PHYSICAL AND INORGANIC CHEMISTRY

Microwave Absorption and Molecular Structure in Liquids. XLII. Molecular and Group Rotation in Aromatic Methoxy and Ethoxy Compounds[1,2]

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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. and temperatures of 20 and 40° or 20, 40 and 60° have been measured for anisole, p-dimethoxybenzene and α- and β-methoxy and α- and β-ethoxynaphthalene in solution in decalin and in Nujol, and for p-methyl-, p-chloro-, and p-phenylanisole in solution in Nujol. The two solvents were used in order to facilitate the analytical separation of the effects of the molecular and the intramolecular relaxation processes. The equations used by Bergmann, Roberti and Smyth to calculate the relaxation times for simultaneously occurring molecular and intramolecular relaxation processes have been employed in analyzing the results for the decalin solutions, but the equations have been modified to take care of the large distribution of molecular relaxation times occurring in the Nujol solutions. The calculated molecular relaxation times show dependence on the liquid viscosity, the dependence being greater the larger the molecule. The much smaller relaxation times for the rotation of the polar methoxy group within the molecule are virtually equal in the two solvents, and the same is true for the ethoxy group. The larger size of the ethoxy group gives it a relaxation time longer than that of the methoxy group. The shorter relaxation times of the methoxy and ethoxy groups in the 2-position as compared to the 1-position in the substituted naphthalenes give evidence of steric hindrance exerted by the hydrogen in the 8-position upon the rotation of a group in the 1-position.

Methoxy group rotation has been found to lower the dielectric relaxation times of several aromatic compounds.[3,4] A few results have been obtained of a sufficiently quantitative nature to make possible definite characterization of the individual relaxation processes.[5-7] A viscous medium, such as Nujol, tends to increase the relaxation time of over-all molecular rotation by a large factor, whereas the internal rotation process is rather insensitive to viscosity.[8] Therefore, with a highly viscous medium there is a greater possibility of separation of two relaxation processes into their respective components. Nujol (viscosity[8] = 211 c.p.s. at 20°), due to its inherent complexity,

usually gives a distribution of relaxation times when used as solvent, making detailed analysis difficult. On this account, it is desirable to use a second solvent that is less complex than Nujol but still slightly viscous. Decalin (viscosity[8] = 2.61 c.p.s. at 20°) is a solvent which fulfills these requirements.

Purification of Materials.—All substances measured were obtained from Eastman Kodak Company except β-methoxynaphthalene and β-ethoxynaphthalene, which were obtained from Matheson, Coleman and Bell.

α-Methoxynaphthalene was purified by fractional distillation. The purest fraction obtained was redistilled. This procedure was repeated four times. The sample resulting from the final distillation was collected over a range of 0.2°.

α-Ethoxynaphthalene was fractionally distilled under vacuum. The purest fraction was redistilled under vacuum. The resulting material was dried with sodium and then redistilled under vacuum over sodium in order to obtain the driest material possible. The resulting material was colorless.

β-Methoxynaphthalene was recrystallized once from absolute ethanol and twice from n-heptane. The resulting material was dried under vacuum in an Abderhalden pistol. The observed melting point was 72.4–72.7° compared to a literature value[9] of 72.5–73.0°.

β-Ethoxynaphthalene was recrystallized three times from n-heptane followed by one recrystallization from pe-

(1) This research was supported by the U. S. Army Office of 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 Eugene L. Grubb to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) E. Fischer, Z. Naturforsch., 4a, 707 (1949).

(4) H. Hase, ibid., 8a, 695 (1953).

(5) D. M. Roberti and C. P. Smyth, J. Am. Chem. Soc., 82, 2106 (1960).

(6) D. M. Roberti, O. F. Kalman and C. P. Smyth, ibid., 82, 3523 (1960).

(7) K. Bergmann, D. M. Roberti and C. P. Smyth, J. Phys. Chem., 64, 665 (1960).

(8) O. F. Kalman and C. P. Smyth, J. Am. Chem. Soc., 82, 783 (1960).

