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

JAAKKO K. ELORANTA *

Institut für Physik der Johannes-Gutenberg-Universität Mainz, Abteilung Mikrowellenphysik

(Z. Naturforsch. **27 a**, 1652—1662 [1972]; received 30 August 1972)

The dielectric absorption of dilute solutions of aniline, methyl substituted anilines, chlorine substituted anilines, N,N,N′,N′-tetramethyl-p-phenylene diamine and 4-aminobiphenyl in various solvents has been measured between 0.3 and 135 GHz. The measurements have been carried out at 20 °C and for some mesitylene solutions also at −30 °C and 60 °C. The absorption curves have been resolved into multiple absorption regions. A far infrared (FIR) term had to be included in each analysis. Its contribution to the total dipole reorientation depends on the solvent and on the mobility of the substituted groups in the phenyl ring. The obtained group relaxation times are longer than those reported previously and also their weight factors are smaller. Differences in the mobility of the amino group are observed in methyl substituted anilines. Methyl substituents in the amino group itself strongly reduce the mobility. The decrease in the group mobility parallels the increasing mesomeric interaction between the lone pair electrons in the nitrogen and the π-electrons of the phenyl ring. In addition to the reorientation of the amino group of 4-aminobiphenyl another internal reorientation process is found which is attributed to a mesomeric charge shift. Indications are obtained for weak association between some amino compounds and mesitylene.

The dielectric loss of meter waves[1] already indicated the nonrigid character of some amino compounds like aniline and diphenylamine. Later measurements, extended to higher frequencies, allowed to resolve two distinct relaxation regions for a great number of amines in dilute solutions of nonpolar solvents[2–6]. As a rule, the relaxation time of the high frequency process was shorter than the ones obtained for the molecular group rotations. On the basis of this and the relatively small activation energy, an ammonia-like inversion of the nitrogen bonds was proposed as a possible dipole reorientation mode for p-phenylene diamine and aniline instead of the group rotation about the C–N bond[7]. That idea was further experimentally confirmed and extended to other molecules[6] by the very short relaxation times obtained for triphenylamine[8, 9], diphenylamine, and related compounds in which other fast mechanisms are unlikely.

Corresponding high frequency regions have been resolved for the amines also in their pure liquid state[10–13] and a theoretical discussion on the multiple relaxation mechanisms of amines has been given[14].

The conclusions drawn by KRAMER[3, 4] and KNOBLOCH[6] suffer from too law a number of measured loss values especially at the high frequency region. The substantial improvement in the instrumentation in this laboratory has made it possible to extend the measurements to higher frequencies and to make more accurate measurements at more frequencies over the absorption bands. Therefore, some of the substances studied in the papers mentioned above have been reinvestigated in this work. The solvent dependence of the relaxation processes observed by KRAMER[3] has been reinvestigated using aromatic and nonaromatic solvents with varying viscosities. Also measurements at different temperatures are of great interest.

The extension of the range of the measurements also makes it possible to estimate the contribution of the so called farinfrared (FIR) absorption to the total dielectric absorption. This very high frequency absorption has been observed for a considerable number of polar molecules[15] in dilute solutions. The origin of the FIR process is not yet well understood. It has been suggested to originate from damped rotational oscillations of the permanent dipoles or from dipole moments induced by molecular collisions.

1. Experimental

All the dielectric measurements were made with dilute solutions, the mole fraction x of the solute being less than 4%. The difference $\Delta\varepsilon''$ between the dielectric

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Reprint requests to Prof. Dr. G. KLAGES, Abt. Mikrowellenphysik, Institut für Physik der Johannes-Gutenberg-Universität, *D-6500 Mainz*, Jakob-Welder-Weg 11.

* Alexander von Humboldt Fellow 1971; present address: Department of Physics, University of Oulu, SF-90100 Oulu 10, Finland.

losses of the solution and the solvent at a given frequency was measured and the increment of the loss with concentration $\Delta\varepsilon''/x$ was determined. No concentration dependence was observed for the substances investigated. The dielectric loss was measured, as a rule, at 9 or 10 frequencies ranging from 0.3 to 135 GHz (1 m – 2.2 mm). The methods of the measurements have been described elsewhere[16–18]. With all the instruments an accuracy of the measurements about 1% can be reached in favorable conditions. The practical accuracy is, however, about 2% at room temperature and somewhat less at other temperatures.

The increment of the dielectric permittivity was determined at MHz frequencies to obtain the static value $\Delta\varepsilon_0/x$ and also, for control purpose only, at some frequencies in the range from 0.3 to 3.0 GHz and at 135 GHz. The high frequency limit of the permittivity $\Delta n_D{}^2/x$ was determined from the optical refractive indices.

The substances investigated were of the purest commercial grade. Most of the liquids were destilled under reduced pressure and the solids were recrystallized. The solvents were of p.a. grade and decalin a technical mixture of trans- and cis-decalins. Four solvents were used: n-heptane, benzene, mesitylene (1,3,5-trimethylbenzene), and decalin (decahydronaphthalene). The viscosities are 0.41, 0.65, 0.85, and 2.6 cP at 20 °C, respectively.

2. Results and Analysis

The measured loss data were plotted in double logarithmic plots of $\Delta\varepsilon''/x$ against wavelength λ. This form of representation allows to compare the shapes of the curves independent of the total dielectric increment[16], which in many instances is conclusive when making decisions on the band composition.

