curves are compared in Table I. The final results are as follows.

	$[(CH_3)_2SiS]_2$	$[(CH_3)_2SiS]_3$
Si–S, Å.	2.18 ± 0.03	2.15 ± 0.03
∠SSiS	105°	115°
∠SiSSi	75°	110°
∠CSiC	110° (assumed)	110° (assumed)

TABLE I

		$[(CH_3)_2SiS]_2$			$[(CH_3)_2SiS]_3$	
Max.	Min.	$q_{obsd.}$	$q_B/q_{obsd.}$	$q_{B'}/q_{obsd.}$	$q_{obsd.}$	$q_E/q_{obsd.}$
1		13.4	(0.934)	(0.927)	7.7	(0.934)
	2	17.1	(1.027)	(0.958)	10.4	(0.826)
2		20.1	1.009	1.009	13.1	(0.938)
	3	23.1	1.021	1.013	16.6	(1.005)
3		25.6	1.003	0.996	19.7	1.031
	4	28.7	0.986	.984	22.6	1.017
4		31.6	0.989	.977	25.0	0.968
	5	34.7	0.994	.997	27.5	0.981
5		38.1	1.005	.998	30.0	1.009
5′		..	...	...	33.4	1.008
	6	43.2	1.006	1.002	35.9	1.008
6		48.5	0.988	0.994	39.2	1.026
	7	53.0	0.995	0.987	44.2	0.998
7		57.4	0.993	0.989	48.3	1.009
	8	61.7	1.005	1.011	53.2	1.004
8		66.3	1.004	1.004	57.7	1.000
	9	70.8	1.005	1.003	62.7	0.991
9		75.5	1.003	1.006	67.1	1.010
	10	..	...	...	72.7	0.984
10		..	...	...	76.6	1.003
	11	..	...	...	81.0	1.009
11		..	...	...	86.1	1.007
Av.			1.000	0.998		1.003
Av. dev.			±0.008	±0.008		±0.011

The values 2.18 and 2.15 Å., obtained for the bonded Si–S distance of these compounds, agree within the limits of error with the value of 2.15 Å. given by Schomaker and Stevenson's rule.[4]

The crystal structure of silicon disulfide was studied by Bussen, *et al.*,[5] who found that it had a two-dimensional fibrous structure composed of cyclic four-membered rings $(Si–S)_2$. They obtained 2.14 Å. for the Si–S bond length and 100 and 80° for the bond angles of silicon and sulfur, respectively. Our values for the bond length and bond angles of the disilthiane are in comparatively good agreement with those of silicon disulfide; these data suggest that the Si–S bond of silthianes is largely ionic, a characteristic which may be responsible for the ready cracking of trisilthiane to disilthiane.

Kurita and Kondo,[6] assuming the atomic polarization of trisilthiane to be of the same magnitude as that of the corresponding oxygen compound, hexamethylcyclotrisiloxane, estimated the dipole moment of trisilthiane as 1.03 *D*. As this large moment rules out a planar symmetrical structure similar to that of trisiloxane, they suggest that trisilthiane has predominantly a chair configuration; their conclusion is consistent with the results of our electron diffraction study.

This investigation was supported by the Grant-in-Aid for Fundamental Scientific Research of the Ministry of Education.

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[CONTRIBUTION NO. 1290 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Dynamic Electrical Birefringence of Rigid Macromolecules

BY IGNACIO TINOCO, JR.[1]

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Benoit's theory of the dynamic electrical birefringence of rigid macromolecules under the action of a rectangular electrical pulse has been extended to include the effect of a transverse component of the permanent dipole moment, and the effective orienting field acting on the permanent dipole has been explicitly considered. The proton polarizability contribution to the induced dipole moment introduced by Kirkwood and Shumaker has also been considered. A new interpretation of Benoit's electrical birefringence measurements on nucleic acid has been made.

