Intramolecular Dipole Reorientation of Amino Compounds and their Interaction with Solvent Molecules II

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The dielectric absorption of dilute solutions of chlorocyclohexane, cyclohexylamine, dicyclohexylamine, diphenylamine, N-methyldiphenylamine, and triphenylamine in various solvents has been measured between 0.3 and 135 GHz. The measurements have been carried out at 20 °C and for some solutions also at −30 and 60 °C. The previous measurements made for the compounds have been extended to higher frequencies and improved by a greater number of frequencies. The loss curves have been resolved into multiple absorption regions. A rather much contributing far infrared (FIR) term was necessary to be involved in each analysis. The intramolecular dipole reorientation process in cyclohexylamine is considerably slower than in aniline because of the lack of the mesomeric interaction. In dicyclohexylamine only the overall relaxation was observed at microwave frequencies. Two large regions were resolved for N-methyldiphenylamine at microwave frequencies whilst in diphenylamine the second region likely contributes to the very large FIR region. Evidences for weak association between diphenylamine and the aromatic solvents were obtained.

In the first part of this investigation[1] indications were obtained, in accordance with previous results[2–4], that the mesomeric interaction between the lone pair electrons in the nitrogen and the π-electrons of the phenyl ring plays an important role in the intramolecular dipole reorientation process of aniline and its simple methyl and chlorine substituted derivatives. Methyl substitutions in the amino group itself change the dielectric behavior of the compound, not only through removed specific solvent interactions, but also through intramolecular interactions.

To gain further information on these phenomena amino compounds in which two or three phenyl rings take part in the mesomeric interaction as well as molecules with one or two cyclohexyl rings have been investigated in this part of the research. The improved instrumental facilities allow to extend the previous measurements made for the compounds[2–4] to higher frequencies and to make more accurate measurements at a higher number of freqencies over the absorption bands. Thus more detailed analyses can be obtained from the experimental data. Especially the so called far infrared (FIR) absorption, is considered, the significance of which was pointed out by KLAGES and KRAUSS[5]. The solvent dependence of the relaxation processes[2] is reinvestigated using aromatic and aliphatic solvents with varying viscosities. The previously reported dielectric data of the compounds are completed by measurements at different temperatures.

The experimental methods and the basis of the analyses have been described in the first part of this investigation [1].

Results and Analyses

a) Cyclohexylamine and Chlorocyclohexane

Solutions of rigid *chlorocyclohexane* were measured to obtain reference parameters for the analyses of the loss curves of cyclohexylamine. The relaxation parameters are given in Table 1. The overall relaxation times in heptane, benzene, and decalin solutions are slightly longer than the ones obtained by KREUTER [6]

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[1] J. K. ELORANTA, Z. Naturforsch. **27a**, 1652 [1972].
[2] H. KRAMER, Z. Naturforsch. **15a**, 66 [1960].
[3] G. KLAGES and P. KNOBLOCH, Z. Naturforsch. **20a**, 580 [1965].
[4] P. KNOBLOCH, Ber. Bunsenges. phys. Chem. **69**, 296 [1965].
[5] G. KLAGES and G. KAUSS, Z. Naturforsch. **26a**, 1272 [1971].
[6] K. KREUTER, Z. Naturforsch. **23a**, 1728 [1968].

because of the FIR contribution not considered by him. The part of the FIR contribution approximated by a Debye curve has a time constant around 1 ps and corresponds to a dipole moment of 0.7 ± 0.1 D. The respective parameters obtained for chlorobenzene are 1.5 ps and 0.44 D [5]. The total dipole moment of chlorobenzene, 1.58 D, is also smaller than the dipole moment of chlorocyclohexane, 2.18 D. It is to note that the experimental dielectric data of chlorocyclohexane can be represented much closer in terms of the chosen component curves than the data of any other molecule in this work. This is seen in the small G_4 values in Table 1.