(9) F. Radt, Ed., "Elsevier's Encyclopedia of Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1955.

troleum ether. The resulting material was dried under vacuum in an Abderhalden pistol. The observed melting point was 35.5° compared to a literature value[9] of 35.6–36.0°.

p-Dimethoxybenzene was recrystallized four times from benzene and then dried under vacuum in an Abderhalden pistol. The melting point observed was 57.2–57.8° compared to a literature value[10] of 56.0°.

Anisole was fractionally distilled and gave a refractive index at 20° of 1.5179 compared to a literature value[11] of 1.5179.

p-Chloroanisole was fractionally distilled, the purest sample of which was collected at 196.8°.

p-Methylanisole was fractionally distilled, the purest sample of which was collected at 176.0–176.2°.

p-Phenylanisole was recrystallized three times from a mixture of benzene and petroleum ether. The resulting material was dried under vacuum in an Abderhalden pistol. The observed melting point was 89.9–90.1° compared to a literature value[12] of 89.0°.

Decalin, obtained as the practical grade from Matheson, Coleman and Bell, was fractionally distilled. The sample to be used was stored under Drierite (W. A. Hammond Drierite Company) until used.

Nujol, purchased from a local drugstore, was placed under vacuum for an hour in order to remove any dissolved gases which might be present. It was then used without further purification.

Experimental Methods and Results

Measurements of dielectric constant and loss were carried out on the solvent and on the solutions of each substance in decalin or Nujol at the temperatures and wave lengths indicated in Table I by methods described in previous papers.[13–15] Refractive indices were measured by means of a Pulfrich refractometer, normally at only one temperature.

The experimental results were treated in the manner previously described,[16] the dielectric constants ϵ' and losses ϵ'' being plotted against mole fraction for the decalin solutions and against weight fraction for the Nujol solutions. The slopes of the straight lines obtained in this manner, a''. corresponding to ϵ'', and a', corresponding to ϵ', were plotted against each other in order to see if the experimental data conformed to a Cole–Cole plot.[17] The compounds

TABLE I

SLOPES OF DIELECTRIC CONSTANT AND LOSS FOR COMPOUNDS MEASURED IN DECALIN

λ (cm.)	—20°—		—40°—		—60°—	
	a'	a''	a'	a''	a'	a''
α-Methoxynaphthalene (0–0.030)						
D-line	0.36					
1.25	.65	0.12	0.70	0.13		
3.22	.72	.26	0.79	.26		
10	1.08	.41	1.02	.25		
25	1.42	.30	1.39	.23		
50	1.55	.18	1.50	.11		
575 m.	1.61		1.53			
α-Ethoxynaphthalene (0–0.024)						
D-line	0.36					
1.25	.61	0.08	0.63	0.075		
3.22	.64	.16	.67	.19		
10	.76	.41	.86	.39		
25	1.31	.43	1.35	.30		
50	1.51	.29	1.46	.16		
575 m.	1.61		1.48			
β-Methoxynaphthalene (0–0.020)						
D-line	0.33					
1.25	.60	0.17	0.61	0.20		
3.22	.74	.27	0.82	.29		
10	1.06	.29	1.08	.26		
25	1.28	.21	1.25	.16		
50	1.38	.12	1.30	.09		
575 m.	1.41		1.32			

β-Ethoxynaphthalene (0–0.026)

D-line	0.33					
1.21	.61	0.11	0.63	0.13		
3.22	.74	.25	0.85	.30		
10	.97	.31	1.10	.31		
25	1.33	.25	1.36	.16		
50	1.49	.13	1.42	.10		
575 m.	1.55		1.44			

p-Dimethoxybenzene (0–0.030)

D-line	0.08					
1.20	1.10	0.48	1.18	0.51	1.27	0.52
3.22	1.81	.72	1.87	.64	1.93	.50
10	2.39	.37	2.22	.30	2.07	.24
25	2.50	.20	2.29	.16	2.12	.10
50	2.52	.11	2.30	.08	2.12	.04
575 m.	2.55		2.31		2.13	

[a]Anisole (0–0.060)

D-line	0.05					
1.28	0.57	0.39	0.58	0.39	0.51	0.39
3.19	1.08	.40	1.09	.34	1.02	.26
10	1.26	.24	1.16	.15	1.05	.13
25	1.36	.07	1.21	.05	1.09	.04
575 m.	1.38		1.25		1.13	

[a] Measured by Mr. W. S. Lovell.

