Theory of Optical Activity of Helical Structures and its Application to the α-Helix

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The theory of optical activity presented in an earlier paper has been applied to helical structures, obtaining a compact formula for the residue rotation $[m']_{\lambda_0}$. In particular, the theory has been applied to the α-helix, and this theory consists of two parts: firstly the calculation of the magnitude and orientation of the polarisability tensor ellipsoid of the peptide residue from the locations of the atoms in it and secondly the calculation of optical activity. The calculated value of $[m']_{\mathrm{D}}$ for a right handed α-helix is about +100° which is in excellent agreement with the experimental value for most L polypeptides. Also the sign of the optical rotation does not change on varying the polarisability tensor over a wide range. Consequently the absolute configuration of the α-helix in those L polypeptides which have a positive value for $[m']_{\mathrm{D}}$ is shown to be right handed.

1. General formulation

In an earlier paper[1] the polarisability theory of optical activity has been fully worked out in tensor notation giving formulae for birefringence and optical activity of a crystal kept in an arbitrary orientation in a beam of light. The same theory has also been applied to a simple molecule, and by averaging over all orientations of the molucule a formula for the specific rotation of a solution has been obtained in the form

$$[\alpha]_{\lambda_0} = -\frac{4800\,\pi^2}{\lambda_0^2}\,\frac{N_0}{M}\,\frac{n^2+2}{3}\,L \tag{1}$$

with

$$L = \sum_{k=j+1}^{N}\,\sum_{j=1}^{N-1} L_{(jk)} \tag{2}$$

and

$$L_{(jk)} = \varepsilon^{lsq}\,\alpha_{sm}^{(j)}\,T_{(jk)}^{mp}\,\alpha_{pq}^{(k)}\,R_l^{(jk)} \tag{3}$$

where λ_0 is the wavelength of light in vacuo, N_0 is Avogadro's number, M is the molecular weight of the solute, n is the refractive index of the solution and N is the number of polarisable groups in the molecule; $\alpha_{sm}^{(j)}$ is the polarisability tensor of group j, $T_{(jk)}^{mp}$ is the dipole-dipole interaction tensor and $R_l^{(jk)}$ is the position vector of group k with respect to j; ε^{lsq} is the permutation tensor given by

$$\varepsilon^{lsq} = \frac{1}{\sqrt{a}}\,e^{lsq} \tag{4}$$

with

$$a = \det(a_{jk}) \tag{5}$$

where e^{lsq} is the weighted tensor skew symmetric in all its indices and whose non-vanishing components are ±1 according as $l\,s\,q$ is an even or odd permutation of 123, and a_{jk} is the metric tensor. The interaction tensor may be written in the form

$$T_{(jk)}^{mp} = r^{-5}\,(3\,R_{(jk)}^{m}\,R_{(jk)}^{p} - r^2\,a^{mp}) \tag{6}$$

and

$$r^2 = a_{st}\,R_{(jk)}^{s}\,R_{(jk)}^{t} \tag{7}$$

i. e., r is the distance between the groups j and k.

2. Application to helical structures

We may now apply the above theory to a helical chain. Equation (2) expresses L as the sum of contributions $L_{(jk)}$ arising from the interactions between the polarisable groups j and k, and equation (3) shows that $L_{(jk)}$ is a pseudo-scalar under coordinate transformations, its magnitude depending only on the orientation, anisotropy and the distance between the groups. Consequently in a helical chain pairs of groups which are related to one another by the operation of a screw give the same contribution to L. If the groups are all alike, we may classify the interactions according to the separation between the groups along the chain, adjacent groups giving rise to first neighbour interactions and so on.

Now consider a finite helical chain consisting of N identical residues, numbered 0, 1, 2, . . . , $(N-1)$, say. Treating each residue as a polarisable group equation (2) may be written in the form

$$L = \sum_{\nu=1}^{N-1} (N-\nu)\;L_{(0\nu)} \tag{8}$$

where

$$L_{(0\nu)} = \varepsilon^{lsq}\,\alpha_{sm}^{(0)}\,T_{(0\nu)}^{mp}\,\alpha_{pq}^{(\nu)}\,R_l^{(0\nu)}. \tag{9}$$

Since $L_{(0\nu)}$ decreases rapidly with increasing distance between the groups, only the first few terms contribute significantly to L. Consequently if N is large we may, without appreciable error, replace the co-

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[1] S. Venkataraman, Z. Naturforschg. **16 a**, 356 [1961].