Introduction

The theory of the dynamic double refraction in a sinusoidal electric field was developed by Peterlin and Stuart.[2] Subsequently Benoit[3] considered the birefringence produced by a rectangular electrical pulse acting on a dilute solution of rigid macromolecules. As a model for the macromolecule he chose an ellipsoid of revolution with a permanent dipole moment along the axis of revolution whose principal geometrical, optical and electrical axes coincided. His very thorough treatment of this system has been used to interpret the electrical birefringence of protein solutions.[3,4]

Benoit's model of a protein molecule can be improved by removing the restriction that the dipole moment be along the axis of revolution and by including the Kirkwood–Shumaker[5] concept of the mobile proton contribution to the polarizability. Consideration of this model shows that electrical birefringence (Kerr effect) measurements, unlike dielectric dispersion,[5] can be used to determine unambiguously rotary diffusion coefficients for pro-

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[1] Public Health Service Research Fellow of the National Cancer Institute.

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teins, and that both the mean permanent dipole moment and the fluctuating dipole moment due to proton migration can in principle be determined.

Theory

The birefringence of a solution of non-interacting rigid macromolecules under the action of a rectangular electrical pulse will be considered. Benoit's model for the macromolecule will be used, except for the modifications mentioned previously.

Consider a rigid ellipsoid of revolution with rotary diffusion coefficients[6] Θ_1 and $\Theta_2 = \Theta_3$ for rotation about the symmetry and transverse axes, respectively. The components of the mean permanent dipole moment along these axes are μ_1 and $\mu_2 = \mu_3$. The principal axes of polarizability (which lie along the geometrical axes) also define an ellipsoid of revolution. The principal polarizabilities are a function of the frequency of the applied electrical field; they are determined by the refractive indices n_1, $n_2 = n_3$ at the optical frequencies of the incident light, and the permittivities ϵ_1, $\epsilon_2 = \epsilon_3$ at the lower frequencies comprising the Fourier spectrum of the applied electrical pulse. Both the refractive indices and the permittivities may show dispersion in their respective frequency ranges.

The ellipsoid is immersed in a continuous medium with refractive index n_0 and permittivity (equal to the dielectric constant) ϵ_0. Its position with respect to a fixed external coördinate system is determined by the three Eulerian angles θ, χ and ϕ. The angle between the direction of the homogeneous parallel electric field and the symmetry axis of the ellipsoid is θ; χ measures the rotation about this axis; and ϕ is the colatitude of this axis.

Orientation.—The potential energy W of the ellipsoid in the electric field consists of a term linear in the electric field strength E and a quadratic term. The quadratic term is[3]

$$W_2 = (-1/2)v(g_1^\circ \cos^2\theta + g_2^\circ \sin^2\theta)E^2 \qquad (1)$$

v = vol. of ellipsoid
$g_i^\circ = (\epsilon_i - \epsilon_0)/[4\pi + (\epsilon_i - \epsilon_0)L_i/\epsilon_0]$ = polarizability per unit vol. of ellipsoid
L_i = a form factor which depends only on the axial ratio of the ellipsoid; it is defined in references (2) and (3)
i = 1 and 2 along the symmetry axis and transverse axes, respectively
E = the external field strength.

The linear term is

$$W_1 = -\mu_1 E_{r_1}\cos\theta - \mu_2 E_{r_2}\sin\theta(\sin\chi - \cos\chi) \qquad (2)$$

If the dipole moment is assumed to be a point dipole situated at the center of symmetry of the ellipsoid,[7] the orienting field acting on the dipole is[9] $E_{ri} = E/[1 + (\epsilon_{ei} - \epsilon_0)L_i/4\pi\epsilon_0]$, where $\epsilon_{e,i}$, the electronic contribution to the permittivity, is equal to n_i^2 extrapolated to infinite wave length. For a sphere with a permittivity of unity the orienting field reduces to the Onsager field.[10]

