measurements, the parameter a has a value ranging from 4 to 8 A and increasing as the ions are larger. In other words, the K values are in reasonably good accord with Bjerrum's theory. In water, however, the a values derived from the K_a values of Table 1 are not in accord with this theory. For Bu_4NI the value found for a, calculated on the basis of $K_a = 3.87$, is only 1.02 A. Clearly, in this instance, the parameter a no longer has physical meaning. For Bu_4NBr, the value of a is found to be 1.93 A. In other words, the parameter a for the bromide is nearly twice that of the iodide.

We are presently carrying out an analysis of conductance data for solutions in dioxane-water mixtures. We shall report the results in a later communication.

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THE OPTICAL ROTATORY DISPERSION OF SIMPLE POLYPEPTIDES. I

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In a recent communication[1] the optical rotatory powers of helical macromolecules were investigated. It was shown that, under favorable circumstances, an abnormal frequency dependence should lead to marked departures from the simple Drude equation.

The purpose of the present note is twofold. In the first place, we shall propose an alternative phenomenological equation to describe the more complex dispersion that is sometimes observed for helices. The equation involves three constants, two of which should be more or less invariant properties of the helical skeleton itself; the latter should be independent of temperature, solvent, and the nature of the side chains for a given skeletal conformation. We shall then describe the observed dispersion for poly-γ-benzyl-L-glutamate and for poly-α-L-glutamic acid, a preliminary account of which has been published elsewhere.[2, 3] There is strong experimental evidence that, under the right conditions, both polymers exist in the α-helical configuration;[4, 5] it also seems clear that the screw senses of the helices are well defined, though whether these are right- or left-handed for given side chains remains to be established. The rotatory dispersion curves are anomalous in both cases, as had been predicted. Their more detailed analysis is also in satisfactory accord with the phenomenological equation proposed as a result of the theory.

In a forthcoming note,[6] the molecular theory is applied in greater detail to the α-helix. On the basis of dichroic studies of myristamide by Peterson and Simpson,[7] it is suggested that the experimental evidence presented here is consistent with the view that the screw sense of both helices is right-handed.

ANALYSIS OF THE DISPERSION

It is profitable, at first, to consider why so many systems which are transparent through the near ultraviolet should show the simple dispersive behavior of a single-term Drude equation. In order to facilitate comparisons with the formulas of molecular optics, we shall begin by defining the most convenient quantities with which to work.

Instead of the specific rotation $[\alpha]$, it is preferable to use what may be called "effective molecular rotations" $[m']$ defined by the relations

$$[m'] = \left(\frac{3}{n_\nu^2 + 2}\right)[m] = \left(\frac{3}{n_\nu^2 + 2}\right)\frac{[\alpha]M}{100}. \tag{1}$$

Here n_ν is the refractive index of the medium, the dispersion of its polarizability for light of different frequencies ν being thereby eliminated. M is the molecular weight of the optically active solute species; for polymers it is the molecular weight per residue, when $[m']$ is called the "effective residue" or monomer rotation.

If the asymmetric molecules are in their ground states and interact neither with themselves nor with the solvent, then the frequency dependence of the effective molecular rotation is given by the quantal formula[8]

$$[m'] = \sum_i \frac{a_i\nu^2}{\nu_i^2 - \nu^2}, \qquad a_i = \frac{96\pi N_0}{hc}\, r_i, \tag{2}$$

where r_i is a molecular parameter (the rotational strength) associated with the ith absorption band, which occurs at frequency ν_i in the electronic spectrum. Under these conditions, the identity[8]

$$\sum_i a_i = 0 = \sum_i r_i \tag{3}$$

holds. However, since measurements are almost always conducted under less idealized circumstances, equation (2) may be used only if it is acknowledged that the rotational strengths r_i of the various absorption bands are functions not only of the solute molecules but also of the temperature and of the solvent. Moreover, since asymmetric molecules may be expected to have asymmetric solvation shells, equation (2) cannot describe the dispersion through regions of incident light frequency where the solvent itself absorbs.

