[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Dipole Moment and Dielectric Relaxation Time of Acepleiadylene[1,2]

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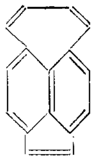
The dipole moment and dielectric relaxation time of acepleiadylene have been measured in dilute benzene solution at 30°. The values were found to be $\mu = 0.49 \times 10^{-18}$ e.s.u.-cm. and $\tau = 20.7 \times 10^{-12}$ sec., respectively. The moment is 50% of the value predicted by quantum mechanical calculations. Possible reasons for the low moment are discussed. The relaxation time is comparable to other aromatic compounds of similar size.



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The dipole moment of acepleiadylene (I) was calculated by Pullman, Pullman, Berthier and Pontis[4] using quantum mechanical methods. Their calculations indicated a value of $5.7 \times 10^{-18}$, which they corrected empirically to $1 \times 10^{-18}$ on the basis of previous correlations between calculated and experimental values. The recent synthesis of this compound by Boekelheide and Vick[5] and subsequent study of some of its properties[5,6] has led to qualitative substantiation of the properties predicted by Pullman, *et al.*[4] Professor Boekelheide suggested the experimental determination of the moment of the molecule and kindly provided us with a sample of the compound for dielectric measurements.

## Experimental Methods

Analytical reagent grade benzene, obtained from Merck and Company, was dried over sodium hydride and fractionally distilled from it as needed. The fraction used boiled at 79.9° at 757.8 mm. and had the following physical properties: $n^{30}\text{D}$ 1.49521, $d^{30}{}_4$ 0.86823, $\epsilon_{30}$ 2.2635.

The acepleiadylene was recrystallized from benzene and dried in an Abderhalden pistol at 80° *in vacuo*. The solid melted sharply at 162°. Solutions for measurement were prepared at mole fractions between 0.004 and 0.016.

All measurements were made at 30°. The low frequency dielectric constants, $\epsilon_0$, were measured by a heterodyne beat method described elsewhere.[7-10] The high frequency dielectric constants, $\epsilon'$, and losses, $\epsilon''$, were measured at 1.25[11] and 3.22[12] cm. wave lengths by a wave guide reflection method, and at 10.0, 25.0 and 50.0 cm. wave lengths with a coaxial resonant cavity cell.[13] The dielectric constants and losses were found to be linear functions of the mole fractions according to the equations

$$\epsilon_0 = \epsilon_1 + a_0c_2$$
$$\epsilon' = \epsilon_1' + a'c_2$$
$$\epsilon'' = a''c_2$$

The slopes $a_0$, $a'$ and $a''$ plotted in the complex plane gave an arc dispersion diagram[14] yielding the relaxation times and the slope $a_\infty$ of the infinite frequency dielectric constant defined by the equation

$$\epsilon_\infty = \epsilon_1 + a_\infty c_2$$

Densities were measured with a graduated pycnometer[15] having an accuracy of ±0.002%. Refractive indices were measured with a Pulfrich refractometer using the sodium D line. The specific volumes and the squares of the refractive indices were found to be linear functions of the mole fractions according to the equations

$$v = v_1 + \beta' c_2$$
$$n^2 = n_1^2 + \gamma' c_2$$

The $a_0$ and $\beta'$ values were used to calculate the polarization of the solute at infinite dilution, $P_\infty$, by the method of Halverstadt and Kumler.[16] The values of $\beta'$ and $\gamma'$ were used to calculate the molar refraction of the solute at infinite dilution, $R$, by the same method, substituting $\gamma'$ for $a_0$. The dipole moment was calculated by the Debye equation

$$\mu = 0.01281 \times 10^{-18}[(P_\infty - R)T]^{1/2}$$

## Experimental Results

The experimental results and values calculated from them are listed in Table I.

TABLE I

EMPIRICAL CONSTANTS, MOLAR POLARIZATIONS AND REFRACTIONS (SODIUM D LINE) AND DIPOLE MOMENTS AT 30°

| | $a_0$ | $\beta'$ | $\gamma'$ | $P_\infty$ | $R$ | $\mu$ ($\times 10^{-18}$) |
|---|---|---|---|---|---|---|
| Acepleiadylene | 2.695 | −0.833 | 2.357 | 89.76 | 84.42 | 0.51 ± 0.02 |
| Pyrene | 1.446 | −0.713 | 1.484 | 74.00 | 74.03 | 0 |

The use of $R$ instead of the actual sum of the electronic and atomic polarizations can lead to considerable error in the value of the dipole moment. If the moment is small, it is especially necessary to avoid assigning an arbitrary increment to $R$ in order to account for the unknown atomic polarization. An attempt was made to circumvent this difficulty by measuring the molar polarization and refraction of pyrene, the non-polar $\pi$-isomer of acepleiadylene. The difference between $P_\infty$ and $R$ for pyrene might then be a measure of the unknown fraction of

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[2] Portions of this paper represent a part of the work to be submitted by Mr. D. A. Pitt to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Monsanto Fellow in Chemistry, 1956–1957.