The distribution function $f(\theta, \chi, t)$ of ellipsoids in the electric field is determined by the general diffusion equation[11,12]

$$Lf - \frac{\partial f}{\partial t} = -Qf \qquad (3)$$

$$Lf = -\frac{\Theta_2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \left(\Theta_2\frac{\cos^2\theta}{\sin^2\theta} + \Theta_1\right)\frac{\partial^2 f}{\partial\chi^2} \qquad (4)$$

$$Qf = \frac{\Theta_2}{kT}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(f\sin\theta\frac{\partial W}{\partial\theta}\right) + \frac{\partial}{\partial\chi}\left[f\frac{\partial W}{\partial\chi}\left(\cot^2\theta + \frac{\Theta_2}{\Theta_1}\right)\right]\right\} \qquad (5)$$

$$\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\frac{f}{8\pi^2}\sin\theta d\theta\, d\chi d\phi = 1 \qquad (6)$$

k = Boltzmann constant
T = absolute temperature

The equation can be solved using the perturbation method of Kirkwood[11] in which both the operator Q and the distribution function f are expanded in powers of the field strength. Only the first two terms in the expansion were considered in this work.

$$f = 1 + f^{(1)}E + f^{(2)}E^2 \qquad (7)$$

$$Q = Q^{(1)}E + Q^{(2)}E^2 \qquad (8)$$

The inhomogeneous differential equations obtained by equating the coefficients of powers of the field strength are then solved by expanding the distribution function in terms of the eigenfunctions ψ_λ of the operator L. The eigenfunctions in this case are the spherical harmonics.

$$L\psi_\lambda + \lambda\psi_\lambda = 0 \qquad (9)$$

$$f = \sum_\lambda a_\lambda(t)\psi_\lambda(\theta,\chi) \qquad (10)$$

To determine f completely only the boundary conditions are needed. We shall consider f in two parts: (a) after the application of an electric field as a step function, (b) after the removal of the electric field. The boundary conditions are: (a) $f = 1$ at $t = 0$, (b) f = any function $f'(\theta, \chi)$ at $t = 0$.

Birefringence.—The birefringence of the system of ellipsoids, obtained by applying the familiar formula, $n^2E = E + 4\pi P$, is given by[3]

$$n_z - n_x = \frac{n_z^2 - n_x^2}{2n_0} = \frac{V(g_1 - g_2)}{8\pi n_0}\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} f(3\cos^2\theta - 1)\sin\theta d\theta d\phi d\chi \qquad (11)$$

n_z = refractive index in the direction of the electric field
n_x = refractive index perpendicular to the electric field
V = vol. fraction of ellipsoids in solution
$g_i = g_i^\circ$ except n_i^2 is substituted for ϵ_i

If the f obtained in the previous section is substituted in the equation, it is apparent (as $(3\cos^2\theta - 1)$ is a spherical harmonic) that only one term in the expansion of f in spherical harmonics contributes to the integral. The birefringence is thus

(a) Rise of the birefringence

$$\Delta n - n_z - n_x = (2\pi/15)(g_1 - g_2)VE^2\{p_1 - p_2 + q - (3/2)p_1e^{-2\Theta_2 t} + [6\Theta_2/(5\Theta_2 - \Theta_1)]p_2e^{-(\Theta_1+\Theta_2)t} + [p_1/2 + p_2 - q - 6\Theta_2 p_2/(5\Theta_2 - \Theta_1)]e^{-6\Theta_2 t}\}$$

$$p_i = (\mu'_i)^2/(kT)^2 \quad i = 1 \text{ or } 2$$

$$\mu'_i = \mu_i/[1 + (\epsilon_{ei} - \epsilon_0)L_i/4\pi\epsilon_0]$$

$$q = v(g_1^\circ - g_2^\circ)/kT = \text{induced dipole term} \qquad (12)$$

$$\Delta n(t \rightarrow \infty) = (2\pi/15)(g_1 - g_2)VE^2(p_1 - p_2 + q) = B\lambda E^2 \qquad (13)$$

B = Kerr constant
λ = wave length of light (*in vacuo*) used

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(6) See Edsall's article in "The Proteins," Edited by H. Neurath and K. Bailey, Academic Press, Inc., New York, N. Y., 1953, p. 668, for a discussion of the relation of rotary diffusion coefficients to the semi-axes of the ellipsoid.