The formal analyses of the absorption curves were made in terms of superposition of one FRÖHLICH[19] and two DEBYE[20] curves:

$$\frac{\Delta\varepsilon''}{x} = \frac{S}{x}\left[G_1 F(p_1,\tau_1) + G_2 \frac{\omega\tau_2}{1+(\omega\tau_2)^2} + G_3 \frac{\omega\tau_3}{1+(\omega\tau_3)^2} + G_4\right], \quad (1)$$

where the Fröhlich term is

$$F(p_1,\tau_1) = \frac{1}{p_1}\,\text{arc tan}\left[2\sinh\left(\frac{p_1}{2}\right)\frac{\omega\tau_1}{1+(\omega\tau_1)^2}\right].$$

S/x is the measured dielectric increment of the solute equal to $(\Delta\varepsilon_0/x) - (n_D{}^2/x)$ and the G's are the relative weight factors of the absorption regions described by the relaxation times τ_1, τ_2, and τ_3. A fourth weight factor G_4 was introduced to represent the difference between the measured dielectric increment and the one computed from the three relaxation regions so that

$$G_1 + G_2 + G_3 + G_4 = 1\,.$$

The Fröhlich parameter $p = \ln(\tau'/\tau'')$ describes the width of the even distribution of the relaxation times in a logarithmic scale between the limiting values τ' and τ''. The mean relaxation time of a Fröhlich process is $\tau = \sqrt{\tau'\,\tau''}$.

Though all the absorption regions very likely have a distribution of relaxation times, the relatively high number of adjustable parameters compelled us to assume a Fröhlich process for one region only. The FIR region, which had to be taken into account in all cases, was approximated by a high frequency Debye region together with the additional contribution G_4.

The analyses of the measured loss curves were carried out with a Hewlett-Packard calculator 9100 A equipped with a plotter 9125 A. The calculator was programmed to draw the log-log plots of the function (1). The relaxation times and the weight factors were varied until the measured curve was obtained. The method appeared to indicate sensitively even rather small changes of the parameters.

a) Aniline and Methyl Substituted Anilines

Among the substituted anilines measured in this work *p-toluidine* (p-methylaniline) is discussed first because it provides the best sight into the dielectric absorption of the internal reorientation of the anilines. The group moment of the para methyl group partly compensates the NH_2 group moment making the contribution of the overall rotation to the total dielectric absorption rather low.

The obtained dielectric parameters of p-toluidine are given in Table 1. The overall relaxation time of p-toluidine in benzene solution, τ_1, agrees well with the one reported by KRAMER[4] but he finds a slightly higher weight factor $G_1 = 0.45$. The group relaxation time $\tau_2 = 0.9$ ps given by him differs remarkably from our value 1.9 ps. The measurements, extended to higher frequencies in this work, allowed to resolve the FIR contribution which makes the obtained parameters to differ from Kramer's extrapolated values throughout the work.

The overall relaxation time τ_1 of p-toluidine in different solvents increases with the viscosity of the solvent. The group relaxation time τ_2, however, behaves in quite a different way. Figure 1 illustrates

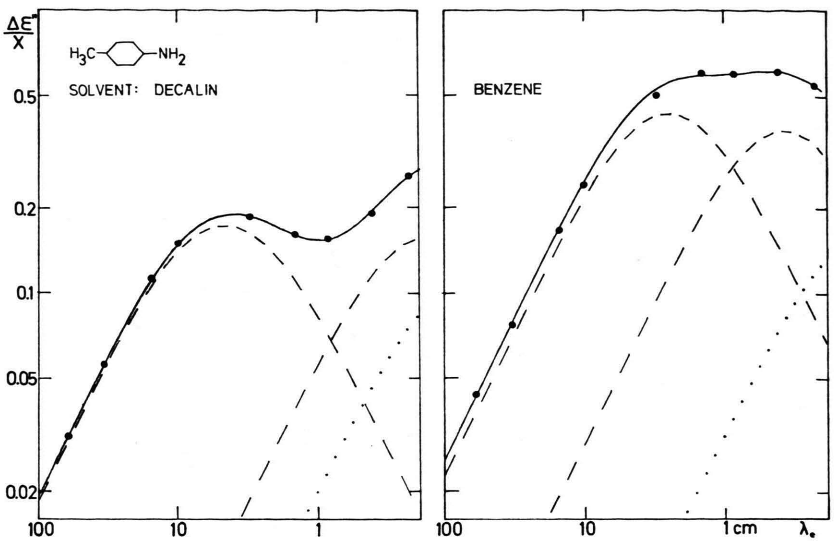

Fig. 1. Decalin and benzene solutions of p-toluidine at 20 °C. The broken curves from left to right illustrate the overall and group relaxation regions. The FIR regions have been marked with dotted curves.

the composition of the measured loss curves in the two most strikingly differing cases. In decalin solution τ_2 is substantially shorter than in benzene solution. Also the weight factor G_1 in decalin solution is distinctly smaller than in the aromatic solvents. KRAMER [3] has found similar differences in G_1 in many other primary amines. The ratio G_2/G_1 is 0.90, 0.83, and 0.42 in decalin, benzene, and mesitylene at 20 °C, respectively. At −30 °C in mesitylene the obtained ratio, 0.36, is still smaller. The considerably smaller ratio in mesitylene solution is verified by the clearly different curve shapes of benzene and mesitylene solutions (Figures 1 and 2). One could attribute the difference in the ratios to the high G_3 in mesitylene. There is, however, no way to analyze the curves according to Eq. (1) keeping the ratios equal in different solvents. The obtained FIR contributions, $G_3 + G_4$, do not show any aromatic vs. aliphatic features. They are high in decalin and in mesitylene, 0.39 – 0.43, and somewhat lower in benzene, 0.27.