efficients $(N-1)$, $(N-2)$, etc. in these terms simply by N, and write

$$L = N \sum_{\nu} L_{(0\nu)} \qquad (\nu = 1, 2, 3, \ldots). \tag{10}$$

Also $$M = N R \tag{11}$$

where M is the molecular weight and R is the weight of one residue or group of atoms in the chain (residue weight). Substituting these results in (1) we obtain the formula

$$[\alpha]_{\lambda_0} = -\frac{4800\,\pi^2}{\lambda_0^2}\,\frac{N_0}{R}\,\frac{n^2+2}{3}\sum_{\nu} L_{(0\nu)} \tag{12}$$

which gives the specific rotation of a solution containing long helical chains.

If the residues are optically active, for example by the presence of asymmetric carbon atoms, and carry also side groups as in polypeptides, we may, as a first approximation neglect the vicinal interactions involving the side groups. Formula (12) then gives the contribution to the specific rotation by the helical structure of the backbone as such, and this will be superposed on the intrinsic specific rotation.

It is usual to express the optical rotation in a more standard form by multiplying the specific rotation by two factors which eliminate the residue weight R and the refractive index n of the solution. The corrected specific rotation $[m']_{\lambda_0}$ is generally referred to as the effective residue rotation, and it is defined by

$$[m']_{\lambda_0} = [\alpha]_{\lambda_0}\,\frac{R}{100}\,\frac{3}{n^2+2}\,. \tag{13}$$

From (12) and (13) we therefore have

$$[m']_{\lambda_0} = -\left(\frac{48\,\pi^2}{\lambda_0^2}\right) N_0 \sum_{\nu} L_{(0\nu)}\,. \tag{14}$$

If we insert numerical values for the constants, the effective residue rotation for the D line of sodium ($\lambda_0 = 5893\cdot 10^{-8}$ cm) is given by the formula

$$[m']_{\mathrm{D}} = -821.2\cdot 10^{32} \sum_{\nu} L_{(0\nu)} \tag{15}$$

where $L_{(0\nu)}$ must be expressed in units of $(\mathrm{cm})^4$. However in equation (9), if we express polarisability in cubic Ångstroms and length in Ångstroms $L_{(0\nu)}$ will be obtained in units of $\mathrm{Å}^4 = 10^{-32}(\mathrm{cm})^4$. We may then write (15) in the form

$$[m']_{\mathrm{D}} = -821.2 \sum_{\nu} L_{(0\nu)}\,. \tag{16}$$

If we now introduce the symbol $[m']_{\mathrm{D}}^{(\nu)}$ to denote the contribution to $[m']_{\mathrm{D}}$ by the ν-th neighbour interactions, we have

$$[m']_{\mathrm{D}}^{(\nu)} = -821.2\, L_{(0\nu)} \tag{17}$$

and $$[m']_{\mathrm{D}} = \sum_{\nu} [m']_{\mathrm{D}}^{(\nu)}. \tag{18}$$

3. Methods for calculating $L_{(0\nu)}$

We shall now consider the methods available for evaluating the terms $L_{(0\nu)}$ which determine the residue rotation. For this purpose we may either choose a fixed orthogonal cartesian coordinate system or employ the coordinate system of the principal axes of the polarisability ellipsoid of group 0. There are some advantages in both, and as a matter of fact the numerical data obtatined with one system have been checked by working in the other system, in the present series of calculations.

(a) *The fixed coordinate system*

Let A_0, A_1, A_2, ... represent the optical centres of the groups 0, 1, 2, ... respectively and let them lie on a right handed helix of radius r' with angular separation Φ and rise per residue c. Now set up an orthogonal cartesian coordinate system with origin O at A_0, x-axis perpendicular to the helix axis along the outward drawn radius through A_0, y-axis perpendicular to the x-axis in the plane at right angles to the axis of the helix and z-axis parallel to the helix axis, the system $0\,x\,y\,z$ being right handed.