TABLE II

DISTRIBUTION PARAMETERS, RELAXATION TIMES (10^{-12} SEC.), AND CONTRIBUTIONS BY THE INTRAMOLECULAR ROTATION PROCESS FOR COMPOUNDS MEASURED IN DECALIN

Temp., °C.	α	a_∞	τ_0	τ_1	τ_2	C_2
α-Methoxynaphthalene						
20	0.12	0.61	55.2	79.4	27.5	0.39
40	0.12	0.64	44.7	63.1	25.0	0.41
α-Ethoxynaphthalene						
20	0.00	0.61	105	110	36.3	0.18
40	0.00	0.62	75	78	33.9	0.24
β-Methoxynaphthalene						
20	0.27	0.48	33.1	94	15.8	0.51
40	0.27	0.48	23.3	72	14.4	0.54
β-Ethoxynaphthalene						
20	0.29	0.53	56.2	122	24.5	0.55
40	0.19	0.56	38.9	83	20.9	0.57
p-Dimethoxybenzene						
20	0.04	0.94	17.5	31.6	13.8	0.81
40	.00	.95	13.5	27.5	11.0	.83
60	.00	.95	9.8	21.9	9.6	.84
Anisole						
20	0.20	0.18	10.8	21.9	7.0	0.65
40	.19	.15	9.0	18.2	6.0	.68
60	.15	.11	7.6	15.0	5.5	.62

(10) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

(11) "Handbook of Physics and Chemistry," Chemical Rubber Publishing Co., Cleveland, Ohio, 1956.

(12) F. Richter, Ed., "Beilstein's Handbuch der Organischen Chemie," J. Springer, Berlin, 1944.

(13) H. L. Laquer and C. P. Smyth, J. Am. Chem. Soc., 70, 4097 (1948).

(14) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, ibid., 74, 3443 (1952).

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

(16) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, J. Am. Chem. Soc., 74, 3447 (1952).

(17) K. S. Cole and R. H. Cole, J. Chem. Phys., 9, 341 (1941).

measured in decalin all give satisfactory Cole–Cole plots as do α-ethoxynaphthalene and α-methoxynaphthalene in Nujol. β-Methoxynaphthalene and the substituted anisoles, when measured in Nujol solution, fail to give satisfactory Cole–Cole plots. Where Cole–Cole plots could be drawn satisfactorily values of the most probable relaxation time, τ_0, and of the distribution parameter, α, were obtained by the usual methods.[18]

In Table I are listed the values of the slopes a' and a''. In Table II are listed the distribution parameters α, the high-frequency intercept a_∞, values of τ_0 and the two relaxation times τ_1 and τ_2, corresponding to over-all and internal rotation, respectively, and the fraction C_2 of the total process which is due to internal rotation. The relaxation times τ_1 and τ_2 have usually been determined by the method of analysis employed by Bergmann, Roberti and Smyth.[7]

Since Nujol has been observed to give a distribution of relaxation times for rigid molecules of various shapes,[6] the equations used for analysis in terms of two relaxation times[7] have been modified by considering an appropriate distribution of relaxation times[17] for the over-all molecular rotation process. It is assumed that only the internal rotation process obeys the Debye equations, and the equations for analysis in terms of more than one relaxation time[7]

$$\frac{a' - a_\infty}{a_0 - a_\infty} = C_1 \frac{1}{1 + (\omega\tau_1)^2} + C_2 \frac{1}{(1 + (\omega\tau_2)^2} \quad (1)$$

$$\frac{a''}{a_0 - a_\infty} = C_1 \frac{\omega\tau_1}{1 + (\omega\tau_1)^2} + C_2 \frac{\omega\tau_2}{1 + (\omega\tau_2)^2} \quad (2)$$

are modified to

$$\frac{a' - a_\infty}{a_0 - a_\infty} = C_2 \frac{1}{1 + (\omega\tau_2)^2} +$$
$$\frac{C_1}{2}\left[1 - \frac{\sinh(1 - \alpha)x}{\cosh(1 - \alpha)x + \sin(\alpha\pi/2)}\right] \quad (3)$$

$$\frac{a''}{a_0 - a_\infty} = C_2 \frac{\omega\tau_2}{1 + (\omega\tau_2)^2} +$$
$$\frac{C_1}{2}\left[\frac{\cosh(\alpha\pi/2)}{\cosh(1 - \alpha)x + \sin(\alpha\pi/2)}\right] \quad (4)$$

where $x = \log(\omega\tau_1)$ and $C_1 + C_2 = 1$.