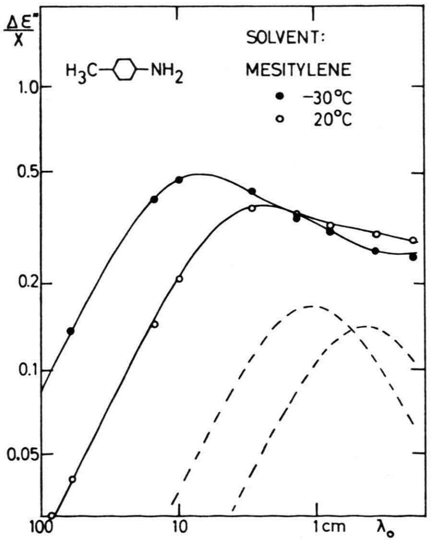

Fig. 2. Mesitylene solution of p-toluidine at −30 °C and 20 °C. The broken curves from left to right are the group relaxation contributions.

The larger molecular volume of *mesidine* (2,4,6-trimethylaniline) shifts the overall relaxation region to lower frequencies than in p-toluidine (Figures 3 and 4). The relative contribution of the group relaxation region in each solvent is smaller in mesidine. The obtained relaxation parameters given in Table 1 show that also the group relaxation times in each solvent are slightly longer than in p-toluidine. The solvent effects in τ_2 and in the weight factors discussed for p-toluidine, are also present here. The ratios G_2/G_1 are 0,43, 0.45, 0.26, and 0.15 in decalin, benzene, mesitylene at 20 °C, and in mesitylene at −30 °C, respectively. The comparison of the loss curves of benzene (Fig. 3) and mesitylene (Fig. 4) solutions again verifies the effect.

The solvent dependence of the weight factors refers to some specific interaction between the solute

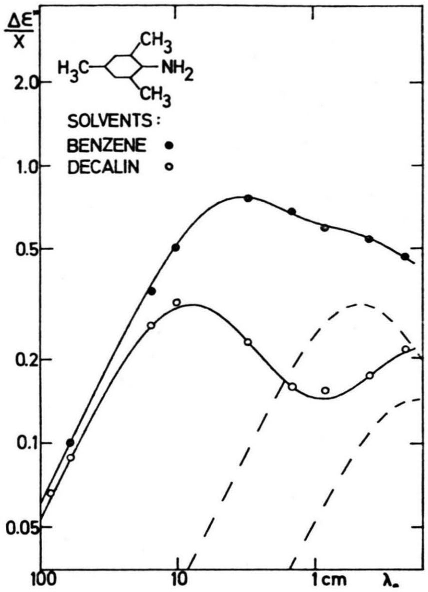

Fig. 3. Benzene and decalin solutions of mesidine at 20 °C. The broken curves from left to right are the group relaxation contributions.

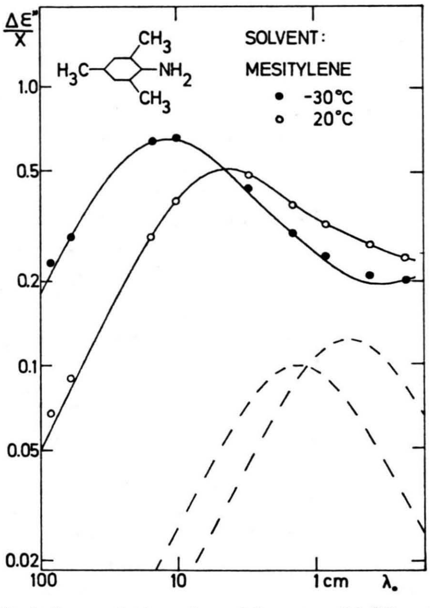

Fig. 4. Mesitylene solution of mesidine at −30 °C and 20 °C. The broken curves from left to right are the group relaxation contributions.

and mesitylene molecules. A possible mode of interaction, already proposed by KRAMER[3], is the association between the amino protons and the π-electron system of the aromatic solvents. For such an association there are both dielectric and spectroscopic evidences[21]. The strength of the association increases with the increasing basicity of the solvent[21]. Presumably, the lower basicity of benzene[22] is too low for a detectable effect in the weight factors. It is also possible that the given G_2's of decalin solutions might be too low. They cannot be determined accurately since the absorption regions of both solutes are too much beyond the range of the measurements.

It should be remarked that the ortho positioned methyl groups in mesidine do not act as a drastic steric hindrance either to the reorientation of the amino group or to the solvent interaction. The activation energies[23] for the overall rotation of p-toluidine and mesidine in mesitylene are both 2.2 kcal/mol and for the group reorientation 1.9 kcal per mol.

In *m-toluidine* and *o-toluidine* the group moment of the methyl group does not compensate the NH_2 group moment as effectively as at the para position, and the contribution of the overall rotation becomes predominant.