Tab. 1. Dielectric parameters of dilute solutions of chlorocyclohexane and cycloheylamine. The relaxation times are all in picoseconds. The given dipole moments have been calculated from the benzene solution data.

Solvent	t(°C)	$\Delta\varepsilon_0/x$	$\Delta n_D^2/x$	τ_1	p_1	G_1	τ_2	G_2	τ_3	G_3	G_4
Chlorocyclohexane, μ = 2.18 D											
Heptane	20	3.76	0.21	5.6	0	0.90			0.8	0.10	—
Benzene	20	6.58	−0.17	9.5	0	0.90			0.7	0.08	0.02
Mesitylene	20	4.08	−0.11	11.6	0.7	0.83			0.7	0.13	0.04
	−30	4.96		27	1.0	0.91			1.5	0.09	—
Decalin	20	3.55	−0.05	11.4	1.0	0.86			1.0	0.11	0.03
Cyclohexylamine, μ = 1.34 D											
Heptane	20	1.37	0.20	$5_{.5}$	0	0.24	1.8	0.61	1.0	0.10	0.05
	−30	1.72		$8_{.5}$	1.5	0.22	4.5	0.57	1.5	0.09	0.12
Benzene	20	2.44	−0.12	$9_{.5}$	1.5	0.35	3.5	0.44	0.7	0.13	0.08
Mesitylene	60	1.12		6	0	0.30	2.2	0.38	0.7	0.23	0.09
	20	1.46	−0.11	$11_{.5}$	1.5	0.29	3.5	0.37	1.2	0.22	0.11
	−30	2.21		45	2	0.30	9	0.38	2.0	0.18	0.13

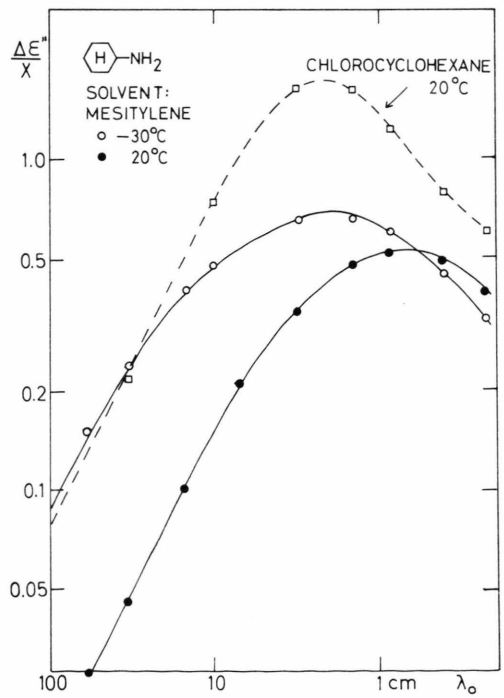

Fig. 1. Mesitylene solution of cyclohexylamine at −30 and 20 °C and of chlorocyclohexane at 20 °C.

The loss curves of *cyclohexylamine* in each solvent have their maxima at much higher frequencies than the respective curves of chlorocyclohexane (Figure1). Also they are rather broad. These features are in agreement with Kramer's finding that the absorption band consists of the overall and group relaxation regions with approximately equal weights. When analyzing our loss curves the overall relaxation times τ_1 as well as the FIR time constants τ_3 of chlorocyclohexane were transferred into the computation. This gave rather good fits to the measured losses after slight modifications of τ_3. However, the overall relaxation time of chlorocyclohexane obtained in mesitylene solution at −30 °C is too short for cyclohexylamine (Table 1). The loss curve of decalin solution could not be measured reliably at low frequencies. Nevertheless, the intermediate and high frequency losses were well reproducable in repeated measurements and τ_2 = 4.3 ps was estimated from these data. Similar difficulties were met with heptane solutions especially at −30 °C but not with the aromatic solvents.