Knowing the principal components of the polarisability tensor of group 0 and the directions of the principal axes, the components $\alpha_{sm}^{(0)}$ and $\alpha_{pq}^{(\nu)}$ of the polarisability tensors of the groups 0 and ν respectively in the fixed coordinate system may be readily evaluated. If x, y, z represent the components of the vector $R_l^{(0\nu)}$ in this system, we have (cf. Fig. 1)

$$\begin{aligned} x &= -r' + r'\cos\nu\,\Phi &&= R_1^{(0\nu)}, \\ y &= \phantom{-r' +{}} r'\sin\nu\,\Phi &&= R_2^{(0\nu)}, \\ z &= \phantom{-r' +{}} c\,\nu &&= R_3^{(0\nu)}, \end{aligned} \tag{19}$$

and $$r^2 = x^2 + y^2 + z^2\,. \tag{20}$$

The components of the interaction tensor are then given by

$$T_{(0\nu)}^{11} = (3\,x^2 - r^2)/r^5 \text{ etc.},$$

and $$T_{(0\nu)}^{12} = 3\,x\,y/r^5 \text{ etc.} \tag{21}$$

Also since the coordinate system is orthogonal cartesian, we have

$$\det(a_{jk}) = 1$$

and therefore $\varepsilon^{lsq} = e^{lsq}$

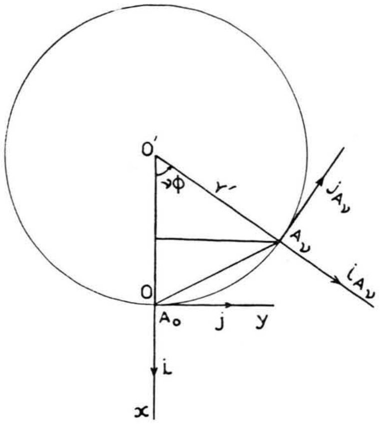


Abb. 1.

according to (4). If we now perform the summations with respect to the coupled indices l, s, q in equation (9), the expression for $L_{(0\nu)}$ may be split into 6 terms as follows:

$$\begin{aligned} t_1 &= +\alpha^{(0)}_{2m}\, T^{mp}_{(0\nu)}\, \alpha^{(\nu)}_{p3}\, R^{(0\nu)}_1 ,\\ t_2 &= -\alpha^{(0)}_{3m}\, T^{mp}_{(0\nu)}\, \alpha^{(\nu)}_{p2}\, R^{(0\nu)}_1 ,\\ t_3 &= +\alpha^{(0)}_{3m}\, T^{mp}_{(0\nu)}\, \alpha^{(\nu)}_{p1}\, R^{(0\nu)}_2 ,\\ t_4 &= -\alpha^{(0)}_{1m}\, T^{mp}_{(0\nu)}\, \alpha^{(\nu)}_{p3}\, R^{(0\nu)}_2 , \qquad (22)\\ t_5 &= +\alpha^{(0)}_{1m}\, T^{mp}_{(0\nu)}\, \alpha^{(\nu)}_{p2}\, R^{(0\nu)}_3 ,\\ \text{and}\quad t_6 &= -\alpha^{(0)}_{2m}\, T^{mp}_{(0\nu)}\, \alpha^{(\nu)}_{p1}\, R^{(0\nu)}_3 . \end{aligned}$$

These terms may be readily evaluated to give

$$L_{(0\nu)} = \sum_{s=1}^{6} t_s . \qquad (23)$$

(b) *The coordinate system of the principal axes of group 0*

Let us indicate the quantities referred to this system by a horizontal bar over them. Since $\bar{\alpha}^{(0)}_{11}$, $\bar{\alpha}^{(0)}_{22}$, $\bar{\alpha}^{(0)}_{33}$ are the only non-vanishing components of $\bar{\alpha}^{(0)}_{sm}$, the 6 terms constituting $\bar{L}_{(0\nu)}$ may be simply written as

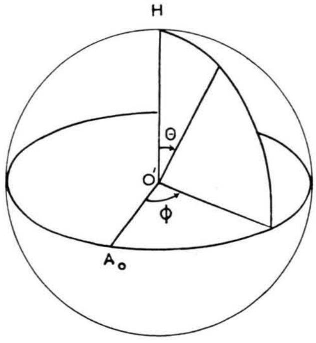
$$\begin{aligned} \bar{t}_1 &= +\bar{R}^{(0\nu)}_1\, \bar{\alpha}^{(0)}_{22}\, \bar{T}^{2p}_{(0\nu)}\, \bar{\alpha}^{(\nu)}_{p3} ,\\ \bar{t}_2 &= -\bar{R}^{(0\nu)}_1\, \bar{\alpha}^{(0)}_{33}\, \bar{T}^{3p}_{(0\nu)}\, \bar{\alpha}^{(\nu)}_{p2} ,\\ \bar{t}_3 &= +\bar{R}^{(0\nu)}_2\, \bar{\alpha}^{(0)}_{33}\, \bar{T}^{3p}_{(0\nu)}\, \bar{\alpha}^{(\nu)}_{p1} ,\\ \bar{t}_4 &= -\bar{R}^{(0\nu)}_2\, \bar{\alpha}^{(0)}_{11}\, \bar{T}^{1p}_{(0\nu)}\, \bar{\alpha}^{(\nu)}_{p3} , \qquad (24)\\ \bar{t}_5 &= +\bar{R}^{(0\nu)}_3\, \bar{\alpha}^{(0)}_{11}\, \bar{T}^{1p}_{(0\nu)}\, \bar{\alpha}^{(\nu)}_{p2} ,\\ \text{and}\quad \bar{t}_6 &= -\bar{R}^{(0\nu)}_3\, \bar{\alpha}^{(0)}_{22}\, \bar{T}^{2p}_{(0\nu)}\, \bar{\alpha}^{(\nu)}_{p1} . \end{aligned}$$