Now suppose that we have to analyze the dispersion of simple molecular systems which only begin to absorb at wave lengths appreciably shorter than those for which the rotatory power has been measured. It will always be possible formally to expand the terms of equation (2) in inverse powers of $(\lambda^2 - \lambda_0^2)$, where the wave length λ_0 is as yet undetermined:

$$[m'] = \frac{\sum_i a_i\lambda_i^2}{(\lambda^2 - \lambda_0^2)} + \frac{\sum_i a_i\lambda_i^2(\lambda_i^2 - \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2} + O[(\lambda^2 - \lambda_0^2)^{-3}]. \tag{4}$$

If $\lambda^2 \gg \lambda_0^2, \lambda_i^2$, this may be expected to converge quite rapidly. Now let λ_0^2 be determined by the relations

$$a_0\lambda_0^4 = \sum_i a_i\lambda_i^4, \qquad a_0\lambda_0^2 = \sum_i a_i\lambda_i^2. \tag{5}$$

The coefficient of $(\lambda^2 - \lambda_0^2)^{-2}$ on the right-hand side of equation (4) vanishes. Accordingly, if this λ_0^2 is positive and appreciably less than λ^2, the dispersion is well described by the simple formula

$$[m'] = \frac{a_0\lambda_0^2}{\lambda^2 - \lambda_0^2}. \tag{6}$$

This is, of course, just a slightly modified form of the single-term Drude equation. Since the dispersion of the factor $3/(n_\nu^2 + 2)$ is relatively small, it is effectively identical with this equation, whose empirical coefficients a_0, λ_0 receive their interpretation from equations (5). The optical rotatory dispersion of a large variety of molecules, including simple amino acids, di- and tri-peptides, obey equation (6) over a wide range of frequencies.[9]

It is difficult to lay down useful conditions for the validity of the simple Drude equation. We may note that, from equation (5), the contributions of the lower excited states are heavily weighted in determining λ_0^2; if these states are fairly close together, and the sum of their rotational strengths is larger than any one of these, then it is clear that λ_0^2 satisfies the required inequalities, particularly since equation (3) will be at least approximately valid. Conversely, if the sum of the rotational strengths of the lower excited states is small with respect to any one, then we may expect the dispersion to be complex, and equation (6) will not be satisfied. It is just this possibility—which must be expected whenever a principal source of the rotatory power is the asymmetric disposition of identical chromophores within a molecule—to which we attribute the anomalous dispersion of certain tartrates and, in particular, of simple polypeptides in a helical configuration.

In a helix of any great length, allowed transitions, which alone contribute to the optical rotatory power, are polarized either parallel or perpendicularly to the screw axis. (By "allowed" we do not imply that the bands need be strong.) For each parallel band there is an associated perpendicular band, and conversely. Moreover, pairs of such associated bands are rarely separated by more than 100 A or so; indeed, owing to their width, they will generally overlap. A single monomeric chromophore, like the peptide bond of a single residue, will appear in the spectrum of the α-helix as just such an overlapping pair of bands. More generally, this will be true for all monomeric chromophores which are prevented, on steric grounds or by the interposition of insulating groups, from conjugative interactions with one another. For these important, longer-wave-length systems the rotational strength of the parallel component may be exceedingly large, but it is almost exactly compensated by the opposing rotational strength of its perpendicularly polarized partner. The partial effective monomer rotation due to such a band pair may therefore be written[1]

$$\begin{aligned}[m_i'] &= \frac{a_{\|i}\lambda_{\|i}^2}{\lambda^2 - \lambda_{\|i}^2} + \frac{a_{\perp i}\lambda_{\perp i}^2}{\lambda^2 - \lambda_{\perp i}^2} \\ &\approx \frac{a_i\lambda_i^2}{\lambda^2 - \lambda_i^2} + \frac{b_i\lambda_i^4}{(\lambda^2 - \lambda_i^2)^2},\end{aligned} \tag{7}$$

since $|a_{\|i} + a_{\perp i}| \ll |a_{\|i}|$, $\lambda^2 - \lambda_i^2 \gg |\lambda_{\|i}^2 - \lambda_{\perp i}^2|$, and

$$\begin{aligned} a_i &= (a_{\|i} + a_{\perp i}) + b_i, & b_i &= (a_{\|i} - a_{\perp i})\Delta_i, \\ \lambda_i &= {}^1/_2(\lambda_{\|i} + \lambda_{\perp i}), & \Delta_i &= \frac{(\lambda_{\|i} - \lambda_{\perp i})}{\lambda_i}. \end{aligned} \tag{8}$$