The obtained loss curves of the compounds are illustrated in Figure 5. The relaxation parameters are given in Table 1. The overall relaxation times τ_1 of both compounds are consistent with the values given by KRAMER[4]. The overall relaxation times of the toluidines decrease in the sequence: p-, m-, and o-toluidine. This is due to the decreasing effective

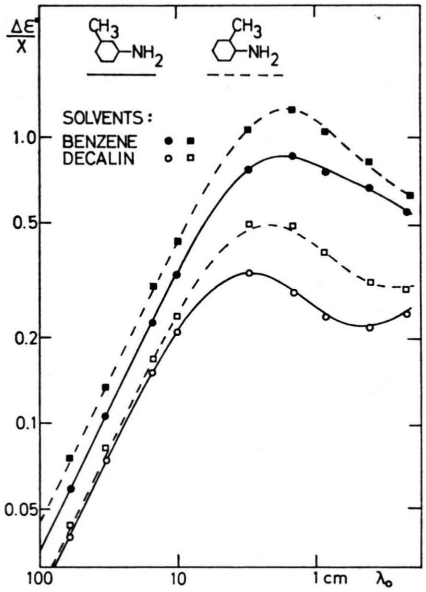

Fig. 5. Benzene and decalin solutions of m- and o-toluidine at 20 °C.

radius of the rotating unit which is also seen in the decreasing effect of the viscosity on the relaxation time when passing from p-toluidine to o-toluidine[24].

The loss curves of decalin and benzene solutions of p-toluidine, mesidine, m-toluidine, and o-toluidine (Figs. 1, 3, and 5) all have the same primary shapes illustrated in Figure 1; only the contribution of the high frequency absorption decreases in the sequence mentioned above. Thus it is evident that τ_2 is shorter in decalin than in benzene solution throughout the series of the methyl substituted anilines. Also G_1 in decalin is smaller than in benzene solution in all these compounds. A similar aliphatic vs. aromatic relation in G_1 has been observed for m- and o-toluidine in cyclohexane and p-xylene solutions[25]. Further, the FIR contribution, $G_3 + G_4$, is higher in decalin solutions of all these compounds.

Aniline, the parent molecule of the compounds discussed above, was measured in all the four solvents (Figure 6). The measurements of heptane solution allow to compare the results with the ones obtained by KRAMER[3] and to check his finding that the contribution of the overall rotation of aniline is smaller in heptane than in benzene.

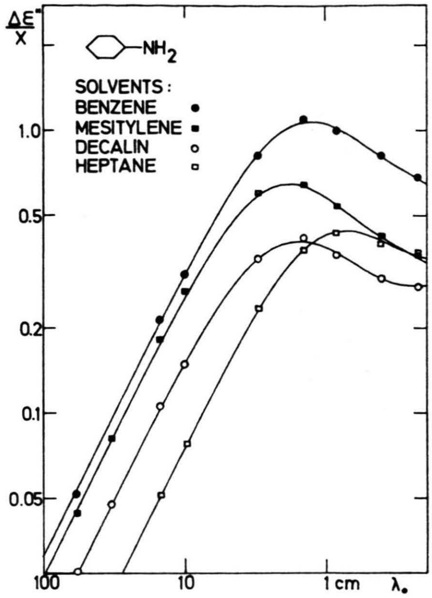

Fig. 6. Benzene, mesitylene, decalin and heptane solutions of aniline at 20 °C.

The magnitude of the dipole moment of aniline (Table 1) would locate the shape of the loss curve between those of m- and o-toluidine in each solvent

Table 1. Dielectric parameters of dilute solutions of aniline and methyl substituted anilines. 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
		p-Toluidine $\mu = 1.31$ D									
Benzene	20	2.66	0.31	13	1.0	0.40	1.9	0.33	0.5	0.13	0.14
Mesitylene	20	1.73	0.15	17	1.0	0.43	2.5	0.18	0.5	0.22	0.17
	− 30	2.22		44	1.0	0.44	6.0	0.16	0.6	0.20	0.20
Decalin	20	1.39	0.12	24	1.5	0.30	0.8	0.27	0.4	0.18	0.25
		Mesidine $\mu = 1.38$ D									
Benzene	20	2.95	0.23	21	1.0	0.51	2.5	0.23	0.5	0.14	0.12
Mesitylene	20	1.96	0.17	25	1.0	0.54	3.0	0.14	0.5	0.17	0.15
	− 30	2.43		65	1.5	0.61	7.0	0.09	0.6	0.16	0.14
Decalin	20	1.58	0.11	43	1.0	0.44	1.0	0.19	0.4	0.12	0.25
		m-Toluidine $\mu = 1.43$ D									
Benzene	20	3.20	0.27	11	1.0	0.52	1.9	0.18	0.5	0.13	0.17
Decalin	20	1.65	0.12	18	1.5	0.44	0.8	0.14	0.4	0.20	0.22
		o-Toluidine $\mu = 1.58$ D									
Benzene	20	3.86	0.31	9.5	1.0	0.69	1.5	0.07	0.5	0.14	0.10
Decalin	20	1.96	0.13	12	1.5	0.57	0.7	0.07	0.5	0.21	0.15
		Aniline $\mu = 1.51$ D									
Heptane	20	1.89	0.34	4.5	1.0	0.52	0.5	0.10	0.4	0.21	0.17
	− 30	2.30		8.6	1.0	0.52	0.8	0.10	0.6	0.17	0.22
Benzene	20	3.52	0.27	7.7	1.0	0.64	1.2	0.12	0.5	0.17	0.07
Mesitylene	60	1.84		6.2	1.0	0.61	1.0	0.11	0.4	0.18	0.10
	20	2.33	0.14	10.5	1.0	0.58	1.5	0.11	0.5	0.14	0.17
	− 30	3.03		32	1.0	0.64	3.5	0.12	0.6	0.15	0.09
Decalin	20	1.75	0.12	9.0	1.5	0.50	0.7	0.10	0.4	0.20	0.20

if equivalent reorientation processes are assumed. In fact this is indicated by a comparison of the curves when the shift of the overall relaxation region, especially in decalin solution, is considered. Consistently, also the values of the weight factors G_1 and G_2 of benzene and decalin solutions (Table 1) range between the respective values of m- and o-toluidine.

