Dipole Moment and Dielectric Relaxation of Some Aromatic Ethylenes and Butadienes

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The dipole moment of 1,1-bis-p-chlorophenylethylene, 1,1-bis-p-bromophenylethylene, 1,1-bis-p-methoxy, -ethoxy, -isopropoxy-phenyl-ethylene, 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 -OCH_3 group in the 1,1-bis-p-methoxy-phenylethylene is hindered to a large extent. The orientation of the -OC_2H_5 and -OC_3H_7 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 ε'' of dilute solutions of the investigated substances 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 ε_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. 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.

Results and Discussion

1. Dipole moment

The dispersion step

$$\frac{S}{x} = \frac{\Delta\varepsilon_0 - \Delta n_D^2}{x}$$

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

$$\mu^2 = \frac{27\,k\,T\,M\,S/x}{4\,\pi\,N_A\,\varrho\,(\varepsilon_s+2)^2}, \qquad (1)$$

where k is Boltzmann's constant, N_A is Avogadro's number, M, ϱ and ε_s are the molecular weight, density and dielectric constant of the solvent and T is the absolute temperature. The experimental values values of the dipole moment μ are given in Table 1.

On the other hand, the formula proposed by Zahn [6] is used to calculate the dipole moment μ^* 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 Φ

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* The contribution of Dr. Jannett E. Risk to this work is the preparation and purification of the investigated ethylenes and butadienes.

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

Substances	μ D	μ^* D				μ_x D
1,1-bis-p-chlorophenyl-ethylene "CPE"	−1.50	−1.81				0.31
1,1-bis-p-bromophenyl-ethylene "BPE"	−1.69	−1.76				0.07
			$\mu_{\parallel}$ D	$\mu_{\perp}^{*2}$	$\sqrt{\mu^2-\mu_{\perp}^{*2}}$ $=\mu_{\parallel}^{*}+\mu_x$	
1,1-bis-p-methoxyphenyl-ethylene "MPE"	3.58	1.73	0.49	2.76	3.17	2.68
1,1-bis-p-ethoxyphenyl-ethylene "EPE"	2.74	1.87	0.53	3.22	2.07	1.54
1,1-bis-p-isopropoxyphenyl-ethylene "IPE"	2.53	1.87	0.53	3.22	1.78	1.25
			$\mu_{\parallel}$ D	$\mu_{\perp}^{**2}$	$\sqrt{\mu^2-\mu_{\perp}^{**2}}$ $=\mu_{\parallel}^{**}+\mu_x$	
1,1,4,4-tetrakis-p-methoxy-phenylbuta-1,3diene "TMPD"	2.42	2.42	0.57	5.52	0.57	0.00
1,1,4,4-tetrakis-p-ethoxy-phenylbuta-1,3diene "TEPD"	2.47	2.61	0.61	⟨6.44	–	0.00
1,1,4,4-tetrakis-p-isopropoxy-phenylbuta-1,3diene "TIPD"	2.52	2.61	0.61	6.44	0.30	−0.31

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 μ_x in a direction opposite to that of the resultant dipole moment. In the same way, μ_x is calculated for "BPE" taking [3] $\mu_1 = -1.53$ D. The results are given in Table 1.

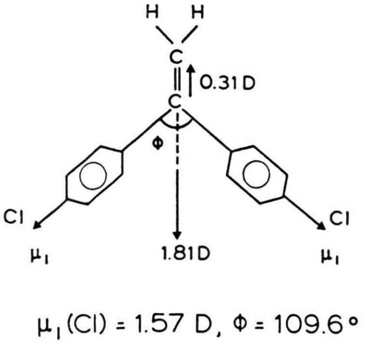

Fig. 1. Illustration of the dipole moment of 1,1-bis-p-chlorophenylethylene CPE.

