tained by using the O'Dwyer and Sack expression, the correspondence obtained by using the Powles expression and then correcting for viscous effects seems more reasonable.

With the notable exception of 2-methylnaphthalene, the agreement among the τ_μ/η values is comparable to that in column 3 of Table IV. The apparent anomaly in the high τ_μ/η value for 2-methylnaphthalene is significant in that it is the only compound listed in which the direction of the dipolar axis is not nearly parallel to the carbon-carbon bond held in common by the two rings. For this reason, therefore, the first six compounds in the table could equally well be grouped together on the basis of "electrical shape," in which case the use of τ_μ/η for purposes of comparison is to be preferred over the use of τ_M/η.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XXII. The Dielectric Relaxation Times of Three Prolate Ellipsoidal Molecules in Benzene Solution[1,2]

BY DONALD A. PITT AND CHARLES P. SMYTH

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The dielectric constants of benzene solutions of anthrone, fluorenone and phenanthrenequinone have been measured at 1.25, 3.22, 10.0, 25.0 and 50.0 cm. wave length at temperatures of 20, 40 and 60°. The relaxation time and its distribution parameter for each solute have been determined from arc plots of the slopes at each wave length of the curves for the dependence of dielectric constant and loss upon the concentration of the solute. Anthrone and fluorenone have values of relaxation time which would be anticipated from their molecular sizes and shapes, but the value for phenanthrenequinone is anomalously high. This may be due to a greater volume swept out by this molecule in orienting about its long axis.

The dielectric relaxation of dipolar molecules in solution provides a means of investigating the viscous drag forces which hinder the rotation of the polar solute molecules. The quantitative effects of solvent viscosity, of the volume and shape of the solute molecule and of position of the dipole moment within the solute molecule are not yet wholly clear. To further the study of the latter factors, the dielectric relaxation properties of three roughly ellipsoidal polar molecules have been examined.

Materials.—Anthrone from Brothers Chemical Co. was successively crystallized from benzene and ethanol and thoroughly dried in an Abderhalden pistol. The purified material retained a pale yellow tint; m.p. 155°; lit.[3] 154–155°.

9-Fluorenone obtained from Brothers Chemical Co., was recrystallized from absolute ethanol, forming flat needles having a bright yellow color. After drying, these melted sharply at 84°; lit.[4] 84°.

9,10-Phenanthrenequinone obtained from Eastman Kodak Organic Chemicals was twice recrystallized from dioxane and dried *in vacuo*. The orange needles melted at 208°; lit.[4] 207°.

Benzene of analytical reagent grade, Merck and Co., was used without purification. The dielectric loss at 20° and 1.25 cm. wave length was less than 10% higher than that obtained with benzene dried over sodium hydride and fractionally distilled immediately before use. The static dielectric constants were 2.2854, 2.2454 and 2.2055 at 20, 40 and 60°, and the refractive indices were 1.5009, 1.4889 and 1.4776.

Methods of Measurement.—The static dielectric constant was measured at a frequency of 520 kilocycles/sec., using heterodyne-beat equipment.[5–7] Microwave measurements of dielectric constant and loss at 1.25 and 3.22 cm. wave lengths were carried out with wave guide apparatus.[8,9] The standing-wave method of evaluating dielectric loss was applicable for all solutions. A coaxial resonant cavity apparatus[10] was employed with radiation of 10.0, 25.0 and 50.0 cm. wave length. The concentrations of solutions used in this apparatus were considerably lower than for the wave guide equipment to keep the loaded cavity loss tangent below 0.02.

Refractive indices were measured with a Pulfrich refractometer for the sodium-D line, and densities were determined with a graduated pycnometer, as described by Robertson.[11]

Experimental Results

The dielectric constant, ϵ', and loss, ϵ'', of dilute solutions of polar molecules in non-polar solvents have been shown[12] to be linear functions of concentration for non-associated solutes, that is

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

where c_2 is the mole fraction of the polar solute, and the subscripts 1 and 2 refer to solvent and solute, respectively. Similarly

$$\epsilon_0 = \epsilon_1 + a_0c_2$$
$$n_D^2 = (n_D)_1^2 + a_Dc_2$$
$$v = v_1 + \beta'c_2$$

where ϵ_0, n_D^2 and v are the static dielectric constants, the square of the refractive index and the specific volume of the solution, respectively.