(7) In a protein molecule the center of drag must be chosen for the center of the coördinate system defining the dipole moment.[5,8]

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(b) Decay of the birefringence

$$\Delta n = \Delta n_0 e^{-6\Theta_2 t} \tag{14}$$

Δn_0 = birefringence at zero time

The decay of the birefringence equation is the same as obtained by Benoit. As the electrical field is not acting on the system during this time, the birefringence must be independent of the electrical properties of the ellipsoids.

If p_2 is set equal to zero, the rise of the birefringence equation reduces to that of Benoit, but with the important difference that what he calls μ is actually equal to μ' the apparent dipole moment in the solution and not the dipole moment of the protein.

Discussion

Although the general equation for the rise of the birefringence looks unmanageable, in practice a few simplifying approximations can be made. The rotary diffusion coefficients are either approximately equal to each other (as in oblate ellipsoids or spheres) or else $\Theta_1 >> \Theta_2$ (as in prolate ellipsoids). In either case the rise of the birefringence depends on time only through Θ_2 which is obtained from the decay of the birefringence. To determine the molecular parameters from the experimental birefringence curve[13] obtained on application of the electrical pulse the rise equation can be used in the following forms

$\Theta_1 = \Theta_2$

$$\frac{\Delta n}{\Delta n_\infty} = 1 - \frac{3\beta e^{-2\Theta_2 t}}{2(\beta + 1)} + \frac{(\beta - 2)e^{-6\Theta_2 t}}{2(\beta + 1)} \tag{15}$$

$$\beta = \frac{p_1 - p_2}{q} = \alpha_1 - \alpha_2$$

Δn_∞ = birefringence finally attained on application of an electrical field

$\Theta_1 > 20\,\Theta_2$, *i.e.*, axial ratio $\geqslant 10$

$$\frac{\Delta n}{\Delta n_\infty} = 1 - \frac{3\alpha_1 e^{-2\Theta_2 t}}{2(\beta + 1)} + \left[\frac{3\alpha_1 - 2\beta - 2}{2(\beta + 1)}\right] e^{-6\Theta_2 t} \tag{16}$$

For a prolate ellipsoid with $20 > \Theta_1/\Theta_2 > 1$ an estimated value of this ratio can be used to give a suitable expression for $\Delta n/\Delta n_\infty$. If q is not a function of time, *i.e.*, the protonic contribution is negligible, β and α_1 can be obtained from the shape of the birefringence curve and the measured Kerr constant if $g_1 - g_2$, the optical factor, is known. This factor can be obtained either from flow birefringence measurements, depolarization of scattered light, or from the Kerr effect measurements themselves by varying the refractive index of the solvent. Furthermore if the protonic contribution is negligible, then for a protein solution in water $\epsilon_i << \epsilon_0$ and q will depend only on the dielectric constant of the solvent so that μ_i' and μ_i can be determined. A short table showing the variation of μ_i'/μ_1 for this case is included to indicate the error that occurs when one neglects the difference between the external field and the orienting field.

Axial ratio p ($p > 1$ for a prolate ellipsoid)	μ_1'/μ_1	μ_2'/μ_2
0.01	∞	1
0.1	8	1.1
1	1.5	1.5
10	1	2
100	1	2