To calculate $\bar{\alpha}^{(\nu)}_{pq}$ we require the direction cosines of the principal axes of group 0 in the coordinate system of the principal axes of group ν. If $\boldsymbol{i}_\nu$, $\boldsymbol{j}_\nu$, $\boldsymbol{k}_\nu$ denote unit vectors parallel to the principal axes of group ν, we may express the direction cosines by the following scheme, where for example β_{12} is the cosine of the angle between $\boldsymbol{i}_0$ and $\boldsymbol{j}_\nu$.

	$\boldsymbol{i}_\nu$	$\boldsymbol{j}_\nu$	$\boldsymbol{k}_\nu$
$\boldsymbol{i}_0$	β_{11}	β_{12}	β_{13}
$\boldsymbol{j}_0$	β_{21}	β_{22}	β_{23}
$\boldsymbol{k}_0$	β_{31}	β_{32}	β_{33}

Now we may set up a spherical polar coordinate system (Fig. 2) in which the colatitude Θ is measured from the helix axis O′H and the longitude Φ from the reference line O′ A_0. From spherical trigonometry we have, for the direction cosines, formulae of the type

$$\beta_{12} = \cos\Theta_{\boldsymbol{i}_0}\cos\Theta_{\boldsymbol{j}_\nu} + \sin\Theta_{\boldsymbol{i}_0}\sin\Theta_{\boldsymbol{j}_\nu}\cos(\Phi_{\boldsymbol{i}_0} - \Phi_{\boldsymbol{j}_\nu}) . \qquad (25)$$



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Since $\bar{\alpha}^{(0)}_{11}$, $\bar{\alpha}^{(0)}_{22}$, $\bar{\alpha}^{(0)}_{33}$ represent also the principal components of the polarisability tensor of group ν, the components of the tensor in the coordinate system of the principal axes of group 0 are given by the transformation formula

$$\bar{\alpha}^{(\nu)}_{pq} = \beta_{p1}\,\beta_{q1}\,\bar{\alpha}^{(0)}_{11} + \beta_{p2}\,\beta_{q2}\,\bar{\alpha}^{(0)}_{22} + \beta_{p3}\,\beta_{q3}\,\bar{\alpha}^{(0)}_{33} . \qquad (26)$$

Also, in the fixed coordinate system of the previous subsection 3(a), if we write (19) in the form

$$\boldsymbol{R}^{(0\nu)} = (-r' + r'\cos\nu\,\Phi)\,\boldsymbol{i} + r'\sin\nu\,\Phi\,\boldsymbol{j} + c\,\nu\,\boldsymbol{k} \qquad (27)$$

where $\boldsymbol{i}$, $\boldsymbol{j}$, $\boldsymbol{k}$ are unit vectors parallel to the axes (cf. Fig. 1), and express $\boldsymbol{i}$, $\boldsymbol{j}$, $\boldsymbol{k}$ in terms of $\boldsymbol{i}_0$, $\boldsymbol{j}_0$, $\boldsymbol{k}_0$, the components of $\boldsymbol{R}^{(0\nu)}$ in the coordinate system of the principal axes of group 0 may be readily obtained. Denoting these by $\bar{x}$, $\bar{y}$, $\bar{z}$ the components of the interaction tensor are given by formulae of the type (21). The terms $\bar{t}_s$ given by (24) may then be evaluated leading to