In Table III are listed the slopes obtained for the compounds measured in Nujol. In Table IV are listed the values of a_∞, α, τ_0, τ_1, τ_2 and C_2. Values of a_∞, α and τ_0 are listed only for those compounds which give a satisfactory Cole–Cole representation. Methods used to calculate τ_1 and τ_2 together with any assumptions used in the calculations will be discussed for individual compounds. The absolute errors in the values of τ_1 and τ_2 are often as large as 20%. The concentration range used in the measurements is given in Tables I and III after the name of the individual compound (mole fractions for decalin measurements and weight fractions for Nujol).

TABLE III

SLOPES OF DIELECTRIC CONSTANT AND LOSS FOR COMPOUNDS MEASURED IN NUJOL

λ (cm.)	−20° a'	−20° a''	−40° a'	−40° a''	−60° a'	−60° a''
α-Methoxynaphthalene (0–0.032)						
D-line	0.30					
1.25	.44	0.10	0.44	0.09	0.44	0.08
3.22	.54	.15	.50	.14	.48	.13
10	.65	.19	.58	.18	.64	.21
25	.73	.21	.89	.25	.96	.23
50	.94	.27	1.05	.26	1.16	.18
575 m.	1.58		1.46		1.46	
α-Ethoxynaphthalene (0–0.029)						
D-line	0.26					
1.20	.43	0.03	0.44	0.04	0.44	0.035
3.22	.46	.05	.49	.075	.48	.10
10	.49	.075	.52	.13	.52	.155
25	.54	.14	.64	.20	.71	.26
50	.64	.21	.80	.27	.94	.30
575 m.	1.47		1.38		1.29	
β-Methoxynaphthalene (0–0.030)						
D-line	0.32					
1.21	.40	0.07	0.40	0.09	0.41	0.11
3.22	.46	.12	.54	.14	.60	.16
10	.54	.13	.58	.165	.68	.17
25	.87	.12	.85	.14	.84	.15
50	.92	.135	.94	.15	.96	.135
575 m.	1.61		1.49		1.38	
β-Ethoxynaphthalene (0–0.029)						
D-line	0.25					
1.25	.34	0.065	0.40	0.10	0.43	0.14
3.22	.44	.105	.51	.145	.59	.18
10	.57	.115	.64	.135	.71	.17
25	.71	.12	.83	.13	.94	.165
50	.78	.14	.89	.145	1.02	.15
575 m.	1.42		1.36		1.29	
p-Dimethoxybenzene (0–0.033)						
D-line	0.07					
1.29	0.98	0.49	1.03	0.61	1.12	0.64
3.19	1.37	.59	1.53	.58	1.68	.52
10	2.04	.50	2.03	.35	2.03	.24
25	2.34	.32	2.22	.25	2.09	.11
50	2.50	.23	2.35	.11	2.15	.07
575 m.	2.57		2.36		2.14	
Anisole (0–0.036)						
D-line	0.05					
1.28	.64	0.35	0.70	0.36	0.74	0.38
3.30	.86	.44	0.94	.41	0.99	.36
10	1.29	.33	1.29	.26	1.31	.23
25	1.39	.23	1.36	.17	1.34	.15
50	1.47	.18	1.42	.13	1.39	.10
575 m.	1.72		1.57		1.45	
p-Chloroanisole (0–0.047)						
D-line	0.10					
1.28	.465	0.285	0.51	0.35	0.55	0.41
3.22	.76	.35	0.87	.49	0.93	.63
10	1.05	.51	1.26	.70	1.58	.96
25	1.53	.83	2.17	.97	2.58	.89
50	2.33	.99	2.90	.93	3.22	.66
575 m.	3.95		3.64		3.34	
p-Methylanisole (0–0.029)						
D-line	0.05					
1.28	.46	0.315	0.56	0.35	0.63	0.36
3.30	.84	.375	0.95	.38	1.01	.37
10	1.18	.25	1.20	.21	1.16	.20
25	1.26	.19	1.24	.09	1.19	.06
50	1.37	.12	1.27	.06	1.19	.03
575 m.	1.41		1.28		1.19	
p-Phenylanisole (0–0.037)						
D-line	0.30					
1.28	.52	0.125	0.51	0.145	0.50	0.175
3.22	.64	.18	.66	.20	.69	.215
10	.79	.19	.85	.16	.88	.15
25	.94	.16	.97	.13	.98	.10
50	1.07	.16	1.08	.11	1.07	.06
575 m.	1.25		1.17		1.085	

