Microwave Absorption and Molecular Structure in Liquids. XLIII. Dielectric Relaxation and Intramolecular Rotation in Ten Aromatic Amines[1,2]

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The dielectric constants and losses at all or most of the wave lengths, 1.2, 3.2, 10, 25 and 50 cm., and 575 m., and temperatures 20, 40 and 60°, have been measured for pure aniline and N,N-dimethylaniline, for dilute benzene solutions of aniline, p-toluidine, benzidene, N,N,N′,N′-tetramethylbenzidene, α-naphthylamine, β-naphthylamine, diphenylamine, N-phenyl-1-naphthylamine and N-phenyl-2-naphthylamine and for dilute solutions of diphenylamine in Nujol and N-phenyl-1-naphthylamine and N-phenyl-2-naphthylamine in decalin. The refractive indices for the D sodium line have also been measured for most of the solutions. The data have been used to calculate the most probable dielectric relaxation times and have been analyzed to obtain relaxation times for dipole orientation by molecular and intramolecular rotation. The molecular relaxation times calculated from the measurements are of the magnitudes to be expected from the sizes and shapes of the molecules. A second relaxation time obtained for each substance in solution is associated with intramolecular motion—the slightly hindered rotation of an NH_2 or $N(CH_3)_2$ group, or the more hindered rotation of a phenyl or naphthyl group, or a combination of the two relaxation times of a phenyl and a naphthyl group rotation.

Early measurements[3,4] on a few amines carried out at frequencies far removed from their regions of maximum dielectric absorption gave short dielectric relaxation times apparently arising in part or in whole from dipole orientation by some kind of intramolecular motion. As the need of microwave measurements was evident, several measurements at centimeter wave lengths were carried out by Dr. K. Fish in this Laboratory about six years ago. The results of these measurements are included, as indicated, in the present paper together with more extensive microwave measurements on aromatic amines containing groups of different sizes in solvents of different viscosities. In the meantime, microwave measurements on several aromatic amines at more than one frequency have been reported.[5,6] The experimental results reported in the present paper have been given preliminary analysis by the arc-plot method of Cole and Cole[7] to obtain a rough value for a most probable relaxation time, which is useful for qualitative comparison with the values obtained for substances giving a more nearly symmetrical distribution of relaxation times about a most probable value. The data then have been analyzed by methods[8,9] designed to yield two relaxation times when two distinct relaxation mechanisms exist.

Purification of Materials.—All solid substances were purified by recrystallization and dried under vacuum in an Abderhalden pistol after being recrystallized.

α-Naphthylamine, obtained from Matheson, Coleman and Bell, was recrystallized twice from absolute ethanol and once from ethyl ether. The observed melting point of the purified material was 50.8–51.2°.

β-Naphthylamine, obtained from Brothers Chemical Company, was recrystallized three times from benzene. The observed melting point of the purified material was 110.2–110.7°.

Benzidine, obtained from Matheson, Coleman and Bell, was recrystallized twice from absolute ethanol and once from ethyl ether. The observed melting point of the purified material was 128.7–129.0°.

N,N,N′,N′-Tetramethylbenzidine, obtained from Eastman Kodak Company, was recrystallized twice from petroleum ether and once from a mixture of petroleum ether and benzene. The observed melting point of the purified material was 195.4–195.6°.

Diphenylamine, obtained from the Fischer Scientific Company, was recrystallized twice from petroleum ether. The observed melting point of the purified material was 62.0–62.5°.

N-Phenyl-1-naphthylamine, obtained from Eastman Kodak Company, was recrystallized three times from absolute ethanol and once from petroleum ether. The observed melting point of the purified material was 63.7–64.0°.

N-Phenyl-2-naphthylamine, obtained from Eastman Kodak Company, was recrystallized three times from benzene followed by successive recrystallizations from absolute ethanol and benzene. The observed melting point of the purified material was 110.6–110.8°.