An essential feature in the results of the analyses is the temperature dependence of the distribution p_1 of the overall relaxation times. The second relaxation region is in each case approximated by a Debye term,

however, it could have a temperature dependent distribution of relaxation times as well. When this is not considered it may be partly reflected in p_1. The temperature dependence of p_1 in mesitylene solution may indicate an association between solute and solvent molecules but p_1 seems to be temperature dependent also in heptane solution. The idea of association is in agreement with the longer overall relaxation time of cyclohexylamine compared to chlorocyclohexane at −30 °C and with the smaller ratio G_1/G_2 in heptane than in the aromatic solvents [2].

In each solvent the group relaxation times τ_2 are about three times longer in cyclohexylamine than in aniline. Also they seem to increase along with the viscosity of the solvent unlike in aniline. Moreover, in cyclohexylamine the group relaxation region contributes much more to the total dielectric absorption.

b) Dicyclohexylamine, Diphenylamine, and N-Methyldiphenylamine

The dielectric loss curves of *dicyclohexylamine* are illustrated in Figure 2. They are rather symmetric for aromatic solvents but distinctly broader than a Debye curve. For aliphatic solvents the high frequency slope is smaller. The analyses of the curves were made in terms of a Fröhlich curve at low frequencies and a Debye curve at high frequencies (Table 2). The differences in the slopes result in a lower contribution of the Debye term for aromatic solvents.

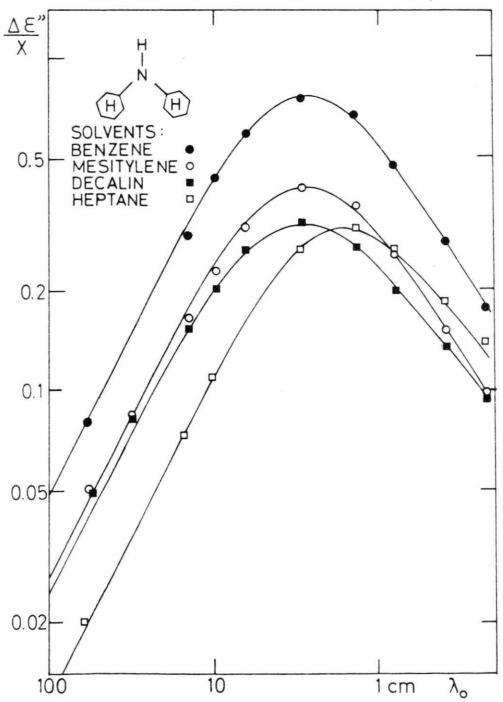

Fig. 2. Benzene, mesitylene, decalin, and heptane solutions of dicyclohexylamine at 20 °C.

The obtained overall relaxation time τ_1 in benzene solution is shorter than reported previously [2, 4], whilst the weight factors agree very well. This is due to the distribution of the relaxation times, $p_1 = 1.3$, adopted in the present analysis. The distribution is observed in each solvent and it increases along with viscosity consistently with the data of related rigid molecules [6]. Thus it rather indicates a real distribution of the overall relaxation times than overlapping discrete absorption regions.

The dipole moment components calculated from the weight factors $G_3 + G_4$ are 0.45 and 0.30 D in the aliphatic and aromatic solvents, respectively. Their order of magnitude as well as the solvent dependence are typical of the FIR processes obtained in the first part of this work. The region is attributed to the FIR process since no second Debye term was needed to obtain a good fit to the experimental dielectric data. This shows that the molecule is almost rigid which is in agreement with the conclusion drawn by KNOBLOCH [4] from consistent dielectric data [2].

The semilogarithmic loss curves of *diphenylamine* in all the four solvents are illustrated in Fig. 3. The quantities $\Delta\varepsilon''/x$ were normalized with the respective dielectric increment $S/x = \Delta\varepsilon_o/x - n^2_D/x$ in each solvent. In the semilogarithmic representation superimposed curves are directly additive and one can easily see the solvent dependence of the loss curves. The maximum normalized losses are about 0.33 and 0.25 in the aromatic and aliphatic solvents, respectively. For a single Debye process it would be 0.50. This together with the shapes of the double logarithmic curves (Figs. 4 and 5) indicates that a large part of the whole absorption must lie beyond the range of the measurements.