These experimental data, obtained from measurements of two to five solutions at each frequency, are given in Table I. Heterodyne-beat measurements of ϵ_1 were used in the calculation of a' at all frequencies. Measurements of the dielectric loss of the pure solvent were used to correct the ϵ'' data of solutions for combined wall and solvent losses.

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(1) This research has been supported by the Office of Naval Research. Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

(2) This article represents a portion of the work submitted by Mr. Donald A. Pitt to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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The solvent loss was of the order of half the wall conductivity loss at 1.25 cm. wave length.

TABLE I

SLOPES FOR THE DEPENDENCE OF THE DIELECTRIC CONSTANT AND LOSS OF SOLUTIONS ON MOLE FRACTION OF SOLUTE

Solute	Wave length, cm.	20° a'	20° a''	40° a'	40° a''	60° a'	60° a''
Anthrone	1.25	3.7	4.5	4.4	5.1	5.3	5.4
	3.22	7.4	7.0	8.7	6.9	9.5	6.2
	10.0	14.9	6.2	14.7	5.0	14.5	3.7
	25.0	18.0	3.3	16.8	2.5	15.5	1.7
	50.0	18.9	2.2	17.3	1.4	15.6	0.9
Fluorenone	1.25	3.6	4.4	4.2	4.7	4.8	4.9
	3.22	7.5	6.3	8.5	5.9	9.2	5.2
	10.0	13.6	5.0	13.1	3.8	12.8	2.5
	25.0	15.8	2.4	14.6	1.8	13.6	1.4
	50.0	16.3	1.6	14.9	1.1	13.6	0.8
Phenanthrenequinone	1.25	7.4	8.5	8.4	9.4	9.5	10.0
	3.22	12.8	13.4	15.8	13.4	18.7	12.2
	10.0	27.6	13.5	29.5	11.2	28.2	8.3
	25.0	36.6	8.9	34.3	6.2	32.1	4.6
	50.0	38.3	5.0	35.7	3.5	32.3	2.4

The relaxation times, τ, were obtained by the arc plot method of Cole and Cole.[12,13] The distribution parameter, α, was obtained from the arc plot, the radius between a_0 and the arc center being depressed $\alpha\pi/2$ below the abscissa axis. The high-frequency intercept of the arc with the abscissa axis is designated as a_∞ and is listed with values of τ and α in Table II.

TABLE II

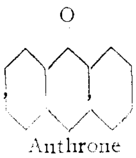
SLOPES FOR THE DEPENDENCE OF STATIC DIELECTRIC CONSTANT, SQUARE OF REFRACTIVE INDEX AND SPECIFIC VOLUME ON MOLE FRACTION, WITH INFINITE-FREQUENCY INTERCEPTS, DISTRIBUTION PARAMETERS, RELAXATION TIMES (10^{-12} SEC.) AND DIPOLE MOMENTS (10^{-18} E.S.U.-CM.)

Solute	Temp., °C.	a_0	a_D	a_∞	β'	α	τ	μ
Anthrone	20	19.55	0.90	1.3	−0.794	0.14	24.8	3.63
	40	17.66	0.96	1.4	− .843	.11	18.4	3.63
	60	15.87	1.09	1.5	− .921	.09	13.6	3.60
Fluorenone	20	16.78	0.87	1.0	− .691	.13	19.9	3.38
	40	15.18	0.98	1.1	− .735	.12	14.9	3.38
	60	13.74	1.10	1.2	− .778	.09	11.5	3.34
Phenanthrenequinone	20	40.50	1.27	2.8	−1.097	.15	31.3	5.36
	40	36.67	1.52	3.0	−1.082	.12	22.2	5.36
	60	32.97	1.72	3.1	−1.177	.12	16.1	5.31

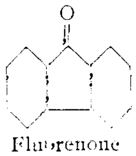
The dipole moment was calculated from the refractive indices and static dielectric constant values by using the equation of Halverstadt and Kumler[14] to evaluate the molar refraction and molar polarization. The resulting moment values, μ, are listed in Table II.