The benzene used as solvent was obtained from the Allied Chemical Corporation and was of the reagent grade, thiophene-free quality. The benzene was dried with "Drierite" before being used in the measurements.

Decalin, obtained from Matheson, Coleman and Bell as the practical grade, was fractionally distilled through a four-foot column. Fractions to be used in the measurements were dried with "Drierite."

Nujol, purchased from a local drugstore, was placed under vacuum for an hour in order to remove any dissolved gases which might be present. No further purification was attempted.

Aniline was fractionally distilled twice from zinc dust.

p-Toluidine was fractionally distilled three times and fractionally recrystallized once.

N,N-Dimethylaniline was fractionally distilled twice from barium oxide and fractionally recrystallized once.

Experimental Results

Measurements were carried out at wave lengths of 1.2, 3.2, 10, 25 and 50 cm., and 575 m. utilizing methods described in previous papers.[10-12] Those compounds having small relaxation times were not measured at the lower frequencies. Refractive indices for the sodium D line were measured by means of a Pulfrich refractometer, normally at only one temperature. The dielectric measurements were carried out at 20, 40 and 60°. The experimental results were treated in the manner previously described.[13]

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(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. Elektrochem., 53, 16 (1949); Z. Naturforsch., 4a, 707 (1949).

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

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Cole-Cole plots were made in order to determine the most probable relaxation time τ_0 and the distribution parameter α.

In Table I are listed the values of the slopes, a' and a'', of the lines obtained by plotting the various quantities against mole fraction of polar solute, for the primary aromatic amines and the diamines, all of which have been measured in benzene solution. a' for the D line is the slope for the square of the refractive index, a' and a'' for the centimeter wave lengths are for the dielectric constant and loss, and a' at 575 m. is taken as a_0, the slope for the static dielectric constant. In Table II are listed the values for the distribution parameter α, the most probable relaxation time τ_0, the relaxation time for molecular rotation τ_1, and the relative amount of the contribution from internal rotation C_2, obtained for these compounds. The contribution from molecular rotation is $C_1 = 1 - C_2$. The methods used in calculating the τ_1 and C_2 values are given in the subsequent discussion of results. Results obtained for aniline and N,N-dimethylaniline as pure liquids are listed in Table III. In Table IV are listed the values of the slopes a_0, a', a'' and a_D obtained for the secondary aromatic amines. Table V contains values for α, τ_0, τ_1, τ_2, a_∞ and C_2 obtained for these compounds. a_∞ values listed in these tables have been determined as the high-frequency intercepts on the Cole–Cole plots. The concentration range in mole fraction over which the solution measurements were carried out is listed in Tables I and IV after the name of the particular compound.

TABLE I

SLOPES OF DIELECTRIC CONSTANT AND LOSS FOR THE
PRIMARY AROMATIC AMINES AND DIAMINES IN BENZENE

λ (cm.)	—20°— a'	a''	—10°— a'	a''	—30°— a'	a''
Benzidine (0–0.10)						
D-line	1.24					
1.28	4.43	0.76	4.22	0.68	4.00	0.61
3.16	4.59	0.30	4.40	0.26	4.16	0.20
575 m.	4.63		4.40		4.16	
N,N,N',N'-Tetramethylbenzidine (0–0.020)						
D-line	1.36					
1.20	2.77	0.43	2.65	0.37	2.54	0.31
3.16	2.84	0.18	2.74	0.15	2.63	0.13
575 m.	2.90		2.78		2.67	
α-Naphthylamine (0–0.026)						
D-line	0.91					
1.28	2.08	0.88	2.16	0.84	2.20	0.69
3.17	3.08	.86	3.08	.76	2.90	.57
10	3.92	.53	3.66	.36	3.34	.26
25	4.16	.16	3.86	.14	3.42	.10
575 m.	4.25		3.88		3.44	
β-Naphthylamine (0–0.027)						
D-line	0.89					
1.28	2.42	1.02	2.44	1.08	2.50	1.10
3.30	3.40	1.50	3.58	1.34	3.84	1.22
10	4.82	0.90	4.54	0.68	4.45	0.45
25	5.18	0.42	4.86	0.30	4.52	0.20
575 m.	5.25		4.84		4.50	
Aniline[a] (0–0.050)						
D-line	0.32[b]					
1.24	2.42	1.18	2.70	0.99	2.50	0.84
3.22	3.28	0.75	3.07	0.55	2.77	0.44
575 m.	3.72		3.37		3.04	
p-Toluidine[a] (0–0.057)						
1.24	1.98	0.56	1.97	0.47		
3.22	2.35	0.49	2.25	0.37		
575 m.	2.83		2.58			