Formally, we therefore adopt the modified equation

$$[m'] = \sum_i \frac{a_i\lambda_i^2}{\lambda^2 - \lambda_i^2} + \sum_i \frac{b_i\lambda_i^4}{(\lambda^2 - \lambda_i^2)^2}, \tag{9}$$

where relation (7) has been extended over all pairs of band systems; in so doing, however, we recognize that b_i may occasionally be very small but that for certain terms a_i and b_i are quite comparable. It is evident that, in the latter eventuality, the dispersion cannot be represented by a simple expression like equation (6) over any sizable range of wave lengths, except in very special circumstances.

A phenomenological form for the anticipated dispersion is obtained in much the same way as equation (6) is derived from equations (2). It takes the form

$$[m'] = \frac{a_0\lambda_0^2}{(\lambda^2 - \lambda_0^2)} + \frac{b_0\lambda_0^4}{(\lambda^2 - \lambda_0^2)^2}, \tag{10}$$

where the constants a_0, b_0, λ_0 are chosen so that

$$\begin{aligned} a_0\lambda_0^2 &= \sum_i a_i\lambda_i^2, \\ b_0\lambda_0^4 &= \sum_i [a_i\lambda_i^2(\lambda_i^2 - \lambda_0^2) + b_i\lambda_i^4], \\ \sum_i [a_i\lambda_i^2(\lambda_i^2 - \lambda_0^2)^2 &+ 2b_i\lambda_i^4(\lambda_i^2 - \lambda_0^2)] = 0. \end{aligned} \tag{11}$$

It will be valid whenever λ_0^2, so determined, is positive and considerably less than λ^2. We note that the last relation involves the sixth powers of the wave lengths. In such systems, even more than for the more simple systems discussed earlier, the dispersion is heavily dependent on the long-wave-length absorption bands and is only slightly influenced by the bands lying far out in the ultraviolet. In the event that λ_0 lies in the region of the longer-wave-length spectrum, it may happen that $|\lambda_i^2 - \lambda_0^2|$ is small with respect to λ_i^2, and equations (11) may be replaced by the simpler relations

$$\begin{aligned} a_0\lambda_0^2 &= \sum_i a_i\lambda_i^2, \\ b_0\lambda_0^4 &= \sum_i b_i\lambda_i^4, \\ b_0\lambda_0^6 &= \sum_i b_i\lambda_i^6. \end{aligned} \tag{12}$$

According to the molecular theory underlying the statements made in this paragraph, the parameters b_i, and the wave lengths λ_i for which these parameters are sizable, should be intrinsic properties of the helical skeleton; they should be insensitive—as should the constants b_0, λ_0 which they, in large measure, determine—to environmental factors such as arise from changes in solvent, temperature, and the nature of the side chains, always provided that this helical skeleton is not destroyed.

We do not, of course, claim that this analysis is any more than formal. Any results based on it are not unique. But it is no more possible at the present time to give an operational prescription for the validity of the Drude equation (6) than it is to say when our equation (10) may be expected to hold. Less so, for if it is found that b_0, λ_0 are indeed invariant properties for a given helical skeleton, under modifications affecting a_0 appreciably, our interpretation of these parameters in terms of equations (11) or equations (12) is greatly strengthened.

EXPERIMENTAL RESULTS

a) *Poly-γ-benzyl-*L*-glutamate* (*MW, 130,000*).—At 20° C. this polypeptide exists as a helix in 1,2-dichloroethane, N,N-dimethylformamide, 1,4-dioxane, and chloroform. Its optical rotatory power in these solvents is in sharp contrast to that which the polymer displays when dissolved in dichloroacetic acid at the same temperature. In the latter solvent the intramolecular hydrogen bonds are destroyed and the molecular configuration assumes a randomly coiled form.