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the induced polarization of acepleiadylene. The results are listed in Table I. Since the $P_\infty$ and $R$ values are identical within our experimental error, it may be assumed that the $R$ value for acepleiadylene represents the total induced polarization. This assumption is supported by the value of $a_\infty$ from Table II in spite of the fact that the sodium-D line is close to an absorption band of acepleiadylene ($\lambda$ = 555 m$\mu$), a condition which might lead to an abnormal refraction.

TABLE II

SLOPES OF DIELECTRIC CONSTANT AND LOSS, AND RELAXATION TIMES OF ACEPLEIADYLENE IN BENZENE SOLUTION AT 30°

| $\lambda$, cm. | $\alpha'$ ± 0.01 | $\alpha''$ ± 0.001 | $\tau \times 10^{12}$, sec. |
|---|---|---|---|
| 1.25 | 2.42 | 0.097 | 20.2 |
| 3.22 | 2.52 | .140 | 19.2 |
| 10.0 | 2.63 | .114 | 23.2 |
| 25.0 | 2.69 | .058 | 21.2 |
| 50.0 | 2.69 | .029 | 19.7 |
| | $a_\infty$ = 2.37 | Av. | 20.7 ± 1.2 |

The results of the measurements at microwave frequencies are listed in Table II. While Debye behavior remains a possibility, in view of the uncertainty cited for $a'$, the most probable values of $a'$ and $a''$ indicate $\alpha$ = 0.09 and $\tau$ = 20.7 ± 1.2 $\mu\mu$sec. Assuming Debye relaxation ($\alpha$ = 0), $\tau$ = 24.3 ± 2.1 $\mu\mu$sec. which may be considered a maximum value.

## Discussion

The most probable value for the dipole moment of acepleiadylene appears to be $0.49 \times 10^{-18}$. This was obtained by comparing the value of $0.47 \times 10^{-18}$ calculated from $a_\infty$ with the value of $0.51 \times 10^{-18}$ calculated from $\gamma'$, both by the Halverstadt-Kumler method.[16] The moment is about 50% of the value predicted by Pullman, *et al.*,[4] indicating the approximate character of the molecular orbital calculations. The inadequacy of the calculation may possibly be ascribed to steric factors. The dipole moment of azulene has been found[17] to be $1.0 \times 10^{-18}$. Since the distance between the seven- and five-membered rings is smaller than in acepleiadylene, the separation of a greater quantity of charge is indicated in azulene. The distorting influence of the relatively rigid naphthalene nucleus in acepleiadylene apparently affects the ease of displacement of charge from the seven- to the five-membered ring as a result of the geometrical requirements of the acepleiadylene ring system.

The relaxation time of the acepleiadylene molecule in benzene solution is in reasonable agreement with values obtained for other planar aromatic compounds of similar size and shape. Fischer[18] has reported values, at 23°, of 17.7, 15.7 and 19.2 ($\times 10^{-12}$ sec.) for $\alpha$-bromonaphthalene, $\alpha$-chloronaphthalene and 1-chloroanthraquinone, respectively. That these are of the same order of magnitude is to be expected since the longest dimension of acepleiadylene is comparable to that of anthraquinone. A more detailed comparison is not warranted because of complications introduced by the position of the dipole axis relative to the major axes of the molecule and by the possibility of a distribution of relaxation times.

**Acknowledgment.**—The authors are indebted to Professor V. Boekelheide of the University of Rochester for his extensive work in synthesizing a quantity of acepleiadylene sufficient for dielectric characterization.

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# Electric Properties of Macromolecules. I. A Study of Electric Polarization in Polyelectrolyte Solutions by Means of Electric Birefringence[1]

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An investigation was made of electric birefringence in dilute solutions of a homogeneous preparation of the rod-like Tobacco Mosaic Virus (TMV). Variables studied included TMV and electrolyte concentrations, *p*H, field strength and frequency of the polarizing field, and the behavior in various transient fields. Some new experimental methods are described. The sign and magnitude of the intrinsic Kerr constant, its frequency dependence and the transient behavior show that orientation is produced by an induced polarization about 50 times greater than expected from electronic and atomic effects, and that the permanent dipole coupling is negligible. It is proposed that the large electric anisotropy arises because of polarizability of the ion atmosphere. The phenomena are interpreted with the aid of calculations on models incorporating a surface conductivity related to the relatively high local concentration of counterions at low ionic strengths. Results are in order-of-magnitude agreement with theoretical expectations on this basis. They cannot be explained with Jacobson's proposal of an ice-like hydration shell. Relaxation properties are qualitatively accounted for with the proposed model. No evidence could be found in the experimentally accessible *p*H region for a large contribution from the proton polarization of Kirkwood and Shumaker, which can be incorporated as an additional term in the surface conductivity. The significance of the counterion polarization in interpretation of the dielectric properties of proteins and other polyelectrolytes is discussed.

## Introduction

Although a large number of investigations of the dielectric properties of macromolecular solutions have been reported in the last two decades, interpretations of the experimental results for polyelectrolytes such as the proteins and nucleic acids have been seriously limited by the inadequate understanding of the mechanisms by which electric polarization is produced in such systems. Aside

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[1] This work is based upon the Thesis submitted by A. J. Haltner for the Ph.D. degree in Chemistry, January, 1955. Presented at the 131st meeting of the American Chemical Society in Miami, April, 1957.

[2] National Science Foundation Fellow, 1953–1954.