(18) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, Chap. II.

TABLE IV

DISTRIBUTION PARAMETERS, RELAXATION TIMES (10^{-12} SEC.) AND CONTRIBUTIONS BY THE INTRAMOLECULAR ROTATION PROCESS FOR COMPOUNDS MEASURED IN NUJOL

Temp., °C.	α	a_∞	τ_0	τ_1	τ_2	C_2
α-Methoxynaphthalene						
20	0.55	0.30	347	640	27.5	0.30
40	.51	.30	155	316	24.6	.32
60	.50	.30	100	159	23.4	.34
α-Ethoxynaphthalene						
20	0.34	0.43	1050	1100	33.1	0.08
40	.32	.43	562	575	31.6	.13
60	.25	.42	245	330	30.2	.14
β-Methoxynaphthalene						
20				912	20.0	0.42
40				648	19.0	.48
60				450	18.2	.51
β-Ethoxynaphthalene						
20	0.67	0.26	290	1212	24.5	0.40
40	.62	.26	120	755	21.9	.43
60	.55	.27	60	471	20.0	.51
p-Dimethoxybenzene						
20	0.32	0.49	20.0	112	14.0	0.78
40	.28	.50	14.8	97	10.5	.82
60	.20	.51	11.6	40	7.2	.85
Anisole						
20				69	7.2	0.60
40				46	6.6	.60
60				36	6.3	.62
p-Chloroanisole						
20				380	10.5	0.21
40				210	10.0	.23
60				91	10.0	.27
p-Methylanisole						
20				100	11.5	0.70
40				63	10.6	.78
60				38	10.0	.78
p-Phenylanisole						
20				345	14.6	0.56
40				195	14.2	.65
60				85	12.1	.62

Discussion of Results

The τ_0 values for α-ethoxynaphthalene in decalin are so large as to indicate a large contribution from over-all molecular rotation. In comparison, the τ_0 values for β-ethoxynaphthalene are only about half as large, in sharp contrast to the difference observed for the rigid α-substituted naphthalenes.[19] This indicates that the lower value of τ_0 for β-ethoxynaphthalene relative to that of α-ethoxynaphthalene is due to a larger contribution from internal rotation of the ethoxy group in β-ethoxynaphthalene. This same tendency is observed for α-methoxynaphthalene and β-methoxynaphthalene, but the relaxation time decrease is smaller than that observed for the ethoxy compounds. The τ_0 value of α-methoxynaphthalene is only about half that of α-ethoxynaphthalene, a much

(19) R. W. Rampolla and C. P. Smyth, J. Am. Chem. Soc., 80, 1057 (1958).

larger difference than would be expected from the difference in size of the two molecules if they were rigid. This indicates that the α-methoxynaphthalene molecule possesses more internal rotation than the α-ethoxynaphthalene molecule. For these compounds, the distribution parameter α is considerable in size when both molecular and intramolecular rotation make large contributions to the relaxation process. When one rotation process is heavily predominant, as in α-ethoxynaphthalene (molecular) and p-dimethoxybenzene (intramolecular), α is small in decalin solution.