The specific rotation of polybenzylglutamate in dichloroacetic acid decreases monotonically from −10° at 7500 A to −65° at 3400 A; the dispersion is simple and obeys the Drude equation, with λ_0 in the neighborhood of 1900 A, throughout this range of wave lengths. In the "helical" solvent, ethylene dichloride, however, the specific rotation is around $+8^1/_2°$ at 7000 A, rises to a maximum value of about $+10^1/_2°$ at 5700 A, and then decreases markedly, attaining the value of −181° at 3130 A. The behavior in chloroform, dimethylformamide, and dioxane is also anomalous, showing the same qualitative features as the ethylene dichloride solution. However, $[\alpha]$ is solvent-dependent: at 4360 A it takes the values +11°, −11°, −3°, and +1° for these respective solutions.

Our results for the "helical" solvents were fitted to equation (10) in the following manner. The specific rotations $[\alpha]$ were first converted to effective monomer rotations $[m']$, using Sellmeyer's formula to obtain suitable extrapolations for the dispersion of the refractive indices n_ν. $[m'](\lambda^2 - \lambda_0^2)$ was then plotted as a function of $(\lambda^2 - \lambda_0^2)^{-1}$ for trial values of λ_0 until a straight line was obtained. The procedure is illustrated for the ethylene dichloride solution in Figure 1. It is seen that the curvature depends fairly strongly on λ_0, whose value is therefore determined as 2120 ± 50 A. The slope of the line determines b_0, and its intercept on the ordinate axis determines a_0. For the other solutions λ_0 was found to be 2120 A also, within the limits of experimental errors. The results for these are collected in Figure 2 (*solid lines*). They may be expressed analytically in terms of equation (10), using $\lambda_0 = 2120$ A, together with the parameters assembled in Table 1. It will be remarked that, in addition to the approximate constancy of the critical wave length, the slopes of the lines are almost the same for all four solutions: both b_0, λ_0 appear to be substantially independent of the nature of the solvent, provided the helical configuration is maintained. The solvent-dependent term is clearly a_0.

Solutions of polybenzylglutamate in 1:3 ethylene dichloride:dichloroacetic acid show a most interesting behavior.[2] At 21° C. the rotatory dispersion is normal and much the same as in pure dichloroacetic acid at the same temperature: the polypeptide is randomly coiled. On raising the temperature to 41° C., however, it has been shown that the viscosity increases markedly (and reversibly) and that the optical rotatory power becomes anomalous: the helix is now the stable form. At the

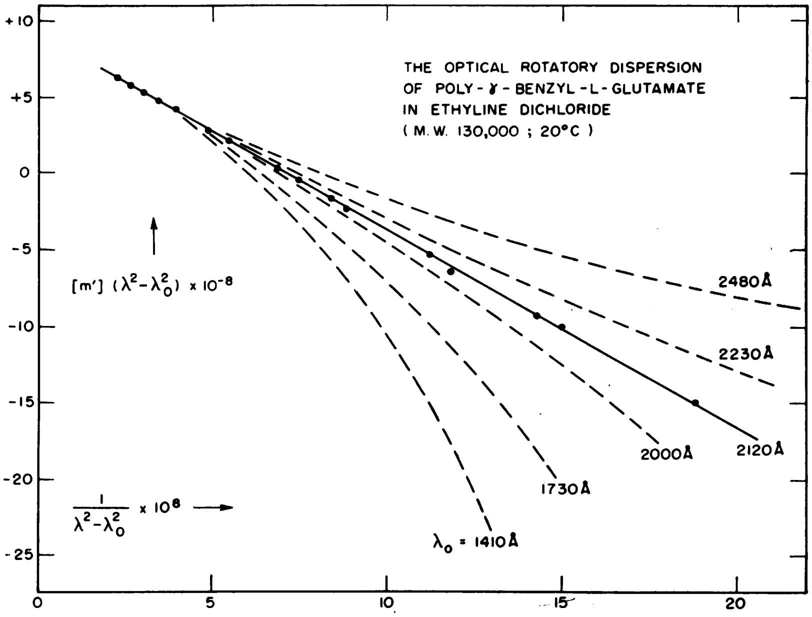
THE OPTICAL ROTATORY DISPERSION
OF POLY-γ-BENZYL-L-GLUTAMATE
IN ETHYLINE DICHLORIDE
(M.W. 130,000 ; 20°C)
$[m'] (\lambda^2-\lambda_0^2) \times 10^{-8}$
$\frac{1}{\lambda^2-\lambda_0^2} \times 10^8$
2480Å
2230Å
2120Å
2000Å
1730Å
λ_0 = 1410Å
+10
+5
0
-5
-10
-15
-20
-25
0
5
10
15
20