[a] Measured by Dr. K. Fish. [b] H. Kramer, Z. Naturforsch., **15a**, 66 (1960).

TABLE II

DISTRIBUTION PARAMETERS, RELAXATION TIMES $(10^{-12}$ SEC.) AND THE CONTRIBUTIONS BY THE INTRAMOLECULAR PROCESS FOR THE PRIMARY AROMATIC AMINES AND DIAMINES IN BENZENE SOLUTION

Temp., °C.	α	a_∞	τ_0	τ_1	C_2
Benzidine					
20	0.00	1.30	1.61		
40	.00	1.30	1.49		
60	.00	1.30	1.38		
N,N,N',N'-Tetramethylbenzidine					
20	0.00	1.40	2.17		
40	.00	1.40	1.95		
60	.00	1.40	1.82		
α-Naphthylamine					
20	0.28	1.18	11.8	16.6	0.37
40	.26	1.19	10.0	13.3	.43
60	.25	1.21	8.3	10.5	.37
β-Naphthylamine					
20	0.08	1.88	16.6	19.1	0.30
40	.05	1.84	13.4	15.9	.30
60	.02	1.90	11.0	13.1	.30
Aniline					
20	0.13	0.80	4.3	8.0	0.4
40	.11	.87	2.6		
60	.09	.88	2.4		
p-Toluidine					
20	0.22	1.20	7.4	13.8	0.6
40	0.20	1.26	4.2		

TABLE III

DIELECTRIC CONSTANTS AND LOSSES, DISTRIBUTION PARAMETERS AND RELAXATION TIMES $(10^{-12}$ SEC.) FOR PURE LIQUID ANILINE[a] AND N,N-DIMETHYLANILINE[a]

Temp., °C.	α	ϵ_∞	λ (cm.)	ϵ'	ϵ''	τ_0
Aniline						
20	0.14	3.50				19.1
			1.24	4.12	1.03	
			3.22	5.13	1.40	
			575 m.	7.00		
40	.10	3.50				12.6
			1.24	4.36	1.17	
			3.22	5.40	1.29	
			575 m.	6.59		
60	.04	3.50				8.0
			1.24	4.55	1.22	
			3.22	5.56	1.05	
			575 m.	6.14		
N,N-Dimethylaniline						
20	.02	2.87				25.7
			1.24	3.01	0.50	
			3.22	3.53	0.95	
			575 m.	4.96		
40	.01	2.87				20.6
			1.24	3.04	0.54	
			3.22	3.64	0.92	
			575 m.	4.74		
60	.00	2.79				15.3
			1.24	3.06	0.64	
			3.22	3.77	0.89	
			575 m.	4.54		

[a] Measured by Dr. K. Fish.

