Dipole Moment and Dielectric Relaxation of Some Aromatic Ethylenes and Butadienes

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Z. Naturforsch. 35a, 623—627 (1980) ; received May 5, 1980

The dipole moment of 1,1-bis-p-chlorophenylethylene, 1,1-bis-p-bromophenylethylene, 1,1-bis-p-methoxy, -ethoxy, -isopropoxy-phenylethylene, 1,1,4,4-tetrakis-p-methoxy, -ethoxy, isopropoxy-phenylbuta-1,3dienes was measured and compared with the calculated value. The mesomeric moment was estimated and found to decrease in the case of the ethylenes with the increase in volume of the substituted group. For the butadienes, the mesomeric moments compensate each other.

Investigations of the dielectric relaxation times of the ethylenes showed that the orientation of the -OCH₃ group in the 1,1-bis-p-methoxy-phenylethylene is hindered to a large extent. The orientation of the -OC₃H₅ and -OC₅H₇ groups in the corresponding molecules are restricted due to steric hindrance.

Introduction

The effect of electron repelling and electron attracting groups on the electrical conductivity and thermoelectric power of some ethylenes and butadienes had been studied [1, 2]. In that work, it was concluded that, in the case of ethylenes, both type and magnitude of the conductivity and also the thermoelectric power are sensitive to the character of the attached groups, while they seemed not to be affected by the groups in the case of butadienes.

The aim of this work is to complete these investigations by studying the dipole moment and dielectric relaxation of these molecules.

Experimental

The dielectric loss \(\varepsilon''\) of dilute solutions in benzene was measured at wavelengths 1.3, 3.1 and 7.3 cm. The apparatus and procedure used in the measurements had been described previously [3—5]. The accuracy of the measurements is better than 2%.

The static dielectric constant \(\varepsilon_0\) was measured at 70 kHz to an accuracy of 1% by a decameter of the Schering bridge type. The refractive index for the Na-D-line was measured by an Abbé refractometer.

Results and Discussion

1. Dipole moment

The dispersion step

\[
\frac{S}{x} = \frac{\Delta \varepsilon_0 - \Delta \varepsilon_0^2}{x}
\]

(where \(x\) is the concentration in mole fraction and \(\Delta\) means the difference between solution and solvent) is obtained and used to calculate the dipole moment \(\mu\) using the equation:

\[
\mu^2 = \frac{27 k T M S}{x} \cdot \frac{4 \pi N_A \varepsilon (\varepsilon_0 + 2)}{}
\]

where \(k\) is Boltzmann's constant, \(N_A\) is Avogadro's number, \(M\), \(\varepsilon\) and \(\varepsilon_0\) are the molecular weight, density and dielectric constant of the solvent and \(T\) is the absolute temperature. The experimental values of the dipole moment \(\mu\) are given in Table 1.

On the other hand, the formula proposed by Zahn [6] is used to calculate the dipole moment \(\mu^*\) using the partial dipole moments of the substituents.

The molecule "CPE" illustrated in Fig. 1 contains two similar polar substituents of group moment \(\mu_1 = -1.57\) D. The calculated dipole moment depends much on the value of the angle \(\phi\)

Measurements were carried out at temperatures ranging between 20 and 40 °C.

The investigated materials had been recrystallised several times from BDH glacial acetic acid and the resistivity measured till no change in its value was observed by further recrystallisation.

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Table 1. Dipole moments of the investigated ethylenes and butadienes. \( \mu \) and \( \mu^* \) are the measured and calculated values of dipole moment. \( \mu_x \) is the estimated mesomeric moment (see Eqs. 2—5 for other symbols).

<table>
<thead>
<tr>
<th>Substances</th>
<th>( \mu ) D</th>
<th>( \mu^* ) D</th>
<th>( \mu_x ) D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1-bis-p-chlorophenylethylene “CPE”</td>
<td>-1.50</td>
<td>-1.81</td>
<td>0.31</td>
</tr>
<tr>
<td>1,1-bis-p-bromophenylethylene “BPE”</td>
<td>-1.69</td>
<td>-1.76</td>
<td>0.07</td>
</tr>
<tr>
<td>1,1-bis-p-methoxyphenylethylene “MPE”</td>
<td>3.58</td>
<td>1.73</td>
<td>0.49</td>
</tr>
<tr>
<td>1,1-bis-p-ethoxyphenylethylene “EPE”</td>
<td>2.74</td>
<td>1.87</td>
<td>0.53</td>
</tr>
<tr>
<td>1,1-bis-p-isoproxyphenylethylene “IPE”</td>
<td>2.53</td>
<td>1.87</td>
<td>0.53</td>
</tr>
<tr>
<td>1,1,4,4-tetrakis-p-methoxyphenylbuta-1,3diene “TMPD”</td>
<td>2.42</td>
<td>2.42</td>
<td>0.57</td>
</tr>
<tr>
<td>1,1,4,4-tetrakis-p-ethoxyphenylbuta-1,3diene “TEPD”</td>
<td>2.47</td>
<td>2.61</td>
<td>0.61</td>
</tr>
<tr>
<td>1,1,4,4-tetrakis-p-isoproxyphenylbuta-1,3diene “TIPD”</td>
<td>2.52</td>
<td>2.61</td>
<td>0.61</td>
</tr>
</tbody>
</table>