FIG. 1

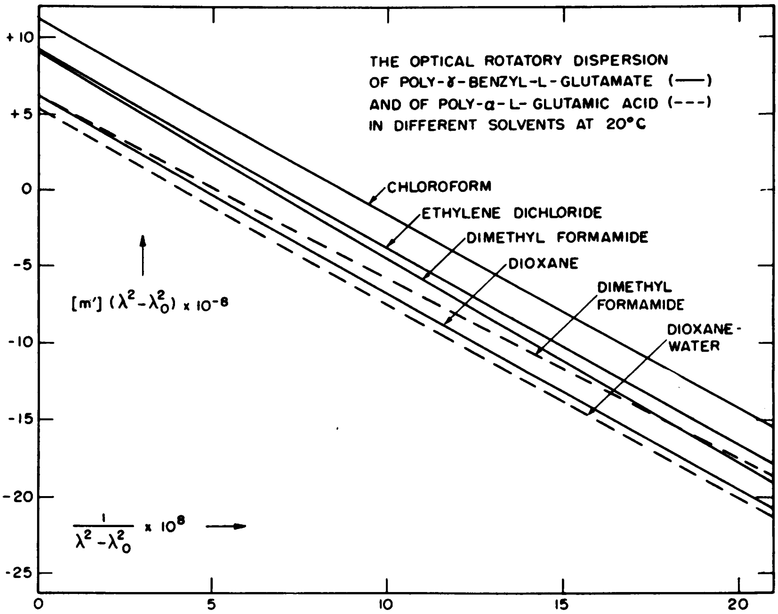
THE OPTICAL ROTATORY DISPERSION
OF POLY-γ-BENZYL-L-GLUTAMATE (——)
AND OF POLY-α-L-GLUTAMIC ACID (---)
IN DIFFERENT SOLVENTS AT 20°C
CHLOROFORM
ETHYLENE DICHLORIDE
DIMETHYL FORMAMIDE
DIOXANE
DIMETHYL FORMAMIDE
DIOXANE-WATER
$[m'] (\lambda^2-\lambda_0^2) \times 10^{-8}$
$\frac{1}{\lambda^2-\lambda_0^2} \times 10^8$
+10
+5
0
-5
-10
-15
-20
-25
0
5
10
15
20

FIG. 2

higher temperature the effective monomer rotation is very closely fitted by means of equation (10) with $\lambda_0 = 2120$ A, as before; b_0 is almost identical with that for solutions in pure ethylene dichloride at 20° C., although the intercept parameter a_0 is different. Their values are listed in Table 1.

TABLE 1*

PARAMETERS DESCRIBING THE OPTICAL ROTATORY DISPERSION (DEGREES)

	a_0	b_0
Poly-γ-benzyl-L-glutamate in		
Ethylene dichloride	205	−635
Dioxane	135	−630
Chloroform	250	−625
Dimethylformamide	200	−660
1:4 Ethylene dichloride:dichloracetic acid (44°C)	190	−630
Poly-α-L-glutamic acid in		
Dimethylformamide	135	−580
1:2 Dioxane:water (0.2 *M* NaCl, pH 4.72)	120	−625

* $\lambda_0 = 2120$ A in all cases; $T = 20°$ C. unless otherwise stated.

b) *Poly-α-L-glutamic acid* (*M.W.*, *35,000*).—Again at 20° C., polyglutamic acid exists as a helix in dimethylformamide. Its optical rotatory dispersion is anomalous in this solvent, changing sign near 4900 A to assume the large negative specific rotations at shorter wave lengths which characterize its benzyl ester. In 2:1 mixtures of 0.2 *M* aqueous sodium chloride:1,4 dioxane its behavior is strongly pH-dependent: at pH 6.56 the repulsions between the ionized carbonyl groups break down the helix and the configuration is that of an extended random coil; the rotatory dispersion is normal and closely follows the Drude equation with $\lambda_0 \approx 2100$ A. On acidifying to pH 4.72, however, the helical configuration is attained reversibly and the optical activity displays anomalous dispersion once more.