TABLE IV

SLOPES OF DIELECTRIC CONSTANT AND LOSS FOR THE SECONDARY AROMATIC AMINES

λ (cm.)	-20°		-40°		-60°	
	a'	a''	a'	a''	a'	a''
Diphenylamine (0–0.039 in benzene)						
d-line	0.83					
1.29	1.60	0.29	1.65	0.26	1.69	0.24
3.15	2.03	.42	2.02	.35	2.00	.27
10	2.38	.22	2.29	.19	2.18	.12
575 m.	2.49		2.35		2.23	
Diphenylamine (0–0.033 in Nujol)						
d-line	0.37					
1.29	.66	0.05	0.68	0.05		
3.17	.73	.08	.735	.09		
10	.82	.125	.855	.10		
25	.93	.11	.915	.09		
50	.98	.08	.945	.05		
575 m.	1.02		.965			
N-Phenyl-2-naphthylamine (0–0.016 in decalin)						
d-line			0.81			
1.20			1.14	0.14	1.11	0.105
3.22			1.32	.23	1.26	.195
10			1.51	.225	1.45	.195
25			1.64	.17	1.54	.11
50			1.69	.09	1.56	.06
575 m.			1.71		1.57	
N-Phenyl-2-naphthylamine (0–0.018 in benzene)						
d-line	1.49					
1.20	2.43	0.18	2.44	0.22	2.44	0.255
3.22	2.67	.41	2.70	.40	2.74	.38
10	3.07	.45	3.05	.35	3.03	.19
25	3.34	.29	3.24	.18	3.07	.11
50	3.44	.20	3.27	.08	3.09	.035
575 m.	3.49		3.28		3.08	
N-Phenyl-1-naphthylamine (0–0.018 in decalin)						
d-line	0.79					
1.27	1.10	0.13	1.07	0.12	1.045	0.13
3.30	1.26	.17	1.30	.145	1.285	.14
10	1.42	.14	1.39	.14	1.375	.13
25	1.52	.10	1.48	.08	1.46	.065
50	1.55	.05	1.52	.04	1.48	.03
575 m.	1.57		1.54		1.49	
N-Phenyl-1-naphthylamine (0–0.018 in benzene)						
d-line	1.40					
1.27	1.84	0.29	1.90	0.32	1.99	0.35
3.30	2.30	.42	2.40	.36	2.42	.31
10	2.80	.16	2.72	.15	2.65	.11
25	2.85	.12	2.80	.08	2.69	.05
575 m.	2.89		2.81		2.70	

TABLE V

DISTRIBUTION PARAMETERS, RELAXATION TIMES (10^{-12} SEC.) AND CONTRIBUTIONS BY THE INTRAMOLECULAR PROCESS FOR THE SECONDARY AROMATIC AMINES

Temp., °C.	α	a_∞	τ_0	τ_1	τ_2	C_2
Diphenylamine (in benzene)						
20	0.15	1.41	13.5	22.9	5.0	0.48
40	.14	1.45	12.0	20.0	4.8	.49
60	.12	1.50	10.2	16.6	4.6	.53
Diphenylamine (in Nujol)						
20	0.19	0.65	51.0	159	14.4	0.41
40	0.17	0.66	33.1	93	13.8	0.40
N-Phenyl-2-naphthylamine (in decalin)						
40	0.19	1.05	29.0	54	15.0	0.44
60	0.08	1.07	24.9	38	13.8	0.42
N-Phenyl-2-naphthylamine (in benzene)						
20	0.14	2.36	23.1	56	15.8	0.45
40	.07	2.35	17.3	38	14.8	.46
60	.00	2.35	13.1	20	13.8	.48
N-Phenyl-1-naphthylamine (in decalin)						
20	0.37	0.92	20.8	60	13.2	0.56
40	.36	.93	17.5	48	12.0	.48
60	.36	.94	14.5	36	10.7	.47
N-Phenyl-1-naphthylamine (in benzene)						
20	0.22	1.64	15.1	42	12.6	0.56
40	.22	1.64	12.6	31	11.2	.44
60	.22	1.64	10.0	19	10.0	.54

relaxation due to molecular rotation arising from a mesomeric shift of charge, such as seems possible in p-dimethoxybenzene, must be of negligible importance. Consequently, the relaxation time values obtained for benzidine may be taken as a good approximation to the relaxation times of the NH_2 group. The slightly higher relaxation times obtained for N,N,N',N'-tetramethylbenzidine are as would be expected for the larger $N(CH_3)_2$ group. The extremely small size of the relaxation times for these two compounds further indicates that there can be little double-bond character or stiffening of the C–N bond by π-orbital overlap in these molecules, since this would hinder the amino-group rotation and cause an increase in relaxation time.

