# Dielectric relaxation of some large aromatic molecules in benzene from microwave absorption measurements

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The dielectric constant ($\epsilon'$) and dielectric loss ($\epsilon''$) of three large aromatic molecules namely $\alpha, \alpha, \alpha', \alpha'$, 2, 3, 5, 6-octachloro -*p*-xylene, 9-acetyl anthracene and acridan have been measured at four wavelengths between 0.2 cm and 25 cm and at two or three temperatures between 20° and 60°C. The data have been analysed and two relaxation times have been found in each case. The results obtained are interpreted.

Measurements of $\epsilon'$ and $\epsilon''$ are carried out at wavelengths 0.22, 3.24, 10 and 25 cm. to an accuracy of 2%. The apparatus used have been described before by Garg *et al* (1965), Laquer & Smyth (1949), Pitt & Smyth (1959). The static dielectric constant $\epsilon$ has been measured at 10KHz using General Radio Low Frequency Bridge Type 1615A.

Three large aromatic molecules of grade 'Pure' were measured namely . $\alpha$, $\alpha, \alpha', \alpha'$, 2, 3, 5, 6-octachloro -*p*-xylene, acridan (both obtained from Almdrich Chemical Co Inc.) and 9-acetyl anthracene (obtained from K & K Laboratories Inc.). Benzene "Analar" was distilled twice over sodium and used as a solvent. Dilute solutions of the substances under test in benzene were used.

$\epsilon_0$, $\epsilon'$ and $\epsilon''$ were measured at temperatures ranging between 20° and 60°C with the exception of acridan $\epsilon'$ and $\epsilon''$ for the substances used were plotted in a complex plane (Cole & Cole 1941) and the dispersion step ($\epsilon_0-\epsilon_\infty$) was obtained for each substance at the different temperatures from these arc plots. As an example, the arc plot of 9-acetyl anthracene at 20°C is given in figure 1 Then the
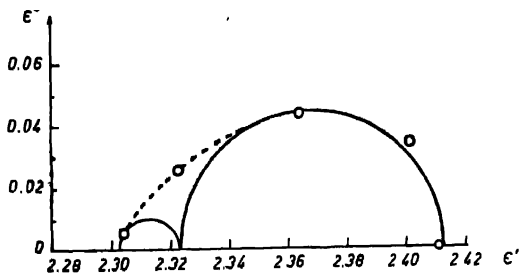


Figure 1. Arc plot for 9-acetyl anthracene in benzene at 20°C (for concentration 0.0099 mole fraction).

reduced absorption $\eta'' = \dfrac{\epsilon''}{\epsilon_0-\epsilon_\infty}$ was calculated for each frequency. The values of $\eta''$ were plotted against log $\lambda$. The absorption curves obtained were analysed into two Deybe terms using the equation

$$\eta'' = (1-G)\,\frac{\omega\tau_1}{1+\omega^2\tau_1{}^2}+G\,\frac{\omega\tau_2}{1+\omega^2\tau_2{}^2}.$$

The numerical analysis has been carried out using a computer IBM 1620.

In case of acridan the variation of $\epsilon'$ with frequency was very small so that it was difficult to draw the arc plots and hence $\eta''$ could not be calculated. $\epsilon''$ was plotted against log $F$ and the results were analysed also into two Debye terms The results of the analyses of all substances are given in table 1.

## Discussion

1. $\alpha, \alpha, \alpha', \alpha', 2, 3, 4, 6\text{-}octachloro\ \text{-}p\text{-}xylene$ :
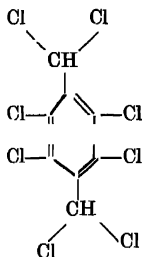


The measurements were carried out at 20° and 40°C only. It was possible to measure $c''$ at a wavelength 1 25 cm at 20°C and so $\eta''$ for this frequency was also calculated. Figure 2 shows the results of analysis at 20°C and 40°C. As shown, the analyses represent the experimental data very well and the absorption curves are found to be composed of two Debye terms having relaxation times $\tau_1$ and $\tau_2$. The availability of the measured values at 2 mm wavelength assure these analyses The longer relaxation time $\tau_1$ is that which may be due to the rotation of a molecule of this size as a whole The short relaxation time $\tau_2$ is due to a complete rotation of the $CHCl_2$ groups. From Stuart & Briegleb model, it is found that no complete rotation of the group is permissible. So, it is concluded that the rotation of the $CHCl_2$-groups is restricted to a slight rotating oscillation by the adjacent Cl-groups. The value of $\tau_2$ (5.18 psec at 20°C) is comparable with the value 3.72 p sec for the $CH_2Cl$-group in $\alpha, \alpha'$, dichloro-$p$-xylene (Purcell et al 1960). $\tau_2$ is very temperature dependent as would be expected for the oscillation of the $CHCl_2$ groups while $G$ does not change much.