The molecule "MPE" is illustrated in Figure 2. If we assume free rotation of the $-\mathrm{OCH_3}$ 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

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

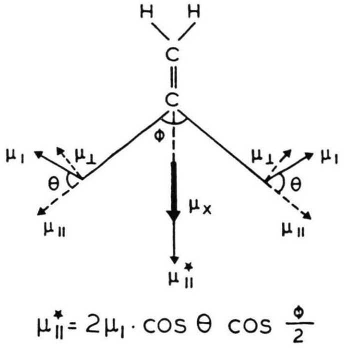

Fig. 2. Illustration of the dipole moment components and mesomeric moment (μ_x) of 1,1-bis-p-methoxyphenylethylene MPE.

leads with $\Phi = 109.6^\circ$ to a value $\mu^* = 1.73$ D. This is far below the experimental value 3.58 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 D), we get a value of 1.27 D for $\mu_\perp$ of the ethoxy group which leads to $\mu_1 = 1.35$ D if we take $\Theta = 70^\circ$ as that of the $-\mathrm{OCH_3}$ group. Using $\Phi = 109.6^\circ$, μ^* is calculated for the "EPE" and "IPE" molecules (see Table 1).

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

$$\mu^{*2} = 2\,(\mu_{\parallel}{}^{*} \cos\gamma)^2 + 2\,\mu_{\perp}{}^{*2} = \mu_{\parallel}{}^{**2} + \mu_{\perp}{}^{**2} \tag{3}$$

(with $\mu_{\parallel}{}^{*}$ 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 μ^* 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 μ^* 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 μ_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].

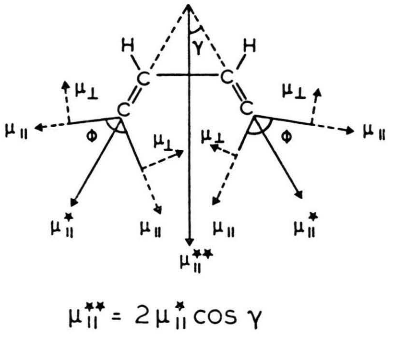

Fig. 3. Illustration of the dipole moment of the butadienes.

So, taking μ_x into account, it may be estimated from:

$$\mu^2 = (\mu_{\parallel}{}^{**} + \mu_x)^2 + \mu_{\perp}{}^{*2} \quad \text{for the ethylenes} \tag{4}$$

and

$$\mu^2 = (\mu_{\parallel}{}^{**} + \mu_x)^2 + \mu_{\perp}{}^{**2} \quad \text{for the butadienes}, \tag{5}$$

where μ 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 $-\mathrm{OCH_3}$ 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 $\mathrm{C}-\mathrm{O}-\mathrm{C}$ 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 μ^* will not be changed considerably thereby, $\mu_{\parallel}{}^{**}$ 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 μ^*. 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 $\Delta\varepsilon''/x$ 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

$$\frac{\Delta\varepsilon''}{\Delta\varepsilon_0 - \Delta n_D{}^2} = G_1 \frac{\omega\,\tau_1}{1 + \omega^2\,\tau_1{}^2} + G_2 \frac{\omega\,\tau_2}{1 + \omega^2\,\tau_2{}^2}, \tag{6}$$

where τ_1 is the relaxation time attributed to the overall rotation of the molecule, τ_2 is the time constant for an inner molecular motion with dipole orientation shorter than τ_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. $\Delta\varepsilon_0/x$, $\Delta n_D^2/x$ 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.