The relaxation times obtained for α and β-naphthylamine in benzene are lower than those observed for analogous rigid molecules, in particular that of α-nitronaphthalene[14] in benzene solution, 22.8 × 10^{-12} sec. at 20°. Large differences between a_∞ and a_D are noted for both compounds. These differences and the low values of τ_0 indicate a second dispersion region at higher frequencies, presumably, due to NH_2 rotation. If it is assumed that the relaxation times obtained for benzidine are characteristic of NH_2 group rotation, it is then possible to characterize the molecular rotation process and determine the relative contributions by the two relaxation processes for other primary aromatic amines. If a plot of a'' vs. log ω is made for the experimental points and a Debye absorption curve corresponding to the relaxation time of the NH_2 group is calculated, then subtraction of the latter

Discussion of Results

Primary Aromatic Amines and Diamines.— From Table II it can be seen that the relaxation times obtained for benzidine, or 4,4'-diaminobiphenyl, are close to the approximate upper limit 1.5 × 10^{-12} previously obtained[3] for benzidine and p-phenylenediamine at 23° from measurement at one wave length, 4.3 m. Since the fixed dipole moment components of the NH_2 groups are equal and oppositely directed along the major axis of the molecule, dielectric relaxation should occur entirely by internal rotation. These observed relaxation times are so low that any contribution to dielectric

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

from the former will yield the absorption curve for molecular rotation. The molecular relaxation time is obtained by determining the frequency corresponding to the maximum of the molecular absorption curve. This procedure has been carried out for α-naphthylamine, β-naphthylamine, p-toluidine and aniline. A comparison of the τ_1 values obtained in this manner with approximate relaxation times obtained for halonaphthalene and halobenzene compounds under similar solvent and temperature conditions indicates the accuracy of the method. At 23°, in benzene solution α-chloronaphthalene[3] has a relaxation time of approximately 15.7×10^{-12} sec. and α-bromonaphthalene,[15] a value of approximately 17.7×10^{-12} sec.,[12] which are close to the τ_1 value obtained for α-naphthylamine at 20°. As observed, the τ_1 values of β-naphthylamine should be larger than those obtained for α-naphthylamine due to the greater length of the molecule of the former.

Values of 7.5×10^{-12} sec. at 19° and 8.3×10^{-12} sec. at 20° have been found for the relaxation time of chlorobenzene[16,17] in benzene solution, which are close to the value 8.0 of τ_1 at 20° for aniline in Table II. The larger τ_1 value obtained for p-toluidine is due to the increased size and elongation of the p-toluidine molecule. The increase in C_2 for p-toluidine as compared to aniline can be explained by considering the moment components of the two molecules. Since the CH_3 bond moment is directed in an opposite direction to the component of the NH_2 group along the major axis, the resulting moment m_1 for over-all rotation will be smaller in the case of p-toluidine. The dipole moment components for NH_2 group rotation m_2 are equal for these two compounds. Since it follows from the theory of Budó[18] that $C_1/C_2 = (m_1/m_2)^2$, the C_1 of p-toluidine must be less than that of aniline. The C_2 values of α-naphthylamine are slightly larger than those of β-naphthylamine, a difference which could arise from the somewhat larger fixed moment of the β-compound, which would cause a smaller C_2. The C_2 values obtained for α-naphthylamine are close to that obtained for aniline, as would be expected in the absence of any significant steric repulsion.