TABLE 1 Dielectric constants, dielectric losses, relaxation times and dipole moments in benzene solutions

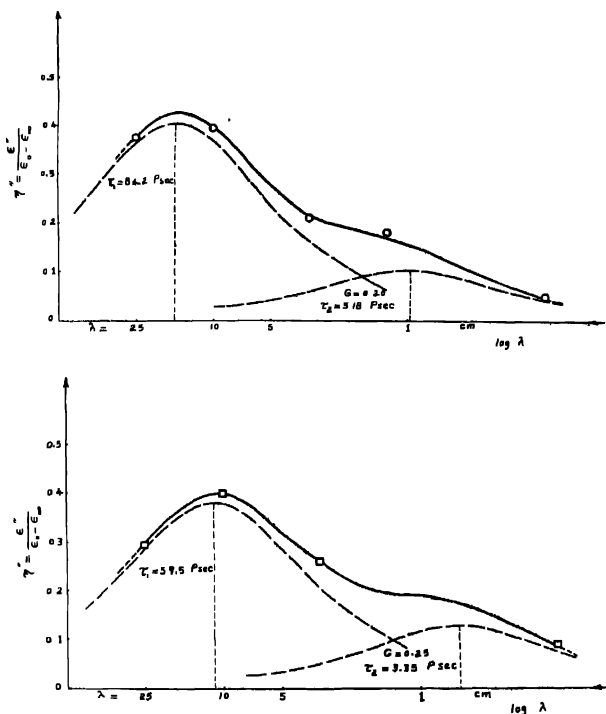| Substance | t°C | $\epsilon_0$ | $\lambda$ cm | $\epsilon'$ | $\epsilon''$ | $\epsilon_0 - \epsilon_\infty$ | $\eta'' = \dfrac{\epsilon''}{\epsilon_0 - \epsilon_\infty}$ | $\tau_1$ psec | $\tau_2$ psec | G | μ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| α, α, α', α', 2, 3, 5, 6 octachloro p-xylene  x = 0.0336 mole fraction | 20 | 2.422 | 0.216  1.25  3.24  10.00  25.00 | 2.320  2.328  2.339  2.362  2.405 | 0.0045  0.0177  0.0212  0.0403  0.0382 | 0.102 | 0.049  0.177  0.206  0.392  0.372 | 84.2 | 5.18 | 0.20 | 1.43 |
|  | 40 | 2.377 | 0.216  3.24  10.00  25.00 | 2.287  2.300  2.332  2.373 | 0.0079  0.0241  0.0371  0.0271 | 0.093 | 0.088  0.258  0.398  0.291 | 59.5 | 3.35 | 0.25 | |
| 9-acetyl anthracene  x = 0.0099 mole fraction | 20 | 2.411 | 0.216  3.24  10.00  25.00 | 2.304  2.323  2.364  2.402 | 0.0062  0.0257  0.0450  0.0340 | 0.108 | 0.048  0.239  0.417  0.315 | 65.3 | 5.10 | 0.20 | 2.75 |
|  | 60 | 2.320 | 0.216  3.24  10.00  25.00 | 2.228  2.253  2.295  2.317 | 0.0087  0.0331  0.0326  0.0176 | 0.093 | 0.093  0.356  0.350  0.188 | 35.1 | 4.40 | 0.30 | |
| Acridan  x = 0.0087 mole fraction | 20 | 2.308 | 0.216  3.24  10.00  25.00 | 2.289  2.306  2.308  2.308 | 0.0012  0.0026  0.0035  0.0028 | — — — — | — — — — | 64.9 | 4.42 | 0.42 | — |
|  | 40 | 2.280 | 0.216  3.24  10.00  25.00 | 2.257  2.267  2.268  2.280 | 0.0034  0.0024  0.0033  0.0023 | — — — — | — — — — | 58.9 | 2.35 | 0.58 | |

Figure 2.  Absorption of α, α, α′, α′, 2, 3, 5, 6—octachloro- p-xylene in benzene at 20° and 40°C for concentration 0.0336 mole fraction obtained from the sum of two Debye terms having relaxation times $\tau_1$ and $\tau_2$

The dipole moment ($\mu$) was calculated at the two temperatures and was found to be 1.43 $D$.