between the two dipoles. Using \( \Phi = 109.6^\circ \) found in literature [7] for the angle F-C-F in 1,1-difluoroethylene, the calculated dipole moment amounts to \( \mu^* = -1.81 \) D compared with the measured value \(-1.50 \) D. This difference may be due to a mesomeric moment \( \mu_x \) in a direction opposite to that of the resultant dipole moment. In the same way, \( \mu_x \) is calculated for “BPE” taking [3] \( \mu_1 = -1.53 \) D. The results are given in Table 1.

The molecule “MPE” is illustrated in Figure 2. If we assume free rotation of the \(-OCH_3\) group around the Ar—O bond and take for the group moment the value of anisol [8] \( \mu_1 = 1.25 \) D and an angle \( \Theta = 70^\circ \), then the Zahn equation

\[
\mu^* = \left( 2 \mu_1 \cos \Theta \cos \frac{\Phi}{2} \right)^2 + 2 \mu_1^2 \sin^2 \Theta = \mu_{\parallel}^* + \mu_{\perp}^* (2)
\]

Fig. 1. Illustration of the dipole moment of 1,1-bis-p-chlorophenylethylene CPE.

Fig. 2. Illustration of the dipole moment components and mesomeric moment (\( \mu_x \)) of 1,1-bis-p-methoxyphenylethylene MPE.
leads with $\Theta = 109.6^\circ$ to a value $\mu^* = 1.73 \text{ D}$. This is far below the experimental value $3.58 \text{ D}$. The moments of the ethoxy and isopropoxy groups are not available in literature. For first approximation, using the dipole moment of p-diethoxy benzene ($1.79 \text{ D}$), we get a value of $1.27 \text{ D}$ for $\mu_2$ of the ethoxy group which leads to $\mu_2 = 1.35 \text{ D}$ if we take $\Theta = 70^\circ$ as that of the $-\text{OCH}_3$ group. Using $\Theta = 109.6^\circ$, $\mu^*$ is calculated for the “EPE” and “IPE” molecules (see Table 1).

For the molecule “TMPD” shown in Fig. 3, the rotation around the $-\text{C} - \text{C} -$ simple bond is possible. If we assume random positions of the two groups, then the Zahn equation:

$$\mu^{*2} = 2(\mu_{||}^* \cos \gamma)^2 + 2 \mu_{\perp}^{*2} = \mu_{||}^{**2} + \mu_{\perp}^{**2}$$

(with $\mu_{||}^*$ and $\mu_{\perp}^*$ from Eq. (2)) holds. Using $2 \gamma = 70^\circ$ like the corresponding angle of propylene and proceeding in the same way as in the ethylenes, the dipole moments $\mu^*$ of the butadienes are calculated and are given in Table 1.

It is evident from Table 1 that the measured dipole moments of MPE, EPE and IPE are higher than the calculated moments $\mu^*$ after Equation (2). An increase in dipole moment was noticed by Smyth and his coworkers and Brooker and his colleagues for 25 dye molecules [9], too. Brooker observed a value of 5.8 D for phenol blue compared with a roughly estimated value of 2.4 D. This was attributed to mesomeric effects.

It seems interesting to estimate the mesomeric moments $\mu_x$ of the investigated ethylenes and butadienes. It is assumed that this moment arises only in the direction of the axis connecting the first atom of the substituent to the benzene ring [10]. So, taking $\mu_x$ into account, it may be estimated from:

$$\mu^2 = (\mu_{||}^{**} + \mu_x)^2 + \mu_{\perp}^{*2}$$

for the ethylenes

$$\mu^2 = (\mu_{||}^{**} + \mu_x)^2 + \mu_{\perp}^{**2}$$

for the butadienes, (5) where $\mu$ is the measured dipole moment. The estimated values are given in Table 1.

The mesomeric moment can be attributed to the contribution of the electrons shifting towards the aliphatic carbon, the conjugated system providing the channel for this charge shift. Without the electron shift, the $-\text{OCH}_3$ group is positive with respect to the benzene ring, so that this shift will leave the group more positive leading to an increase in dipole moment. The shift of electrons will be maximum only when the $-\text{C} - \text{O} - \text{C}$ plane coincides with that of the benzene ring. This may explain the decrease found in the mesomeric moment (Table 1) with the increase in volume of the substituted group which may cause steric hindrance resulting in a deviation from planar position.