In analyzing the loss curves the dielectric increment, calculated from the absorption bands, always tends to be considerably less than the expected increment S/x. GRUBB and SMYTH [7] reported the relaxation times 22.9 and 5.0 ps with $G_2 = 0.48$ for two Debye terms in dilute benzene solution at 20 °C. They assumed a high

[7] E. L. GRUBB and C. P. SMYTH, J. Amer. Chem. Soc. 83, 4879 [1961].

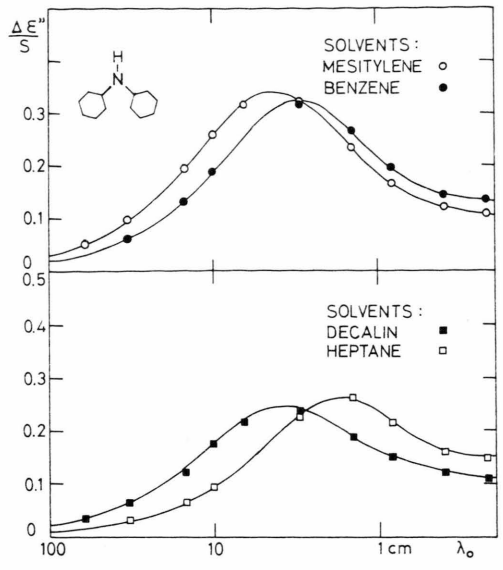

Fig. 3. Mesitylene, benzene, decalin, and heptane solutions of diphenylamine at 20 °C.

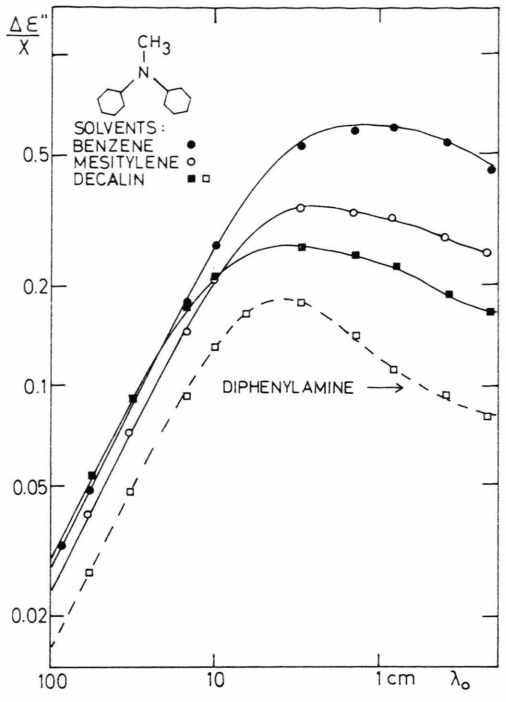

Fig. 4. Benzene, mesitylene, and decalin solutions of N-methyldiphenylamine and decalin solution of diphenylamine at 20 °C.

atomic polarization. Kramer reports the "formal" relaxation times 22 and 0.7 ps with $G_2 = 0.42$. Our new measurements at millimeter waves show that there can be no relaxation around 5 ps with such a high weight factor as 0.48. Also the weight factor 0.42 for a possible Debye term at 0.7 ps is too high.

The double logarithmic loss curves indicate that in any of the four solvents the overall relaxation times of diphenylamine cannot be much distributed. This is obvious from the low temperature curve (Fig. 5) in which the main absorption is least overlapped by high frequency absorptions and the distribution of the relaxation times can be expected to be at a maximum. The unusually large scatter of the measured losses in the curve is due to the precipitation of the solute at the low temperature which compelled to use very low concentrations. The reliability of the measurements was improved by an increased number of solutions used for the measurements. The numerous attempts to analyze the experimental data in terms of two or three regions indicated that only two are needed in the aromatic solvents whereas in decalin three regions are necessary. The results are given in Table 2. The high frequency wing of the heptane solution could be represented with one Debye term as well. The two close lying terms were, however, introduced to obtain consistent weight factors with decalin solutions.