Discussion of Results

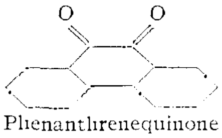
The three polar molecules anthrone, fluorenone and phenanthrenequinone have planar or approximately planar configurations, with the dipole moment of each molecule on one of the minor axes of symmetry, perpendicular to the long axis of the molecule.



Anthrone



Fluorenone



Phenanthrenequinone

The relaxation time of fluorenone in benzene solution has been reported recently by Chau, LeFèvre and Tardif[15] from measurements at a single wave length of approximately 10 cm. Their value of 17.0 $\times 10^{-12}$ sec. at 25° is only 2% above the value of 16.7 $\times$ 10^{-12} obtained by interpolation on the activation energy plot of our data based on measurements at five wave lengths from 1.25 to 50.0 cm. 9-Nitroanthracene in benzene was found by Chau, *et al.*, to have a relaxation time of 28 $\times$ 10^{-12} at 12°. This compound, very similar in molecular size, shape and polarity to anthrone, has a similar relaxation time to anthrone, for which a value 29.4 $\times$ 10^{-12} may be found from extrapolation to 12°. The 1,8-dichloroanthraquinone molecule, measured by Fischer[16] by a calorimetric method at a single frequency, has a relaxation time at 23° of 52.0 $\times$ 10^{-12} sec. Due to the bulk of the protruding chlorine atoms, such a value might be expected from the results of the present study. It is evident that the values of the relaxation times of anthrone, fluorenone and phenanthrenequinone, obtained from data at five high frequencies and the static dielectric constants, are consistent with the results of previous measurements at a single high frequency.

The values of the dipole moments in Table II are in good agreement with earlier measurements in benzene solution for anthrone, 3.66,[17] and for fluorenone, 3.35[18] and 3.29,[19] but are somewhat lower than the earlier value, 5.57,[20] for phenanthrenequinone. As this earlier value was the result of careful dipole moment measurements, the present incidentally calculated value is not to be regarded as superseding it.

From a plot of ln $T\tau$ as a function of reciprocal temperature, the activation energies and entropies for the relaxation process were determined. The values are given in Table III.

TABLE III

MOLECULAR DIMENSIONS (Å.), MOMENTS OF INERTIA AND ACTIVATION ENERGIES (KCAL./MOLE) AND ENTROPIES (E.U.) FOR DIELECTRIC RELAXATION

	Anthrone	Fluorenone	Phenanthrenequinone
A	11.35	11.35	11.2
B[a]	7.2	7.05	7.9
C	3.85	3.4	3.4
Ia	536	576	708
Ib[a]	1960	1430	1510
Ic	2420	2010	2450
$\Delta H^{\ddagger}$	2.1	2.0	2.6
$\Delta S^{\ddagger}$	−2.7	−2.6	−1.6

[a] Axis parallel to the resultant dipole moment.

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Although the measured relaxation times of these three molecules are of the order of magnitude to be expected from their molecular sizes and shapes, the reasons for the differences among the values for the three molecules are not obvious. The Stuart–Briegleb models show their lengths to be practically the same (Table III). The thickness of the anthrone molecule is a little greater and its width a little less than that of fluorenone. The fluorenone and phenanthrenequinone molecules differ by less than 3% in dimensions, so that, qualitatively speaking, one would anticipate little difference in relaxation time for the three substances.