With a protonic contribution[5] to the polarizability of the ellipsoid, q will be time dependent. If we assume a single relaxation time is necessary to describe the time dependence, $q(t)$ may be written as

$$q(t) = q_e + (q_p)(1 - e^{-t/\tau}) \tag{17}$$

q_e = electronic contribution to the induced dipole moment

q_p = protonic contribution to the induced dipole moment

The relaxation time τ is a function of the translational diffusion coefficient of the protons on the protein surface and the size and shape of the molecule. Substitution of this expression into the equation for the rise of the birefringence shows that in general it will be very difficult to separate all the parameters. But if q_p is very large, *i.e.*, the induced dipole due to proton migration is the only important orienting factor, then the general equation reduces to

$$\frac{\Delta n}{\Delta n_\infty} = 1 - e^{-t/\tau} - e^{-6\Theta_2 t} + e^{-(1/\tau + 6\Theta_2)t} \tag{18}$$

and both τ and q_p can be determined It should be pointed out that q_p is a measure of the anisotropy of proton polarization and not the average proton polarization as calculated by Kirkwood.[5]

Application.—A new interpretation of some Kerr effect measurements of Benoit[3] can now be made using the preceding equations. Benoit gives a value of $(B/c)_{c \to 0} = 9.5$ cm.^{4} volt^{-2} g.$^{-1}$ as the intrinsic Kerr coefficient of a sample of thymonucleic acid which had an average length (calculated from the rotary diffusion coefficient) of about 3,200 Å. and therefore corresponded to a molecular weight of about[14] 320,000. From the flow birefringence measurement of Schwander and Cerf[14] on thymonucleic acid a value of $g_1 - g_2 = -1 \times 10^{-2}$ can be estimated.[15] This value is a very approximate one as Schwander's measurements were made in salt solutions containing varying amounts of glycerol and a rough extrapolation had to be made to estimate the desired value. The two data allow one to calculate $(p_1 - p_2 + q)$ equal to -1.3 if an average value of 5000 Å. is used for the wave length of white light.

On application of a rectangular electrical pulse, Benoit found that the rise of the birefringence was symmetrical to the decay of the birefringence, *i.e.*, for a monodisperse system $\Delta n/\Delta n_\infty = 1 - e^{-6\Theta_2 t}$. He interpreted this as indicating the nucleic acid was oriented only by an induced dipole mechanism.

A new interpretation is obtained by comparing the rise curve with the preceding equations. It is seen first that the protonic polarization is not significant so equation 16 can be used. The possibilities are therefore $\alpha_1 = 0$, $\alpha_1 = \alpha_2 = 0$, or $\alpha_2 \to \infty$. In all cases $\alpha_1 = p_1/q$ can be neglected. The induced dipole term q can be calculated from the axial ratio ($p > 100$) and the partial specific volume ($v = 0.55$)[16] of thymonucleic acid, and the dielectric constant of water ($\epsilon_0 = 80$); a value of $q = 4.6 \times 10^{-5}$ is obtained. Both q and p_1 are therefore negligible compared to p_2 which is equal to 1.3. The magnitude of the transverse dipole moment μ_2 is thus calculated to be 22,600 *D*.

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(13) The experimental techniques used in measuring the birefringence are discussed fully in reference 3.

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Dielectric dispersion measurements of Jungner and Jungner[17] on thymonucleic acid show that the component of the dipole moment along the long axis is zero and that the transverse component is directly proportional to the molecular weight. For a sample with a molecular weight equal to that of Benoit's, they give a value of the transverse dipole moment, calculated according to Kirkwood,[18] of 20,800 *D*. This is in very satisfactory agreement.

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NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Dissociation and Ionic Reactions of Dimethylgermanium Dichloride

BY EUGENE G. ROCHOW AND A. LOUIS ALLRED[1]

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In order to contribute information concerning the relative electronegativities of the Group IVB elements, the ionic dissociation and degree of hydrolysis of dimethylgermanium dichloride in water have been investigated. Comparison of the results with those for dimethyltin dichloride shows that germanium has a surprisingly high electronegativity, in keeping with recent predictions and with other experimental evidence. Some metathetic reactions of dimethylgermanium dichloride in aqueous solution also are described.