In order to obtain quantitative results, an analysis in terms of two relaxation times was carried out by means of equations 1 and 2. The values obtained for τ_1 give the general trends shown by rigid molecules, i.e., larger relaxation time for a β-substituted naphthalene than for an α-substituted naphthalene due to the greater length of the β-substituted molecule. The τ_1 values increase with increasing size of the group with the substituent at a given position, as is to be expected. A different trend is noted for the τ_2 values, which, for a given substituent, increase in going from the β- to the α-substituted position. It appears that, for the α-substituted naphthalenes, hindrance of rotation gives rise to increase in the observed internal relaxation time. The observed τ_2 values increase as the group size increases, as is to be expected, since a larger group will experience greater resistance to rotation. Comparison of the C_2 values of these compounds gives further support to these interpretations.

In comparison to the results just discussed for the naphthalene compounds, p-dimethoxybenzene has much smaller values for the most probable relaxation time τ_0. p-Dimethoxybenzene might be expected to give relaxation times characteristic of internal rotation only since the fixed dipole moment components are equal and oppositely directed. However, the relaxation times obtained for this compound are larger than would be expected for a purely internal relaxation mechanism, suggesting that there may be a mesomeric moment along the major axis or that the potential energy barriers hindering rotation of the methoxy groups cause the molecules to exist in unstable cis and trans forms, the cis form contributing to dielectric relaxation by molecular rotation. Dipole orientation by molecular rotation might result from both causes. The results obtained for this compound were further analyzed in terms of two relaxation times. Since the analysis by means of equations 1 and 2 was inaccurate because of the great predominance of the internal rotation process, the high-frequency relaxation time τ_2 was calculated by the chord method[7] and used to calculate a loss-log frequency curve according to Debye. The low-frequency region was then obtained by subtraction of this curve from the experimental loss-log frequency curve. The value of C_2 was varied until the low-frequency curve was most nearly of the Debye type. If the 17% average contribution by over-all rotation arose entirely from a mesomeric moment along the major axis, this moment could be calculated from the relation

$C_1 = \left(\dfrac{\mu_1}{\mu}\right)^2$, where μ_1 is the moment component associated with over-all molecular rotation,[7,20] i.e., the mesomeric moment in the case of this compound, and μ ($= 1.73D$) is the molecular moment measured at radio frequency. This gives $\mu_1 = 0.71D$, compared to values[21,22] of $0.8D$ obtained by other methods.

The relaxation time of anisole in decalin at 20° is slightly larger than that found[23] in benzene at 20°, 7.0×10^{-12} sec., as is to be expected. The large distribution observed for anisole in decalin further is consistent with the importance of internal rotation as shown by the average of $C_2 = 0.65$. Through use of bond moments and group moments a possible mesomeric moment of $0.78D$ was obtained for this compound, which is not far from the values just discussed.

The very large τ_0 values obtained for α-ethoxynaphthalene in Nujol indicate that this molecule has little internal rotation. The τ_0 values for α-methoxynaphthalene are approximately 1/3 those for α-ethoxynaphthalene, too large a difference to be due only to the small difference in size of the two molecules, and indicating that the methoxy group has greater rotational freedom. A rough Cole–Cole plot can be drawn for the β-ethoxynaphthalene results, making possible the determination of τ_0 values. The τ_0 values obtained are much smaller than those observed for α-ethoxynaphthalene, showing the greater ease of ethoxy rotation in β-ethoxynaphthalene. Comparison of the observed α values of these compounds suggests the same conclusions. It should be emphasized that the τ_0 values obtained for β-ethoxynaphthalene are only approximate since the distribution is large and the resulting Cole–Cole plot somewhat inaccurate. It should also be pointed out that the significance of τ_0 values for substances showing two distinct relaxation processes is only qualitative.

Since for most solutes Nujol gives rise to a distribution of relaxation times for over-all rotation, equations 3 and 4 have been employed in the analysis. When a Cole–Cole plot cannot be drawn, it is difficult to assign an accurate value for a_∞ in these equations. A better procedure in this situation is to determine one of the relaxation times as well as possible, as by plotting[24] a' against $a''\omega$, and then calculate a loss–log frequency curve corresponding to this relaxation time value. The loss due to the second relaxation process then can be determined by subtraction of this curve from the experimentally observed curve. The best procedure in the case of the naphthalenes is to determine τ_1 as accurately as possible and then, through use of an appropriate α value, calculate out the molecular rotation absorption curve. The internal rotation curve can then be determined by subtraction of the calculated curve from the ex-

perimental curve, the C_2 and a_∞ values being varied until the curve is of the Debye type.