The obtained overall relaxation time in benzene solution, $\tau_1 = 7.7$ ps, is in agreement with the ones reported by KRAMER[4] and KNOBLOCH[6], 8.25 ps and 7.15 ps, respectively. Kramer reports the weight factors G_1 0.73[3] and 0.69[4] and Knobloch 0.65 which is in good agreement with our value 0.64. Kramer's G_1 value in heptane solution is 0.40 whereas it is 0.52 in this work. In the other aliphatic solvent, decalin, it can be determined more precisely and $G_1 = 0.50$ is obtained. This supports our value in heptane and shows that there is a difference between the G_1 values in heptane and benzene but it is not that large as reported by Kramer. In cyclohexane and p-xylene a similar difference has beeen observed[25].

The overall relaxation times τ_1 of the compounds in Table 1 decrease in each solvent with decreasing effective radius of the rotating unit having the smallest values in aniline. Similarly the viscosity dependence of the relaxation times decreases. In aniline it may be broken by an association of the solute with the mesitylene molecules.

The group relaxation time τ_2 in decalin solution of aniline is within the error limits equal to those obtained for the toluidines. Here the data are available also for another aliphatic solvent, heptane, at two temperatures. Though the loss curves of heptane solution can be analyzed less accurately than the curves where the absorption of the overall rotation lies at lower frequencies, they evidently do not yield any longer group relaxation time at room temperature than the low value obtained in decalin solution. In benzene and mesitylene solutions the group relaxation times of aniline are remarkably shorter than those of the toluidines but still distinctly longer than in decalin and heptane.

b) Molecules with $N(CH_3)_2$ *Group*

N,N,N′,N′-Tetramethyl-p-phenylene diamine even after repeated recrystallization formed some black sediment which had to be filtered out and consequently the concentration was no more exactly known. The measurements had to be carried through during the same day to avoid the increasing low frequency absorption. Therefore the loss curves are illustrated in the form $\Delta\varepsilon''/S$ against wavelength λ in Figure 7.

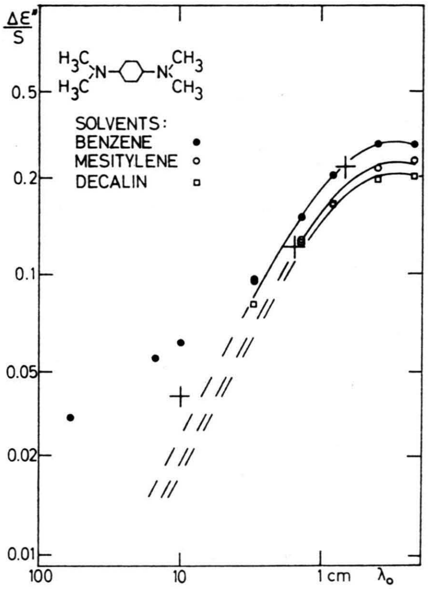

Fig. 7. Benzene, mesitylene and decalin solutions of N,N,N′,N′-tetramethyl-p-phenylene diamine at 20 °C. The points marked with the crosses are from Reference[6].

The obtained dielectric parameters are given in Table 2. Due to the impurities and the low dipole moment of the compound the loss values are not accurate enough for any detailed analyses. The measured losses are in good agreement with the ones measured by KNOBLOCH[6] which have been marked with crosses in Figure 7. The obtained dipole moment is consistent within the error limits, ± 0.05 D, with the value given by Knobloch but is smaller than the other literature values[26]. The new measurements at mm-waves show that the absorption curve does not reach $\Delta\varepsilon''/S = 0.47$ predicted by Knobloch when determining the relaxation time 1 ps of a Debye process. The loss curves are much broader corresponding to a Fröhlich curve with a distribution parameter $p \approx 2$. If the broadness of the curves originate from strongly overlapping FIR absorptions the given mean relaxation times represent the low limit of the relaxation times τ_2. The relaxation region obviously corresponds to the reorientation of the $N(CH_3)_2$ groups. The unaccurate measurements at low frequencies do not allow to decide whether

Table 2. Dielectric parameters of dilute solutions of $N(CH_3)_2$ compounds. 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
		N,N,N′,N′-Tetramethyl-p-phenylene diamine $\mu = 1.09$ D									
Benzene	20	2.11	0.41		—		1.5*	0.72		—	0.28
Mesitylene	20	1.31	0.28		—		1.5*	0.58		—	0.42
Decalin	20	1.20	0.23		—		1.5**	0.55		—	0.45
		N,N-Dimethyl-p-toluidine $\mu = 1.23$ D									
Benzene	20	2.38	0.23	26	0.7	0.75	1.5	0.07	0.5	0.09	0.09
Decalin	20	1.28	0.14	58	1.0	0.70	2.2	0.07	0.5	0.13	0.10
		N,N-Dimethylaniline $\mu = 1.58$ D									
Heptane	20	2.15	0.37	10.3	0.7	0.82	0.4	0.11		—	0.07
Benzene	20	3.84	0.27	15.3	0.7	0.87	0.5	0.12		—	0.01
Mesitylene	60	2.00		11.7	0.7	0.80	0.4	0.15		—	0.05
	20	2.38	0.16	18.9	0.7	0.85	0.4	0.12		—	0.03
	− 30	3.07		46.5	0.7	0.80	1.2	0.07		—	0.13
Decalin	20	1.98	0.15	29.4	0.7	0.82	1.2	0.11		—	0.07

* $p_2 \approx 2.$ — ** $p_2 \approx 2.5.$

there is an overall relaxation region or not. The weight factor G_4 also in this molecule is the smallest in benzene solution.