The relaxation time obtained for pure aniline at 20° is approximately twice as large as a previously reported value,[15] 9.8×10^{-12} sec., which was calculated from a measurement at a very low frequency. In view of the hydrogen bonding and the large viscosity of aniline, 4.47 centipoises, a relaxation time larger than 9.8×10^{-12} sec. would be expected. It appears that the results in Table III for pure aniline should be more accurate than the earlier measurement, since they were obtained at frequencies near to the maximum dielectric absorption. The relaxation times obtained for pure N,N-dimethylaniline agree well with the value 24.5×10^{-12} sec. reported for a 30° measurement[19] at much lower frequencies, 500 to 820 Mc.

Effective relaxation times of 5.8×10^{-12} and 13.7×10^{-12} sec. have been obtained[6] for aniline and N,N-dimethylaniline, respectively, in benzene at 20°, the former value somewhat higher than that for τ_0 in Table II. Since the viscosity of aniline is 6 to 7 times that of benzene and that of N,N-dimethylaniline is about twice that of benzene, the relaxation times should obviously be lower in the solution. Moreover, rotation in pure liquid aniline is hindered by hydrogen bonding. The larger size of the $N(CH_3)_2$ group gives rise to larger values for τ_1 and τ_2.

Secondary Aromatic Amines.—Measurements on the secondary aromatic amines were extended to a medium more viscous than benzene in an effort to study the effect of viscosity on the relaxation mechanism. Since the N-phenylnaphthylamines were not soluble in Nujol, they were instead measured in decalin, which has a viscosity of 2.61 centipoises at 20°, as compared to 0.65 for benzene. Values for τ_1, τ_2, C_1 and C_2 have been calculated by the method of Bergmann, Roberti and Smyth,[20] except for the case of diphenylamine in Nujol, for which the calculations were made by means of equations modified to take account of the distribution of the molecular relaxation time.[21]

The most probable relaxation times for these three compounds in the different solvents are lower than would be expected for rigid molecules of the sizes and shapes involved. Comparison of the relaxation times of N-phenyl-1-naphthylamine in decalin with those of the not wholly rigid 1-ethoxynaphthalene[20] in decalin indicates the extent of this lowering of the τ_0 values. At 40° 1-ethoxynaphthalene has a relaxation time of 75.4×10^{-12} sec., whereas N-phenyl-1-naphthylamine has a value 17.5×10^{-12} sec., indicating that an intramolecular mechanism is important in the latter compound. There is a slight decrease of τ_0 for N-phenyl-1-naphthylamine as compared to the 2-substituted compound. This is quite different from the results obtained previously for the ethoxynaphthalenes[20] where, in decalin at 20°, τ_0 decreased from 105×10^{-12} sec. for 1-ethoxynaphthalene to 55.2×10^{-12} sec. for 2-ethoxynaphthalene. The large difference for these compounds is due to the larger contribution by the internal rotation process in the case of the β-substituted compound, since in the α-substituted compound there is extreme hindrance to ethoxy-group rotation and thus a low contribution by this process. It would appear from the results for the N-phenylnaphthylamines that the intramolecular mechanism is of roughly equal importance in the two compounds. Internal rotation of the phenylamino group would sweep out so large a volume that the corresponding relaxation time would be not very different from that for over-all molecular rotation. In the case of N-phenyl-1-naphthylamine complete internal rotation would occur only occasionally because of steric hindrance in most of the molecular configurations, but some partial rotation of the phenylamino group could contribute to the dipole orien-

(15) E. Fischer, *Z. Physik*, **127**, 49 (1949).
(16) D. H. Whiffen and H. W. Thompson, *Trans. Faraday Soc.*, **42A**, 114 (1946).
(17) D. H. Whiffen, *ibid.*, **46**, 130 (1950).
(18) A. Budó, *Physik. Z.*, **39**, 706 (1938).
(19) B. L. Narayana, *J. Sci. Ind. Research (India)*, **17B**, 173 (1958).