The results lend themselves to quantitative examination in terms of the semi-empirical equations of Chau, LeFèvre and Tardif[15]

$$\tau = 4\pi\eta_1\alpha_0(\exp \Delta_1)(\exp h^2)^2/(\epsilon_1 + 2)kT \qquad (1)$$

$$\tau = \pi\eta_1(\exp \Delta_1)ABC/2(\epsilon_1 + 2)kT \qquad (2)$$

where η_1 is the solvent viscosity, Δ_1 is the depolarization factor of benzene and h is a shape factor.[21] The latter is defined by

$$h^2 = [(A - B)^2 + (A - C)^2 + (B - C)^2]/(A + B + C)^2$$

where A, B and C are the lengths of the molecular ellipsoid along its principal axes. As shown in Table IV, these equations give values of the right order of magnitude and about the right temperature dependence. The calculated differences between anthrone and fluorenone by eq. 1 are, however, in the wrong direction, as are the differences between anthrone and phenanthrenequinone given by eq. 2.

TABLE IV

CALCULATED RELAXATION TIMES (10^{-12} SEC.) BY THE EQUATIONS OF CHAU, LEFÈVRE AND TARDIF (1,2), OF SPERNOL, GIERER AND WIRTZ (3), AND OF FISCHER (4)

t, °C.	Equation	Anthrone	Fluorenone	Phenanthrenequinone
20	1	24.2	25.1	25.3
	2	28.4	24.6	27.2
	3	24.1	19.5	22.8
	4	100.3	90.8	107.3
40	1	17.5	18.5	20.5
	2	20.3	17.6	19.4
	3	17.5	14.1	16.6
	4	71.0	64.3	76.0
60	1	13.6	14.5	15.5
	2	15.3	13.2	14.6
	3	13.4	10.8	12.7
	4	53.0	48.0	56.7

The equation of Wirtz and co-workers[22] (3) gives the relaxation time in terms of the microfriction factor f_r.

$$\tau = 4\pi\eta_1 r_2^3 f_r/kT \qquad (3)$$

$$r_i = (0.556\ M_i/\pi d_i N)^{1/3} \qquad (3a)$$

$$f_r = [(6r_1/r_2) + (1 + r_1/r_2)^{-3}]^{-1} \qquad (3b)$$

In these equations, r_1 and r_2 are the mean radii of the solvent and solute molecules, respectively, as given by eq. 3a, where M is the molecular weight, d the density, N the Avogadro number, and the remaining symbols have their usual significance. The Wirtz equation is very satisfactory for anthrone and for fluorenone. Since the molecular dimensions play a dominant part in these equations, they give nearly equal relaxation times for the three solutes, thus failing to predict the considerably higher values observed for phenanthrenequinone. Based on Perrin's[23] theory, the Fischer[16] equation

$$\tau = \pi\eta f ABC/2kT \qquad (4)$$

with $\eta = \eta_1$ and the friction factor, f, as tabulated by Budó, Fischer and Miyamoto,[24] yields relaxation times which are much higher than those observed. However, the relative order of the three relaxation times is predicted.

While the effect of molecular moment of inertia on the value of the relaxation time has been shown to be insignificant at these frequencies in comparison to molecular volume,[25] it is interesting to note that phenanthrenequinone has a considerably larger moment of inertia about its long axis than the other two molecules. Also, a mean of the moment of inertia about axes a and c, as suggested by Powles,[25] is in the order of progression of the observed relaxation times.

The equations which have been considered are concerned primarily with the over-all molecular volume and do not adequately account for the effects of the differences in volume swept out in rotation around different molecular axes. The effect of these differences has been demonstrated by the relaxation times of trimethylpyridine, in which the molecular dipole lies in the plane of the ring, and trimethyltrioxane,[26] in which the dipole is perpendicular to this plane. Two substituted porphyrazines,[10] with analogous dipole moment directions, have shown similar behavior. In each case, the disk-like molecule having its moment perpendicular to the plane of the disk has about twice the relaxation time of its analog because the dipole orientation can occur only by rotation out of the plane of the disk. The volume swept out by phenanthrenequinone in rotation about the long axis, given approximately by $\pi A^2B/6$, is about 25% greater than that of fluorenone and about 20% greater than that of anthrone. This is in contrast to the fact that the volume of the phenanthrenequinone molecule $\pi ABC/6$ is 10% greater than that of fluorenone and 5% less than that of anthrone. The volumes swept out parallel, in relative magnitude, the observed relaxation times in Table II, indicating their importance in determining the relaxation process.

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