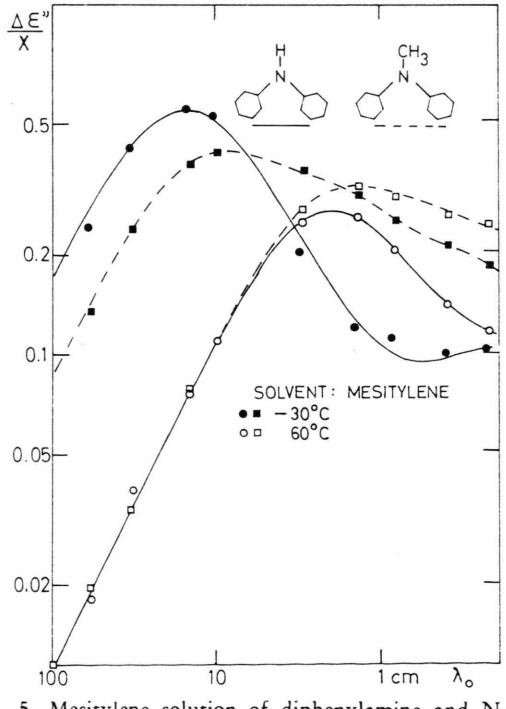

Fig. 5. Mesitylene solution of diphenylamine and N-methyldiphenylamine at −30 and 60 °C.

Figures 4 and 5 illustrate the drastical change in the shape of the loss curves when passed from diphenylamine to *N-methyldiphenylamine*. In each solvent the curves rise appreciably on the high frequency side thus being in agreement with Knobloch's result that there is another strong region besides the overall relaxation region. When our data for the benzene solution were compared with the loss curve given by him [4] his loss values at 3.0 and 0.8 cm wavelengths are shown to exceed our values and the difference is largest at 0.8 cm. This together with our measurements at 0.4 and 0.2 cm wavelengths indicates that Knobloch's extrapolated second region is too high. On the other hand there are indications that in benzene solution the overall relaxation region might be relatively smaller than in the other solvents: Excellent fits to the experimental losses were obtained with the dielectric parameters given in Tab. 2 in all the other solvents but benzene (see Figs. 4 and 5). When the consistent weight factors were constrained into the analysis of the data of benzene solution a satisfactory fit was obtained only with a relatively large distribution parameter $p_1 = 1.5$. The source of the bad fit may also be found in an improper approximation of the FIR region. The experimental data were checked with repeated measurements.

It is known from spectroscopic evidences [8] that diphenylamine enters into hydrogen bonded complexes with aromatic solvents. This is also seen in the longer overall relaxation times of diphenylamine in the aromatic solvents compared to the ones of N-methyldiphenylamine. The hydrogen bond formation can also explain the depressed fast reorientation region of diphenylamine in the aromatic solvents seen in Fig. 3 and in Tab. 2 as decreased values of $1-G_1$.

The ratios G_2/G_1 of diphenylamine and N-methyldiphenylamine in decalin are 9/48 and 26/48, respectively. This indicates that the contribution of the intramolecular dipole reorientation of diphenylamine could be smaller. On the other hand one must bear in mind that the G_1's of both compounds are equal. This means that a great deal of the internal dipole reorientation of diphenylamine may contribute to the exceptionally large FIR region obtained. The combined weight factors $G_3 + G_4$ correspond to the dipole moments 0.56 and 0.70 D in the aromatic and aliphatic

Tab. 2. Dielectric parameters of dilute solutions of dicyclohexylamine, diphenylamine, and N-methyldiphenylamine. The relaxation times are all in picoseconds. The given dipole moments have been calculated from the benzene solution data.