The relaxation parameters of *N,N-dimethyl-p-toluidine* are also given in Table 2. A good fit to the measured loss curve of benzene solution (Fig. 8) was obtained also by taking instead of the two relaxation regions τ_2 and τ_3 (Table 2) only one Debye region at 1 ps along with a weight factor 0.14. This gives an idea of the accuracy of the given short relaxation times.

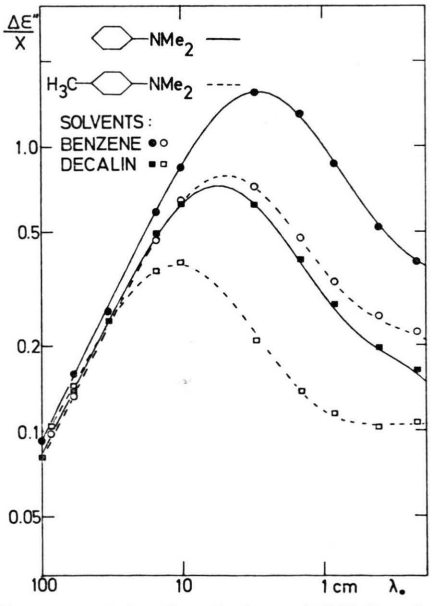

Fig. 8. Benzene and decalin solutions of N,N-dimethylaniline and N,N-dimethyl-p-toluidine at 20 °C.

The ratio of the overall relaxation times τ_1 of dimethyl-p-toluidine and p-toluidine is 2.0 and 2.4 in benzene and in decalin solutions, respectively. This is very consistent with the larger molecular size of the dimethyl compound and with the higher viscosity of decalin [24]. The short relaxation times τ_2 in both the solvents are of the same order of magnitude with the ones obtained for the corresponding tetramethyl compound and can be assigned to the group reorientation process of the dimethyl amino group. In spite of the certain inaccuracy in the τ_2 values it seems very probable that in this compound τ_2 in decalin solution is not shorter than in benzene as is the case with the NH_2 compounds discussed above.

In *N,N-dimethylaniline* the relative contribution of the high frequency regions to the overall loss (Fig. 8) is too low for the analyses of the curves in terms of three regions. Therefore only one high frequency region in each solvent is given in Table 2.

The overall relaxation time and its weight factor G_1 can be determined with rather high degree of accuracy in this case because of the relatively symmetric appearance of the loss curves. KNOBLOCH [6] reports a relaxation time 16.8 ps with the weight factor 0.80 in benzene solution whilst KRAMER [3] gives $G_1 = 0.88$. The dipole moment, 1.64 D, given by Knobloch is slightly higher than the literature values [26] and the one measured in this work, 1.58 D. This refers to too high a dielectric increment and consequently to too low G_1 in Knobloch's work. For heptane solution a weight factor $G_1 = 0.95$ is reported[3]. This is too high when compared to all our values in different solvents.

The resolved FIR contributions $G_3 + G_4$ of dimethyl-p-toluidine exceed the high frequency contributions $G_2 + G_4$ of dimethylaniline in respective solvents. This would lend an idea that there is no group reorientation in dimethylaniline at all. However, the group reorientation contributions G_2 of dimethyl-p-toluidine give

$$\mu_2 = \mu \sqrt{G_2} = 0.33\ \text{D}$$

according to BUDÓ's model[27]. This would correspond to a weight factor as small as 0.04 for the group reorientation process in dimethylaniline. The data of the tetramethyl compound give the respective dipole moment component $\mu_{\perp} = \mu_2/\sqrt{2} = 0.65$ D, corresponding to $G_2 = 0.17$ in dimethylaniline. This obviously represents the upper limit since also a part of the FIR absorptioen is involved in the G_2 obtained for the tetramethyl compound. A conclusion may be drawn, similar to what KRAMER[3] has made, that dimethylaniline is not a rigid molecule but the mobility of the dimethyl amino group both in dimethylaniline and in dimethyl-p-toluidine is much lower than the mobility of the amino group in the respective amino compounds.

c) Chloroanilines and 4-Aminobiphenyl

In the loss curves of *monochloroanilines* the high frequency regions are masked to a large extent by the dominating overall relaxation absorption. In *2,4,6-trichloroaniline* the larger size of the molecule shifts the overall relaxation region to lower frequencies and the symmetrical location of the chlorine atoms in the phenyl ring reduces its prevalence making the high frequency regions easier to resolve.