It has been observed that in decalin solution the α values for α-chloronaphthalene are much larger than those observed for α-ethoxynaphthalene and α-methoxynaphthalene. It has been arbitrarily assumed that this trend also occurs when Nujol is used as solvent. Several trial calculations were carried out for the loss given by the second term of equation 4 as a function of frequency. The best values of α for molecular rotation obtained for α-methoxynaphthalene were 0.13, 0.12 and 0.10 at 20, 40 and 60°, and 0.17, 0.15, 0.12 for α-ethoxynaphthalene at 20, 40 and 60°, respectively. Subtraction of the absorption curves calculated through use of these values from the experimental curves leads to internal rotation absorption regions which are generally Debye-shaped. It was assumed that for β-ethoxynaphthalene and β-methoxynaphthalene the α values should be of the same order of magnitude as those obtained for β-methylnaphthalene.[25] After several trials it was observed that the best α values for molecular rotation for β-methoxynaphthalene were 0.35, 0.32 and 0.28 at 20, 40 and 60°, and 0.31, 0.27 and 0.24 for β-ethoxynaphthalene at 20, 40 and 60°, respectively. It was found that a difference of ± 0.02 for an α value did not cause much change in the resulting τ_2 and C_2 values for two successive trials. In view of the attendant difficulties involved in analysis when Nujol is used as solvent, this is an improvement over any other method which might be used, despite the somewhat arbitrary selection of α values. A comparison of the τ_1 and τ_2 values obtained by this method with those obtained when decalin was used as solvent reveals the same general trend for τ_2 values. The τ_1 values are much larger for the Nujol solutions, as is to be expected in the case of the molecular rotation process. From Table IV it is noted that the same general relationship for C_2 values is obtained as in the decalin measurements, except that the C_2 values are slightly smaller in size. The C_2 values differ for the two solvent systems by no more than the experimental error and the error of the analysis.

The results obtained for p-dimethoxybenzene conform quite well to a Cole–Cole plot, making possible the determination of τ_0 values. The τ_0 values obtained for this compound in decalin average only 14% lower than those in Nujol in spite of the much lower viscosity. This further indicates the predominance of the internal rotation process. However, the values are larger and more temperature-dependent than would be expected for a completely internal rotation process. Values of τ_1 and τ_2 were determined by the same method as that used for this compound in decalin. Using the average value of C_2, a mesomeric moment of $0.73D$ is calculated, which is close to the value previously obtained in decalin.

Since Cole–Cole plots cannot be satisfactorily drawn for any of the other anisoles measured in Nujol, resolution in terms of two relaxation times presents problems similar to those discussed above

(20) See A. Budó, Physik. Z., **39**, 706 (1938); ibid., **40**, 603 (1939); A. Aihara and M. Davies, J. Colloid Sci., **11**, 671 (1956).

(21) L. E. Sutton, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 395.

(22) A. R. Katritsky, E. W. Randall and L. E. Sutton, J. Chem. Soc., 1769 (1957).

(23) W. Maier, Arch. Sci. (Geneva), **14**, fasc. spec. (1959).

(24) R. H. Cole, J. Chem. Phys., **23**, 493 (1955).

(25) E. L. Grubb and C. P. Smyth, J. Am. Chem. Soc., **83**, 4122 (1961).

for the naphthalenes in Nujol. Plots[24] of a' vs. $a''\omega$ for the anisoles gave values of τ_1 much smaller than those obtained for the substituted naphthalenes. The method used to characterize the relaxation processes for the anisoles in Nujol was to determine τ_2, calculate the absorption region corresponding to this relaxation time by means of the Debye equation, and obtain the molecular rotation absorption region by subtraction from the experimentally determined loss–log frequency curve.

