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Dielectric Relaxation Phenomena and Intramolecular Dipole Motion of Anilines in Dilute Solutions. *)

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The effective dielectric relaxation times of molecules like aniline and toluidines are shorter than those of rigid molecules of the same size. Fischer discussed those molecules with intramolecular mobility using two and more Debye absorption terms according to the theory for rotating groups by Budó. But he used measurements at the long wave end of the absorption curve only, assuming the shape of the molecule, its size, and the angle between group moment and CN-bond to calculate the mobility of the group. In order to get more information about the mobility of the NH₂-group and its change by substitutions in the benzene ring, we had measured the microwave absorption of various chloro- and methyl-substituted anilines down to a wavelength of 7 mm, that is often at the decrease of the absorption curve at its high frequency side.

The dipole loss $\Delta\varepsilon''$ (Δ means the difference between solution and solvent) was measured with 4 wavelengths in dilute solutions of benzene at 20° C. With 10,35 cm a coaxial resonator was used, with 3,06 cm an interferometric method, and with 1,392 cm and 0,696 cm a transmission method. The static dielectric constant $\Delta\varepsilon_0$ was determined by means of a low frequency bridge, the optical value Δn^2 by an Abbé refractometer. The dipole moment μ is calculated in the usual way from $\Delta\varepsilon_0 - \Delta n^2$.

It is well known that molecules with intramolecular mobility show flatter absorption curves than predicted by Debye. Therefore it was examined how much the measurements meet an equation:

$$\frac{\Delta\varepsilon''}{\Delta\varepsilon_0 - \Delta n^2} = (1 - G) \frac{\omega\tau}{1 + \omega^2\tau^2} \quad 0 < G < 1 .$$

*) A publication in detail will come out: *Z. Naturforschung*, 15a (1960).

The pair of values τ , G with the minimum sum of the square of deviations was evaluated by a digital computer. But this sum is nearly 100 times larger than the same quantity of the errors of the measurements. The relaxation times are too short compared to those of rigid molecules of similar size.

A sufficient approximation in the investigated range could be obtained by splitting up the absorption curve into two Debye terms:

$$\frac{\Delta\varepsilon''}{\Delta\varepsilon_0 - \Delta n^2} = (1 - G) \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + G \frac{\omega\tau_2}{1 + \omega^2\tau_2^2}$$

Both the relaxation times τ_1 , τ_2 and the weight G of the absorption part at higher frequencies were calculated again. The minimum sum of the square of deviations is small enough this time. Budó had described a molecule with a free rotating group by three parameters, assuming the axis of rotation as the main axis of a spheroid. Accordingly the two relaxation times are given by

$$\tau_1 = 1/2 D_m \quad \tau_2 = 1/(D_m + D_g)$$

D_m and D_g are the mobilities of the entire molecule and of the group. The value D_m of chlorobenzene ($5,2 \cdot 10^{10} \text{ sec}^{-1}$), of aniline and of the two other in shape very similar ortho-derivatives have been found to be nearly the same. The *m*- and *p*- derivatives have smaller mobilities. The proportionality between volume and relaxation time and Perrin's relations for non-spherical molecules are reflected by this quantity D_m .

D_g is almost completely determined by the shorter relaxation time. It fluctuates about $1,1 \cdot 10^{12} \text{ sec}^{-1}$ and does not depend characteristically on any molecular parameter or on the position of substituents.

According to Budo is:

$$G = (\mu_{bew}/\mu)^2$$

μ_{bew} is that component of the entire dipole moment μ which is perpendicular to the CN-bond and which can orientate itself independent of the rest of the molecule. An average of $\mu_{bew} = 0,92 \text{ D}$ has been found for the NH_2 -group. The 6 orthosubstituted anilines have slightly smaller values and the values of o-toluidine and 2,6 dimethylaniline are the smallest ones. Probably there exists a small influence of the substituents on μ_{bew} . With $(1 - G) = (\mu_f/\mu)^2$ we calculate μ_f , which is the part of μ rigidly connected with the molecule. From μ_f and the partial moments of the

CH₃- and the Cl-groups, for which those of toluene and chlorobenzene were assumed, the angle δ between the NH₂-moment and the CN-bond is to be calculated. We have found an average value of $\delta = 38^\circ \pm 3^\circ$ of which o-toluidine and o-chloroaniline deviate again. The entire moment of the NH₂-group agrees with that of aniline (1,54 D). Only the NH₂-moment of the orthosubstituted methyl-derivatives decreases to 1,3 D with an increasing number of substituents in the 2 or 6 position.

So the influence of the substituents on the mobility of the NH₂-group is noticeable only in the ortho position, and only to a small amount. It might be explained by an inductive or mesomeric effect of the substituted group.

DISCUSSION

M. W. Maier. — I should like to ask M. Kramer whether he knows any measurements of dielectric relaxation in the case that the effective relaxation of a molecule is entirely due to the orientation of movable groups on the molecule as for example in 1,4-Di-amino-benzene.

Dr. Kramer. — The solubility of 1,4 Diamino benzene in benzene or another un-polar solvent is so small that no measurements could be done. The benzidine can not be measured exactly.