The dielectric parameters of the chloroanilines are given in Table 3. The overall relaxation times are a few per cent longer than those of the corresponding methyl substituted anilines (Table 1) because of the larger volume of a chlorine atom. The given set of the short relaxation times of the monochloroanilines must be taken as tentative only. The weight factors G_2 of all the chloroanilines correspond to the dipole moment components 0.4 D to 0.6 D, which well agree with the ones of the corresponding methyl substituted anilines, 0.4 D to 0.7_5 D. In trichloroaniline the obtained τ_2 and G_2 are more reliable. The relaxation times τ_2 are comparable with the ones of mesidine (Table 1). However, it cannot with certainty be decided whether in this case the relaxation time is smaller in decalin solution than in benzene.

4-Aminobiphenyl is not soluable enough in aliphatic solvents and was, therefore, measured only in benzene and mesitylene. The loss curves at different temperatures are illustrated in Figure 9. They seem to have an unexpectable shape. In the analyses an additional absorption region had to be introduced between the overall relaxation absorption and the group relaxation region.

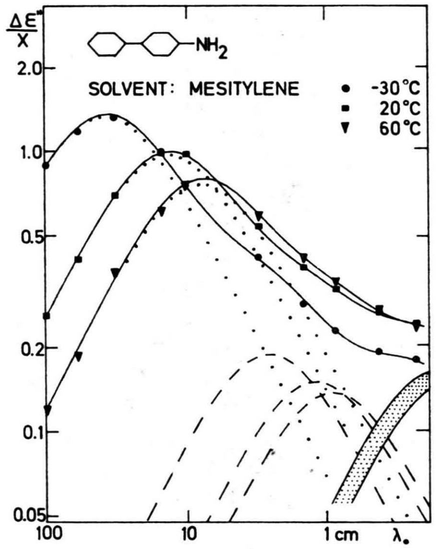

Fig. 9. Mesitylene solution of 4-aminobiphenyl at −30, 20, and 60 °C. The dotted and broken curves from left to right are the overall and intramolecular reorientation (see the text) contributions, respectively. The dotted zone illustrates the approximate location of the curves of the amino group relaxation processes at all the temperatures mentioned above.

The obtained long relaxation times τ_1 (Table 3) are comparable with those of rigid 4-bromobiphenyl[3, 28], 58 ps in benzene (20 °C) and 77 ps and 260 ps in mesitylene (20 °C and −30 °C). The weight factor $G_1 = 0.65$ in benzene solution is lower than 0.80 reported by KRAMER[3], who measured only three loss values rather far from the maximum loss region.

The relaxation times τ_3 are assigned to the reorientation of the amino group since they are of comparable magnitude with the group relaxation times of aniline. The given values may be slightly too short and their weight factors too high since no FIR corrections could be made.

The dipole moment of 4-aminobiphenyl in benzene, 1.78 D, is higher than the one of aniline,

Table 3. Dielectric parameters of dilute solutions of chloroanilines and 4-biphenylamine. 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
		p-Chloroaniline $\mu = 3.01$ D									
Benzene	20	13.24	0.39	17	1.0	0.84	2.0	0.03	0.5	0.07	0.06
		m-Chloroaniline $\mu = 2.66$ D									
Benzene	20	10.46	0.41	16	1.0	0.85	1.5	0.05	0.5	0.07	0.03
		o-Chloroaniline $\mu = 1.76$ D									
Benzene	20	4.77	0.39	10	1.0	0.76	1.0	0.06	0.5	0.07	0.11
		2,4,6-Trichloroaniline $\mu = 1.73$ D									
Benzene	20	4.75	0.48	27	0.7	0.76	2.0	0.09	0.5	0.07	0.08
Decalin	20	2.55	0.21	47	0.7	0.70	1.8	0.06	0.4	0.08	0.16
		4-Aminobiphenyl $\mu = 1.78$ D									
Benzene	20	5.45	0.96	56	0	0.65	5	0.11	0.8	0.15	0.09
Mesitylene	60	2.84		40	0	0.65	4.5	0.12	0.6	0.14	0.09
	20	3.50	0.58	69	0	0.67	6	0.10	0.8	0.11	0.12
	– 30	4.73		195	0	0.65	13	0.09	1.0	0.06	0.20

1.51 D. A phenyl substitution at the para position of dimethylaniline gives rise to even higher an increase in the dipole moment whilst in chloro- and bromobenzenes the equivalent substitution gives no marked difference. This is explained by a strong mesomeric interaction between the lone pair electrons of the nitrogen atom and the π-electron system of the phenyl ring which is able to rearrange the charge distribution as far as in the para phenyl ring[29]. This interaction between the two phenyl rings has its maximum when the rings are coplanar. Thus any change in the coplanarity gives rise to a change in the molecular dipole moment and in the dielectric polarization. The relaxation time of such a process may be expected to be of the order of few picoseconds. It is proposed here that this is the origin of the observed intermediate relaxation time τ_2 of 4-biphenylamine. The solvent and temperature dependence ($\Delta H = 1.6$ kcal/mol) of τ_2 are consistent with the corresponding properties of the other internal dipole reorientation processes of the compounds investigated in this work.

3. Conclusions

The dipole moment component $\mu_\perp$ which is reorienting in an intramolecular motion is according to Budó's model[27] equal to $\mu\sqrt{G_\perp}$. This may be used to compare the internal mobilities of different molecules. In Fig. 10 both the perpendicular and the parallel moment components ($\mu_\parallel$) of methyl substituted anilines in benzene and decalin solutions are plotted against the molecular dipole moments. The relaxation region (τ_2, G_2) alone is taken to be responsible for $\mu_\perp$ and the region (τ_1, G_1) for $\mu_\parallel$, respectively. In both solvents the dipole moment components fall approximately on straight lines. The parallel component increases along with the total dipole moment. Its increase is mainly caused by the rearrangement of the charge distribution in the coplanar part of the molecule.