(20) K. Bergmann, D. M. Roberti and C. P. Smyth, *J. Phys. Chem.*, **64**, 665 (1960).
(21) E. L. Grubb and C. P. Smyth, *J. Am. Chem. Soc.*, **83**, 4873 (1961).

tation. Similar considerations apply to the rotational orientation of the naphthylamino group, but the relaxation time for this group orientation should be as large or larger than that of the molecule as a whole.

The value of τ_0, 13.5×10^{-12}, obtained for diphenylamine in benzene solution at 20° agrees well with the value 12.9 obtained by Kramer[6] but is much higher than the value 6.0 at 25° obtained by Schneider[3] in high-frequency measurements by a comparison method. The low value obtained for τ_2 and its much smaller dependence on temperature and viscosity than that shown by τ_1 show it to be associated with an intramolecular relaxation mechanism and consistent with the previously suggested[22] mechanism of dipole orientation by the change in direction of the π-electron or mesomeric moment accompanying rotation of the rings around their C–N bonds. The rotation of the naphthyl groups should give rise to larger intramolecular relaxation times for the N-phenylnaphthylamines. The τ_2 values obtained for the N-phenylnaphthylamines are two to three times larger than those obtained for diphenylamine. There should actually be two different values for the intramolecular relaxation time by this mechanism, one characteristic of the rotation of the phenyl group and the other characteristic of the rotation of the naphthyl group. However, the number of points on the dispersion curves is insufficient to permit the resolution of these two processes into separate relaxation times. Within the error of the analysis, the τ_2 values obtained for the two N-phenylnaphthylamines are equal, and the same is approximately true of the C_2 values.

By comparison with results for rigid molecules, the values obtained for τ_1 for these compounds appear to be of the expected size. For example, it is expected that the τ_1 values of diphenylamine would be of approximately the same size as the relaxation times obtained for benzophenone, since the two molecules are of approximately similar size and shape. A comparison of the value of τ_1 for diphenylamine in benzene at 20°, 22.9×10^{-12} sec., with the approximate value obtained by

(22) K. Higasi and C. P. Smyth, J .Am. Chem. Soc., 82, 4759 (1960).

Fischer[3] for benzophenone in benzene at 23°, 20.4×10^{-12} sec., confirms this expectation.

Conclusions.—The very short relaxation time of benzidine, or 4,4'-diaminobiphenyl, shows that the dielectric relaxation process consists almost wholly, if not entirely, of the rotation of the NH_2 groups around their C–N bonds. A similar mechanism, the rotation of the $N(CH_3)_2$ groups about their bonds to the rings, is clearly indicated by the somewhat larger relaxation times found for N,N,-N',N'-tetramethylbenzidine. For the four primary aromatic monoamines investigated, the larger relaxation times show large contributions from molecular orientation, but the results indicate contributions of 30 to 60% from the rotational orientation of the amino group within the molecule.

For diphenylamine, two relaxation processes seem to contribute almost equally, a molecular rotation process which is dependent on viscosity to the extent that the molecular relaxation times are increased 4- to 7-fold by the 325-fold increase in viscosity from benzene to Nujol and an intramolecular process which is about half as much influenced by viscosity. The molecular relaxation time has about the value to be expected of a molecule of its size and shape, while the intramolecular relaxation time is consistent with a previous suggestion[22] that orientation occurs by change in direction of the mesomeric moment produced by rotation of the rings around their C–N bonds.

The over-all molecular relaxation times calculated for the phenylnaphthylamines are of the right magnitude for molecules of their sizes and shapes, the longer molecule of N-phenyl-2-naphthylamine having the larger relaxation time. The molecular relaxation times in decalin, which has four times the viscosity of benzene, are from 50 to 100% greater than those in benzene. Any effect of the four-fold increase in viscosity upon the intramolecular relaxation time is within the uncertainty of the values, which are about three times as large as those of diphenylamine in benzene because they include contributions from both naphthyl and phenyl rotations.