Sub-stances	t °C	$\frac{\Delta\varepsilon_0-\Delta n_D^2}{x}$	$\Delta\varepsilon''/x$ at $\lambda=$ 1.3 cm	3.1 cm	7.3 cm
MPE	20	18.25	2.39	4.71	8.10
	30	15.55	2.69	4.84	7.15
	40	14.20	2.86	4.96	6.70
EPE	20	10.74	1.19_3	2.57	4.91
IPE	20	9.13	0.89_5	2.21	4.21
	30	8.42	1.01	2.28	4.05

factor 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 τ_0 and σ given by him, the effective radius of the molecule r_{eff} could be calculated from:

$$\tau_1 = \tau_0 \exp(\sigma\, r_{\text{eff}}) . \tag{7}$$

For the three temperatures, values of r_{eff} 5.0_9, 5.1_6 5.1_9 Å are obtained. The mean value 5.1_5 Å is plausible when considering the molecular model. It is difficult to get an exact value for r_{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 τ_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. τ_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.

Table 3. Relaxation times calculated according to Equation (6). Solvent: Benzene.

Substance	t °C	τ_1 psec	τ_2 psec	G_2
MPE	20	65.1	10.6	0.07
	30	51.8	7.1_7	0.1
	40	41.0	5.3	0.1
EPE	20	68.5	—	0.0
IPE	20	68.5	—	0.0
	30	53.7	—	0.0

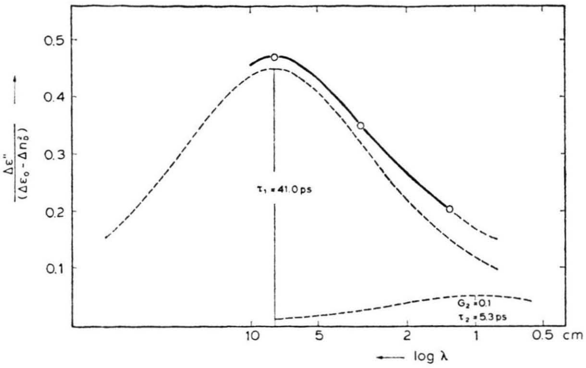

Fig. 4. Absorption curve of 1,1-bis-p-methoxyphenylethylene MPE in benzene at 40 °C obtained from the sum of two Debye terms.

$$\left(\frac{\Delta\varepsilon_0-\Delta n_D^2}{x}=14.20\right).$$

As the group becomes larger by the substitution of the $-\text{CH}_3$ group in the EPE and IPE molecules, the shortwave term do 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 τ_1 for IPE and EPE molecules do not differ much from that of MPE. The molecule does not extend much because r_{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 (ΔH) and entropy (ΔS) of the dipole orientation is calculated for the MPE molecule obtaining values of 5.61 kcal/mole and 7.41 cal/mole/deg respectively.

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[1] B. S. Farag, J. E. Risk, and S. E. Abdou, Mol. Cryst. Liq. Cryst. **26,** 357 (1974).
[2] B. S. Farag and J. E. Risk, ibid **31,** 1 (1975).
[3] F. F. Hanna and K. N. Abdel-Nour, Z. phys. Chem. **246,** 168 (1971).
[4] F. F. Hanna and K. N. Abdel-Nour, Proc. Math. Phys. Soc. U. A. R. **32,** 8 (1968).
[5] A. M. Bishai, Ph. D. Thesis, Cairo 1971.
[6] C. T. Zahn, Phys. Z. **33,** 400 (1932).
[7] R. C. Weast, Handbook of Chemistry and Physics, The Chemical Rubber Co., Ohio 1971, p. F-176.
[8] N. E. Hill et al., Dielectric Properties and Molecular Behaviour, Van Nostrand, London 1969, p. 246.
[9] C. P. Smyth, Dielectric Behaviour and Structure, McGraw-Hill, New York 1955, p. 348.
[10] E. B. Everard and L. E. Sutton, J. Chem. Soc. 1951, 2816.
[11] F. Hufnagel, Z. Naturforsch. **25 a,** 1143 (1970).
[12] F. F. Hanna and A. M. Ghoneim, unpublished.
[13] H. Fröhlich, Theory of Dielectrics, Clarendon Press, Oxford 1958.
[14] G. Klages and G. Krauss, Z. Naturforsch. **26 a,** 1272 (1971).