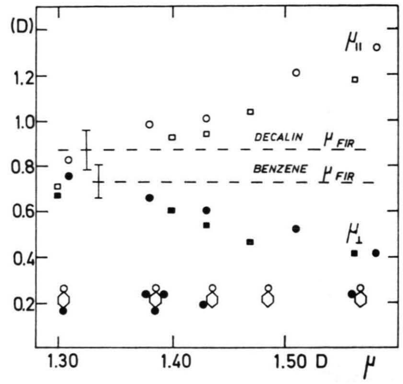

Fig. 10. The dipole moment components $\mu_\parallel$ and $\mu_\perp$ of p-toluidine, mesidine, m-toluidine, aniline and o-toluidine plotted against the total molecular dipole moments. The open circles and squares belong to $\mu_\parallel$ and the full ones to $\mu_\perp$ in benzene and decalin solutions, respectively.

If the polarity of the NH_2 group and its valence angles would stay unchanged in these molecules a constant value for $\mu_\perp$ should be expected. However, there is a remarkable decrease when passing from p-toluidine to o-toluidine. The perpendicular dipole moment component which reorients in the group relaxation process of these molecules consists of two parts: the perpendicular components of the NH_2 group moment and the atomic dipole moment of the nitrogen lone pair electrons. During the reorientation process the overlapping of the lone pair electrons and the aromatic π-electrons is varied. Thus a third contribution is involved in the dipole reorientation process from the varying mesomeric charge shift. This component is, however, parallel to the molecular frame and may not contribute to $\mu_\perp$. All the contributions are dependent on the valence angles and on the electronic state of the nitrogen atom.

From infrared vibrational spectra KRUEGER[30] has calculated changes in the valence angles HNH of these molecules. The decrease of $\mu_\perp$ in Fig. 10 correlates with the increase of the valence angle. The valence angle of p-toluidine, 110.7°, indicates a virtual sp^3 hybridization which changes toward sp^2 when the valence angle increases. This is consistent with increasing mesomeric interaction. In N,N-dimethyl compounds there is a still stronger mesomeric interaction, and lower $\mu_\perp$ values are obtained (0.33 D).

The observed decrease of $\mu_\perp$ with increasing total dipole moment very likely is primarily caused by the increasing mesomeric interaction. In ring methyl substituted anilines the dipole moment may result from a parallel effect. The variation of $\mu_\perp$ is also correlated with the basicity of the compounds. The intramolecular interactions controlling the base strengths are similar to those proposed above[31]. Mesidine is an exception. Its lowest base strength among the methyl substituted anilines has been explained by a shielding effect of the ortho substituents. A similar effect seems not to appear in the obtained $\mu_\perp$ values but the ortho substituents lengthen the group relaxation times (Table 1) with respect to the corresponding values in p-toluidine.

The mean values of the dipole moment components responsible for the FIR contributions have been calculated from the combined weight factor $G_3 + G_4$, Figure 10 demonstrates the significance of the FIR contribution. In Table 4 the dipole moments $\mu_{\mathrm{FIR}} = \mu \sqrt{G_3 + G_4}$ are collected. The heptane values have been obtained only from two polar molecules and are therefore less reliable. They are consistent with the values obtained in decalin. The given data indicate a solvent dependence as well as a dependence on the mobility of the substituted group(s) in the phenyl ring. The methyl groups have no important influence on the FIR absorption. The NH_2 compounds have remarkably higher FIR contribution than the $N(CH_3)_2$ compounds. Also the comparison of the moment values of the chloroanilines with the μ_{FIR} of chlorobenzene, 0.44 D[15], shows that the amino group has a marked influence on the FIR absorption.

On the other hand, the dependence of the FIR contribution on the group mobility may indicate that the resolved high frequency Debye regions might not properly describe the actual distribution of the relaxation times of the group reorientation and the FIR processes. For comparison the $\mu_\perp$ values were calculated from $G_2 + G_3$ and G_4 for the group reorientation and FIR processes, respectively. The new values were less dependent on the molecular properties discussed above. A significant and important difference between the behavior of the NH_2 and $N(CH_3)_2$ group is, however, preserved.

The measurements, extended to higher frequencies, and the introduction of the FIR absorption to the analyses allow a better sight into the composition of the overall loss curves. As a result longer group relaxation times with lower weight factors have been obtained. SMYTH[12] has proposed the shortness of the group relaxation times of the NH_2 group as one of the indications to the inversion process. The new longer relaxation times obtained in this work are of the order of magnitude which have been reported for many rotating small groups[6]. One must, however, bear in mind that in nonassociating solvents the relaxation times are still very short. The

Table 4. Substituent and solvent dependence of the FIR contribution in substituted benzenes. The dipole moments reorienting in the FIR process are given in Debye units.

Substituents		Benzene	Mesitylene	Decalin	Heptane
$N(CH_3)_2$,	CH_3	0.55 ± 0.03	0.61	0.70 ± 0.05	0.67
NH_2,	CH_3	0.73 ± 0.06	0.81 ± 0.04	0.88 ± 0.10	0.94
NH_2,	Cl	0.77 ± 0.07	—	0.85	—

rather low activation energy of the NH_2 group relaxation process, which was employed by DAVIES[7] as the primary basis for the inversion theory has been confirmed here.

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