in the pure liquid state, and their molecular relaxation times, corrected for internal field effects, may be used for comparison. For 2-ethylpyridine $\tau_\mu = 11.3$ and for 4-ethylpyridine $\tau_\mu = 16.4$. These values for over-all molecular relaxation times are similar in magnitude to that found for 2-amino-4-methylpyridine, which seems to confirm the absence of any appreciable contribution from motion of the amino group in the latter molecule. The data for N,N-dimethyl-*p*-nitroaniline may be represented by a Cole-Cole arc plot with α barely distinguishable from zero. The large molecular moment,²⁶ 6.87, lies along the long axis of the molecule and, therefore, end-over-end rotations about the short axes are responsible for the observed dispersion. The shape of the molecule is closely approximated by an ellipsoid and, if the moment lies along one of the molecular axes, no distribution of relaxation times is to be expected, which is consistent with the negligibly small value observed for α . There is no evidence of a high frequency absorption resulting from rotation of the dimethylamino group. This fact is consistent with the high degree of double bond character in the C-N bonds attributed to the molecule. That is, increased double bond character in these bonds resulting from the contributions of resonating polar structures hinders rotation of the dimethylamino group.²⁶ However, as in the case of 2,4,6-trinitroanisole, torsional vibrations of the dimethylamino group about its stiffened bond to the rest of the molecule would give rise to high frequency absorption, which would make itself apparent in an unusually large difference between a_D and a_∞ . For N,N-dimethyl-*p*-nitroaniline a_∞ is over twice as large as a_D (Table II).

In all four of the molecules investigated to determine possible hindrance of relaxation by rotation of a methoxy, amino or dimethylamino group, rotational oscillation of the group was indicated by a large difference between a_∞ and a_D . The effects on relaxation time of possible intramolecular rotation were obscured by the much larger effect of the orientation of the large molecular dipole in 4,4'-bis-(dimethylamino)-benzophenone. The low relaxation times resulting from the presence of the CH₃O group in 1,4-dimethoxybenzene, the NH₂ groups in benzidine and the (CH₃)₂N groups in N,N,N',N'

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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 .

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

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

BY WILLIAM P. PURCELL³ 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 ether⁴⁻¹⁰ 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 suggested¹⁰ 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. Ueyo 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.

(1) This research was supported by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(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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(14) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

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 synthesized¹⁵ 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_D^{20} 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 arcs¹⁷ in the usual fashion¹⁶ 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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