Solvent	t(°C)	$\Delta\varepsilon_0/x$	$\Delta n_D^2/x$	τ_1	p_1	G_1	τ_2	G_2	τ_3	G_3	G_4
Dicyclohexylamine, μ = 1.10 D											
Heptane	20	1.01	0.27	9.3	1.0	0.81			1.5	0.16	0.03
Benzene	20	1.66	−0.05	14.8	1.3	0.94			1.5	0.05	0.01
Mesitylene	20	0.89	−0.04	15.1	1.5	0.93			1.5	0.05	0.02
Decalin	20	0.83	0.03	15.9	1.8	0.86			1.5	0.09	0.05
Diphenylamine, μ = 1.06 D											
Heptane	20	1.52	0.76	9.7	0.7	0.50	0.6	0.10	0.4	0.16	0.24
Benzene	20	2.44	0.84	16.5	0.7	0.63			0.8	0.19	0.18
Mesitylene	60	1.43		11	0.7	0.71			0.7	0.18	0.11
	20	1.55	0.51	24	0.7	0.67			0.9	0.15	0.18
	−30	2.04		83	0.7	0.72			1.0	0.12	0.16
Decalin	60	1.08		13	1.0	0.46	2.0	0.09	0.4	0.26	0.19
	20	1.19	0.43	22	1.0	0.48	2.5	0.09	0.4	0.15	0.28
N-Methyldiphenylamine, μ = 1.24 D											
Heptane	20	1.82	0.80	10	0	0.48	2.0	0.25	0.4	0.27	—
Benzene	20	2.90	0.72	12.5	1.5	0.46	2.5	0.25	0.5	0.20	0.09
Mesitylene	60	1.48		11	0	0.49	2.5	0.25	0.4	0.26	—
	20	1.74	0.49	19	1.0	0.47	3.3	0.24	0.5	0.26	0.03
	−30	2.05		59	1.0	0.47	9.0	0.22	1.2	0.16	0.15
Decalin	20	1.44	0.46	28	1.6	0.48	4.3	0.26	0.4	0.26	—

[8] G. C. PIMENTEL and A. L. MCCLELLAN, The Hydrogen Bond, W. H. Freeman and Co., San Francisco 1960.

solvents, respectively, which are very large compared to the total dipole moment, 1.06 D.

Some measurements of *triphenylamine* were also made. The low dipole moment of the compound, 0.6_5 D, made the measurements difficult and considerably less accurate than those of the other compounds. The obtained losses are given in Fig. 6. The curves have been drawn to connect the experimental points and not to represent any calculated curves. It should be mentioned that in the case of low dipole moments and large molecules the millimeter wave loss of the solute may not be simply the difference between the measured loss of the solution and the solvent. There is a possibility of more complicated terms due to the appreciable loss of nonpolar solvents at millimeter waves. This decreases the reliability of the high frequency data.

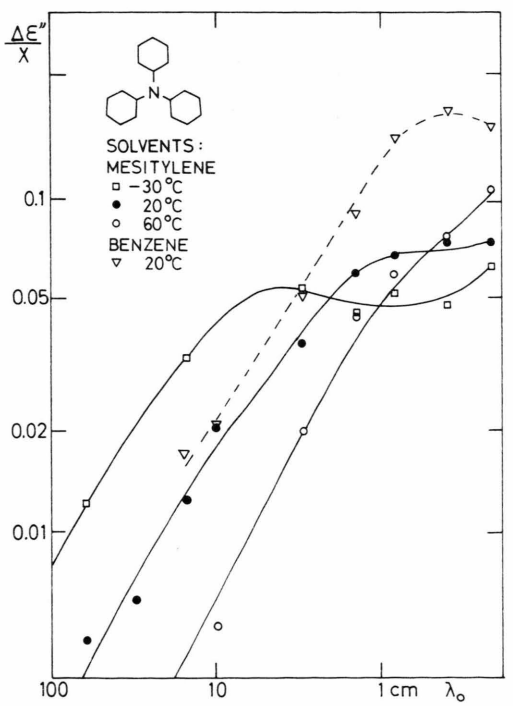

Fig. 6. Triphenylamine in mesitylen and benzene.