For butadienes, it is favourable for the rings to prefer the trans position as the cis position may be sterically hindered. But $\mu^*$ will not be changed considerably thereby, $\mu_{||}^{**}$ being very small. The mesomeric moments almost compensate each other. This is evident from Table 1 when comparing the measured dipole moments with the calculated $\mu^*$. For the first approximation, we can say that no mesomeric moment is noticed in the butadienes. This is in agreement with the observations on conductivity and thermoelectric power of these butadienes [1, 2].

2. Dielectric relaxation

The measured values of $\Delta\varepsilon''/\varepsilon$ for the investigated ethylenes are given in Table 2. The data of the MPE molecule are analysed into two terms of the Debye type using the equation

$$\frac{\Delta\varepsilon''}{\Delta\varepsilon_0 - \Delta nD^2} = G_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + G_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2},$$

where $\tau_1$ is the relaxation time attributed to the overall rotation of the molecule, $\tau_2$ is the time constant for an inner molecular motion with dipole orientation shorter than $\tau_1$ and $G_i$ is the relative weight.
Table 2. Dilute solutions of 1,1-bis-p-methoxy-, ethoxy- and isopropoxyphenylethylene (MPE, EPE, IPE) in benzene. $\Delta \varepsilon_0/x$, $\Delta n^2/x$ and $\Delta \varepsilon'/x$ are the differences between the static dielectric constants, refractive indices and dielectric losses of the solution and solvent and $x$ is the mole fraction.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$t$ °C</th>
<th>$\Delta \varepsilon_0-\Delta n^2/x$</th>
<th>$\Delta \varepsilon'/x$ at $\lambda =$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.3 cm</td>
<td>3.1 cm</td>
<td>7.3 cm</td>
</tr>
<tr>
<td>MPE</td>
<td>20</td>
<td>18.25</td>
<td>2.39</td>
<td>4.71</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>15.55</td>
<td>2.69</td>
<td>4.84</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>14.20</td>
<td>2.86</td>
<td>4.96</td>
</tr>
<tr>
<td>EPE</td>
<td>20</td>
<td>10.74</td>
<td>1.19</td>
<td>2.57</td>
</tr>
<tr>
<td>IPE</td>
<td>20</td>
<td>9.13</td>
<td>0.89</td>
<td>2.21</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>8.42</td>
<td>1.01</td>
<td>2.28</td>
</tr>
</tbody>
</table>

For each process. The relaxation times obtained are given in Table 3. The fitting of the absorption through two Debye terms is shown in Fig. 4 for MPE in benzene at 40 °C.

For the MPE molecule, using the empirical relation of Hufnagel [11] and the values of $\tau_0$ and $\sigma$ given by him, the effective radius of the molecule $r_{\text{eff}}$ could be calculated from:

$$\tau_1 = \tau_0 \exp(\sigma r_{\text{eff}}).$$

For the three temperatures, values of $r_{\text{eff}}$ 5.0, 5.1, 5.1 Å are obtained. The mean value 5.1 Å is plausible when considering the molecular model. It is difficult to get an exact value for $r_{\text{eff}}$ as it depends upon the specific position of the $-\text{OCH}_3$ group. For 4-bromodiphenyl ($r_{\text{eff}}=5.1$ Å) in benzene solution the relaxation times 63.1, 53.0 and 43.2 ps are found at 20, 30 and 40 °C, respectively [12]. These are comparable with those given in Table 3 for MPE. It is not possible to fit the data of MPE by one Frohlich [13] curve.

The values of $\tau_2$ given in Table 3 are only estimated values. However, Klages and Krauss [14] found for anisol and p-dimethoxybenzene in benzene at 20 °C values of $\tau_2=7.8$ and 8.3 ps and $G_2=0.76$ and 0.89 respectively. $\tau_2$ estimated in this work is somewhat larger while $G_2$ is very much smaller than the values obtained by Krauss. As shown by Fig. 4, the value of $G_2$ could not be larger than 0.1. This may be due to the mesomeric effect hindering to a large extent the rotation of the $-\text{OCH}_3$ group in the MPE molecule.

As the group becomes larger by the substitution of the $-\text{CH}_3$ group in the EPE and IPE molecules, the shortwave term does not occur at all. Perhaps steric hindrance may be responsible for the restriction of the orientation of the group. As seen from Table 3, the values of $\tau_1$ for IPE and EPE molecules do not differ much from that of MPE. The molecule does not extend much because $r_{\text{eff}}$ is only slightly increased to 5.14 Å at 20 °C and to 5.20 Å at 30 °C. This also may show that the C–O–C plane is deviated from that of the benzene ring.

The activation energy ($\Delta H$) and entropy ($\Delta S$) of the dipole orientation is calculated for the MPE molecule obtaining values of 5.61 kcal/mole and 7.41 cal/mole/deg respectively.

**Acknowledgement**

The authors would like to thank Prof. Dr. G. Klages, Institut für Physik, Universität Mainz, for his interest and stimulation of this work and for valuable discussions.