Analysis of p-chloroanisole as the pure liquid and in benzene has shown that the molecular rotation process is predominant, although the internal rotation process also occurs.[5,23] The present results show molecular rotation as contributing 79% of the total relaxation process at 20°. The larger fixed dipole moment of p-chloroanisole increases the contribution of the molecular rotation process above that found in the case of anisole where C_1 is 0.40 as compared to 0.79 for p-chloroanisole at 20°. p-Dimethoxybenzene was found to have 78% internal rotation at 20°, as compared to 60% for anisole, where the fixed dipole moment raises the over-all molecular contribution. In p-methylanisole the moment due to the methyl group is in a direction opposite to that of the fixed moment of the methoxy group, so that this molecule would be expected to have more internal rotation than anisole, since the fixed moment is reduced whereas the component capable of internal rotation remains essentially constant. The observed value of C_2, 0.70 at 20°, is in agreement with this prediction. p-Phenylanisole is similar to anisole in regard to the fixed moment component and, therefore, the relative relaxation contributions should be quite similar. The observed values are very close to those found for anisole.

Table V summarizes the mesomeric moments calculated by two methods through use of bond moments, group moments and average C_1 and C_2 values. Considering μ_1 as the dipole moment component associated with molecular rotation and μ_2 as that associated with internal rotation, it can be seen that, for the $para$-substituted anisoles

$$\mu_1 = \mu_{OCH_3} \cos \theta - \mu_m + \mu_g \text{ and } \mu_2 = \mu_{OCH_3} \sin \theta$$

where μ_{OCH_3} is the methoxy group moment which is directed at an angle θ with respect to the major axis, μ_m is the mesomeric moment, and μ_g is the group moment due to the substituent in the $para$ position. The sign of μ_g depends on the direction of this group moment. Since $C_1 = \left(\dfrac{\mu_1}{\mu}\right)^2$ and $C_2 = \left(\dfrac{\mu_2}{\mu}\right)^2$, then $\dfrac{C_1}{C_2} = \left(\dfrac{\mu_1}{\mu_2}\right)^2$.

In Method I, the observed value of c_1 and the dipole moment are used, together with the group moments contributing to μ_1. Then, from the equation $C_1 = \left(\dfrac{\mu_1}{\mu}\right)^2$, the value of μ_m, the mesomeric moment, which satisfies this equation is determined. In Method II, μ_2 and all of μ_1 except μ_m are calculated using group moments. Then using the observed ratio C_1/C_2, the value of μ_m which satisfies this ratio is determined.

TABLE V

MESOMERIC MOMENTS ($\times 10^{18}$) CALCULATED FOR THE SUBSTITUTED ANISOLES

	Method I	Method II
Anisole	0.79	0.72
p-Chloroanisole	0.93	.97
p-Methylanisole	1.10	.94
p-Phenylanisole	0.72	.77

These calculated values are, of course, extremely approximate, but they are of the same magnitude as values estimated by other means for compounds of this type and as the value 0.71 obtained here for p-dimethoxybenzene. This agreement suggests that contributions from unstable polar molecular forms resulting from steric hindrance may be of little importance. The larger values of τ_2 for the substituted anisoles as compared to that for the rotation of the methoxy group in anisole itself may arise in part from increased hindrance of rotation by increased conjugation of π-orbital overlap. In the α-substituted naphthalenes, steric hindrance by the hydrogen in the 8-position raises the relaxation time. The great increase in viscosity from decalin to Nujol seems to have little effect on the intramolecular rotation of the methoxy and ethoxy groups.

The general trend of the τ_1 values is what would be expected from the sizes of the molecules except in the case of p-phenylanisole, which seems to give anomalously small τ_1 values in comparison to relaxation times obtained for other substituted biphenyls in Nujol.[8] This anomaly might possibly arise from rotation of the molecule, to a considerable extent, around its long axis, the rotation of the methoxy group being somewhat hindered. Another factor may be the fact that the center of gravity of 4-bromobiphenyl is closer to the bromine than it is to the methoxy in p-phenylanisole, since the bromine atom is much heavier than the methoxy group. The 4-bromobiphenyl molecule may, therefore, sweep out a greater volume in its rotation than does the p-phenylanisole molecule and thus have a higher relaxation time.