The previous measurements made for benzene solution of triphenylamine yielded a dielectric absorption at very high frequencies which was assigned to the inversion of the molecule [7, 9]. In our loss curves there is a small low frequency contribution in each curve. Its relaxation time is between 50 and 150 ps and the weight factor is less than 0.03 in benzene. This region may be a real overall relaxation region or caused by possible polar impurities. The measured quantities of benzene solution as well as the obtained relaxation time τ_2 = 2 ps (G_2 = 0.6) are consistent with the previous data [7]. The loss curves of mesitylene solution at various temperatures have an unusual behavior. The low and intermediate frequency losses which perhaps define the absorption region of the inversion process increase when the temperature decreases. The obtained loss values increase up to the high frequency limit of our measurements predicting another large region at our measurements predicting another large region at very high frequencies. This is also indicated by the measured dielectric increments (e. g. at 20 °C $S/x = 0.3_6$). Thus the curves in Fig. 6 illustrate only a minor part of the entire absorption and the attempts to analyze the curves would be more or less arbitrary.

Discussion

A comparison between the dielectric data of aniline [1] and cyclohexylamine shows that the mesomeric interaction decreases the relaxation time of the intramolecular dipole reorientation process. In diphenylamine τ_2 is also very short and in dicyclohexylamine it may be equal or longer than τ_1 and therefore cannot be detected by dielectric measurements.

Knobloch has found out that the dipole moment component responsible for the internal dipole reorientation process of primary aromatic amines decreases with increasing mesomeric interaction. This was verified in the first part of this investigation considering also the FIR absorption. KLAGES and KRAUSS [5] approximated the FIR regions of CH_2Cl, OCH_3, and $COCH_3$ substituted benzenes with a Debye term. In the amino compound studied in this work the FIR region is in many instances considerably larger and cannot be adequately approximated with a Debye curve alone.

The hydrogen bonding of diphenylamine with the aromatic solvents was observed primarily as increased overall relaxation times compared to the ones of N-methyldiphenylamine. This is accompanied by depressed high frequency regions in those solvents. In deca-

[9] P. KNOBLOCH and M. STOCKHAUSEN, Angew. Chem. 76, 186 [1964].

lin solution a relatively small region of the internal dipole reorientation around 2 ps was resolved but could not be found in the aromatic solvents. However, this process may contribute to the exceptionally large FIR regions obtained in all the solutions. On the other hand in N-methyldiphenylamine a large intramolecular dipole reorientation region was resolved in all the solvents employed. N-methyl substituents in aniline strongly reduce that region whilst no reduction was observed in N-methyldiphenylamine. This may indicate a different mode of intramolecular dipole reorientation in aniline and in diphenylamine. Measurements at still higher frequencies and better knowledge of the FIR processes are needed to fully understand the dielectric behavior of diphenylamine and triphenylamine.

The activation energy for free rotation [10] of chlorocyclohexane and N-methyldiphenylamine in mesitylene is 2.0 kcal/mol. Only slightly higher an energy, 2.5 kcal/mol, was obtained for cyclohexylamine and diphenylamine for which indications of a specific solvent interaction were found. The activation energies of the internal motion are between 1.5 and 2.0 kcal/mol. The solvent dependence of the relaxation times τ_2 indicates that the intramolecular dipole reorientation processes in these amino compounds are to a great extend controlled by interaction with surrounding solvent molecules.

[10] S. GLASSTONE, K. J. LAIDLER, and H. EYRING, The Theory of Rate Processes, McGraw-Hill Book Co. New York 1941.

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