Both in the aqueous solution at pH 4.72 and in dimethylformamide, $[m']$ is found to obey equation (10) with $\lambda_0 = 2120$ A. On plotting $[m'](\lambda^2 - \lambda_0^2)$ against $(\lambda^2 - \lambda_0^2)^{-1}$, straight lines are again obtained for this critical wave length; these are shown as the broken lines in Figure 2. The parameters a_0, b_0 are listed in Table 1. The value of b_0 for the aqueous solvent falls in nicely with the similar values obtained for polybenzylglutamate, and that for the dimethylformamide solution is within 10 per cent of these: the slopes of the lines in Figure 2 are all much the same. It therefore appears that the constants b_0, λ_0 do not depend appreciably on the nature of the side chains attached to the α-helix. More data are, of course, required to establish this more firmly, but these must await the preparation of further polypeptides.

It has tacitly been assumed that the helical sense of both polypeptides is the same. Since the acid may be prepared from its benzyl ester in anhydrous benzene solution,[5] it seems unlikely that the α-helix should be destroyed and then rebuilt during the process. On forming the sodium salt, in aqueous solution, of the material so obtained, it attains the coiled conformation from which, however, it is possible to recover the acid in its helical conformation with no net change in its optical rotatory power.

The experimental details of the studies summarized in these paragraphs will be published elsewhere. The measurements ranged from 7500 A at the longer wave lengths down to 3340 A in the ultraviolet. It was found that, in each case, the observed rotations over this range could be fitted by the parameters in Table 1 to within 4 per cent or to within the experimental error—whichever is the smaller.

Our samples were kindly provided by Dr. E. R. Blout. We are grateful to him and to Dr. P. Doty for stimulating discussions. The purchase of a Rudolph Model 200 S-80 spectropolarimeter was assisted by a generous grant from the William F. Milton Fund, Harvard University.

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ISOTROPIC MATERIALS WHOSE DEFORMATION AND DISTORTION ENERGIES ARE EXPRESSIBLE BY SCALAR INVARIANTS

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1. *Introduction.*—The deformation energy E per unit mass of an isotropic material with symmetric stress and rate-of-strain tensors given by σ and ϵ, respectively, is determined by the equation

$$\rho \frac{dE}{dt} = tr\, \boldsymbol{\sigma}\boldsymbol{\varepsilon}, \tag{1}$$

where ρ is the density and t denotes the time. If we define the deviation tensors σ^* and ϵ^* by writing

$$\sigma^*_{\alpha\beta} = \sigma_{\alpha\beta} - \frac{1}{3}\,\theta\delta_{\alpha\beta}; \qquad \epsilon^*_{\alpha\beta} = \epsilon_{\alpha\beta} - \frac{1}{3}\,tr\, \boldsymbol{\varepsilon}\, \delta_{\alpha\beta}, \tag{2}$$

with $\theta = tr\, \boldsymbol{\sigma}$, then

$$tr\, \boldsymbol{\sigma}\boldsymbol{\varepsilon} = tr\, \boldsymbol{\sigma}^*\boldsymbol{\varepsilon}^* + \frac{1}{3}\,\theta\, tr\, \boldsymbol{\varepsilon}; \qquad \xi = \xi^* + \frac{1}{3}\,\theta^2, \tag{3}$$

where we have put $\xi = \sigma_{\alpha\beta}\sigma_{\alpha\beta}$ and $\xi^* = \sigma^*_{\alpha\beta}\sigma^*_{\alpha\beta}$. Constructing the relations

$$\rho \frac{de^*}{dt} = tr\, \boldsymbol{\sigma}^*\boldsymbol{\varepsilon}^*; \qquad \rho \frac{de}{dt} = \frac{1}{3}\,\theta\, tr\, \boldsymbol{\varepsilon}, \tag{4}$$