There is some controversy concerning the relative electronegativities of the Group IV elements silicon, germanium, tin and lead. In particular, Sanderson[2] shows a regression of metallic character for the first period of eighteen elements, leading to the values Si 2.6, Ge 3.6, Sn 3.1, and Pb 3.7. Older sources indicate[3] the more uniform values Si 1.8, Ge 1.7, and Sn 1.7. Chemical evidence obtained in the course of experiments on these elements in this Laboratory has indicated that germanium does indeed exhibit an electronegativity considerably higher than that of silicon or of tin.[4] Further conclusions are possible through study of the behavior of the R_2M^{++} ions, such as the dimethyltin ion $(CH_3)_2Sn^{++}$.[5–7] We are concerned here with the electrolytic dissociation, degree of hydrolysis, and metathetic ionic reactions of dimethylgermanium dichloride, particularly as they relate to the corresponding properties of dimethyltin dichloride.

Experimental

Dissociation and Hydrolysis.—Dimethylgermanium dichloride was prepared from germanium as previously described[8] and was purified by distillation. Chlorine was determined by titration with alcoholic KOH.[9] Dilute solutions were prepared and used for the cryoscopic determination of the van't Hoff *i* factor and the *p*H. The results are summarized in Table I.

TABLE I

AQUEOUS SOLUTIONS OF $(CH_3)_2GeCl_2$

Molality	0.0760	0.0350	0.0216	0.0145	0.00478	0.0019
i factor	5.01	5.03	5.21	5.19	[a]	[a]
Obsd. *p*H	1.02	1.20	1.32	1.50	2.11	2.37
Calcd. *p*H	0.82	1.16	1.37	1.54	2.03	2.42

(see Discussion)

[a] Large variations were encountered with these dilute solutions, but the average *i* was 5.0.

A solution of 1.2479 g. of $(CH_3)_2GeCl_2$ in 125.0 ml. of water was titrated with 0.0976 *N* NaOH, measuring the *p*H with a Beckman meter. The result of 125 observations during the titration is given on curve A of Fig. 1, in which the equivalents of base per equivalent of $(CH_3)_2GeCl_2$ are plotted against *p*H. The results of titrating a 0.1016 *N* solution of $(CH_3)_2SnCl_2$ with base by the same technique (from ref. 5) are plotted on the same scale (curve B) for comparison. While precipitation of dimethyltin oxide occurred at approximately one equivalent of base per equivalent of $(CH_3)_2SnCl_2$, in the present work no dimethylgermanium oxide precipitated at any point.

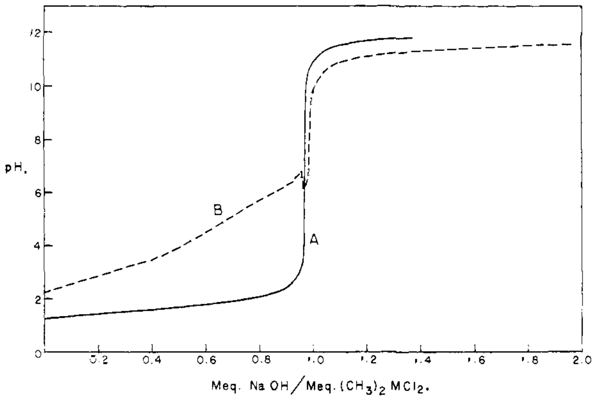

Fig. 1.

Compounds of the Dimethylgermanium Cation.—When an acidified aqueous solution of $(CH_3)_2GeCl_2$ is treated with hydrogen sulfide, a precipitate of white waxy dimethylgermanium sulfide forms at once.[10] The possibility of similar reactions was studied as a rapid means of preparing new organogermanium compounds. Two methods were used: (1) $(CH_3)_2GeCl_2$ was added to an aqueous solution of the desired anion and the product isolated by filtration or evaporation, or (2) an anion-exchange resin was treated with a solution containing the desired anion, washed with water, and then treated with a solution of $(CH_3)_2GeCl_2$.

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