2, 9-*Acetyl Anthracene*
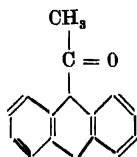


The measurements were carried out in this case at 20° and 60°.   It was found in the case of 1-acetyl naphthalene (Fong & Smyth 1963) that the molecule possesses only one relaxation time due to the blocking of the acetyl group by the 8-hydrogen

atom, the acetyl group in 2-acetyl naphthalene is able to rotate having a relaxation time 7.3 psec. Following this interpretation, it is expected that the acetyl-group in the 9-acetyl anthracene will be more blocked by the 1- and 8-hydrogen atom Anyhow, the relation between $\epsilon'$ and $\epsilon''$ plotted in a complex plane could not be represented by one semicircle. Both absorption curves at 20°C and 60°C are composed of two Debye terms. Figure 1 shows the arc plot obtained at 20°C as an example. The measurements at 2 mm wavelength helped much in obtaining this result. From Stuart & Brieglob model, it is found that the acetyl group may possess a restricted rotation. It is threfore suggested that the longer relaxation time $\tau_1$, is to be attributed to the rotation of the molecule as a whole and the shorter relaxation time $\tau_2$ is due to a restricted orientation of the acetyl group. The values of $\tau_1$, shown in table 1, are reasonable for a molecule of that size The value of $\tau_2$ (5.10 psec at 20°C) obtained for the restricted rotation of the acetyl group in 9-acetyl anthracene is smaller than the value obtained (7.3 psec at 20°C) for the acetyl-group in 2-acetyl naphthalene which is supposed to have free rotation $G$, the weight of $\tau_2$ on the total absorption is not much affected with temperature $\mu$ is also calculated and is found to be 2.75D

3 *Acridan*
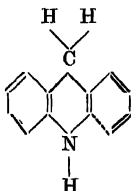


The measurements were taken at 20° and 40°C. No values of $(\epsilon_0 - \epsilon_\infty)$ could be obtained due to the very small variation of $\epsilon'$ with frequency as mentioned before, hence the reduced absorption $\eta''$ could not be calculated. The values of $\epsilon''$ at each temperature are plotted against $\log f$. The measurements of $\epsilon''$ at at 2 mm wavelength (specially at 40°C) show that the absorption cannot be represented by one Debye term. The analysis is carried out as shown in figure 3 using two Debye terms having relaxation times $\tau_1$ and $\tau_2$. The longer relaxation time $\tau_1$, which is about the same as that for 9-acetyl anthracone, (molecule being about the same size) could be attributed to the rotation of the whole molecule. This is a reasonable value for a molecule of that size. While the short relaxation time $\tau_2$ may be due to an internal motion within the molecule. From Stuart & Brieglob model it is seen that the molecule can have an internal motion. This internal motion could not be an orientation but may be due to a tipping over of one of the outer benzene rings. This type of motion, as expected is very temperature dependent.
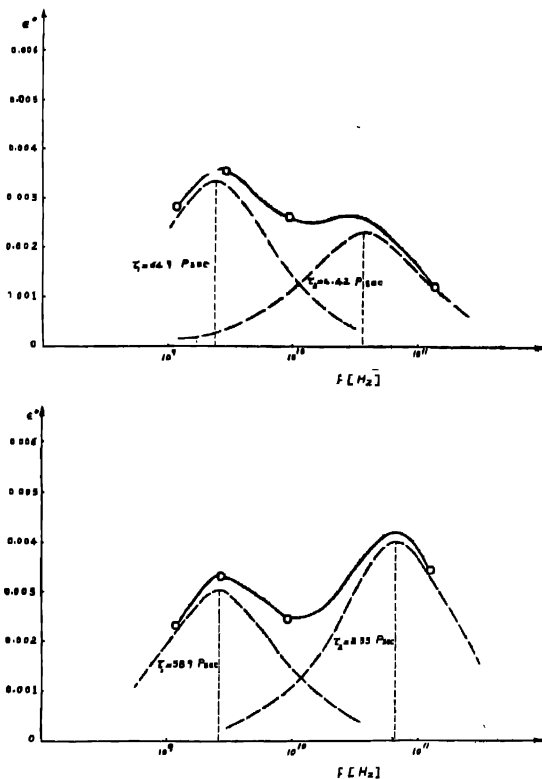
### ACKNOWLEDGEMENT

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