$$\bar{L}_{(0\nu)} = \sum_{s=1}^{6} \bar{t}_s = L_{(0\nu)} \,. \qquad (28)$$

4. Residue rotation of the α-helix

(a) *Introduction*

An intensive study of the optical rotation of the α-helix has been done in recent years because of its relation to the structure of polypeptides and proteins. Experiments with polypeptides having the α-helical structure have shown that the contribution to $[m']_D$ by the helical configuration as such is always positive with L-type residues and the magnitude is about $+100°$ (ref. [2, 3]). An exception seems to be the case of poly-β-benzyl-L-aspartate [4] which has apparently a sense opposite to that for the other L polypeptides for the residue rotation due to the helical content. Thus in the majority of cases the α-helix with L-type residues has the same sense in solution. The absolute configuration in solution is however not yet known with certainty. This can be fixed if the sign of the optical rotation is calculated from theory, say for a right handed helix, and then compared with experiment. If the sign agrees, the helix must be right handed; if not, it must be left handed. FITTS and KIRKWOOD [5] attempted to calculate the specific rotation of a solution containing long polypeptide chains in α-helical form, taking into account the effects of all neighbours on the helix. Unfortunately however, they employed a mathematically simple model in which the polarisability was continuously distributed along the helix, whose line elements were associated with uniaxial polarisability tensors with anisotropy ratio 1/3 and axis directed along the tangent. In a later paper [6] they incorporated ideas of dispersion into the polarisability theory and abandoned the assumption of a continuous distribution of polarisability. They concluded that the sense of the helix must be right handed for those polypeptides which have a positive residue rotation due to helical content. However, recently TINOCO and WOODY [7] arrived at an exactly opposite conclusion from a theoretical study of optical rotatory dispersion of polyalanine. In view of these differences a fresh attempt is made in this paper to estimate the residue rotation of the α-helix. The magnitude and orientation of the polarisability ellipsoid of the peptide residue is first evaluated and this is subsequently used to calculate the optical activity of the α-helix. This leads to the result that for L polypeptides which give a positive residue rotation, the α-helix is right handed. Sections (b) and (c) respectively deal with these and section (d) contains a critical discussion of the results. No attempt is made to bring in ideas of dispersion of optical activity, as they are beyond the scope of the present paper.

(b) *Polarisability ellipsoid of the peptide residue*

The peptide residue $C_{(0)} - NH - C'O - C_{(1)}$ is shown in Fig. 3. The polarisabilities of the constituent groups $C(H_2)$, $C'O$ and NH are taken to be 1.81, 1.82 and 1.42 Å^3 respectively, following KIRKWOOD [5]. In the case of $C_{(0)}$ and $C_{(1)}$ the polarisability was located at the atom concerned, but for $C'O$ and NH, slight variations were made by locating the polarisability of the group $C'O$ either at O or midway between C' and O and similarly that of NH either at N or at H or midway. The polarisability tensor was calculated in each case by the standard method as was adopted by RAMACHANDRAN [8] in calculating the optical activity of quartz and sodium chlorate. The locations for which these calculations were made are shown in Table 1 which contains also the magnitudes of the principal tensor components as well as the inclination β of the direction of $\bar{a}_{22}$ with $C_{(0)}C_{(1)}$, the line joining the α-carbon atoms. Also since the peptide group is planar, two of the principal axes, say $\bar{a}_{22}$ and $\bar{a}_{33}$ will lie in this plane while the third $\bar{a}_{11}$ will be perpendicular to it. Consequently it is sufficient to give the angle β to specify uniquely the orientation of the tensor ellip-

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Locations chosen	$\bar{\alpha}_{11}$	$\bar{\alpha}_{22}$	$\bar{\alpha}_{33}$	β
NH at N, C′O at O	2.49	8.02	4.64	8.2°
NH midway, C′O nearly at O	2.98	6.77	5.40	10.0°
NH at H, C′O midway	3.07	6.92	5.15	28.6°
NH at H, C′O at O	3.61	6.23	5.31	34.6°

Table 1. Polarisability tensor of the peptide residue for different locations of its constituent groups.

soid with respect to the plane of the peptide residue *.

The details of the calculation are omitted, but it may be mentioned that the standard PAULING–COREY [9] dimensions were used for the peptide residue. The full value of 1.81 Å³ was used for the polarisability of both $C_{(0)}$ and $C_{(1)}$ in calculating the interactions and the induced electric moments, but the polarisability of the peptide group was taken to be

$$\alpha = \tfrac{1}{2}\left(\alpha_{C_{(0)}} + \alpha_{C_{(1)}}\right) + \alpha_{C'O} + \alpha_{NH} \,. \qquad (29)$$

Clearly the mean polarisability

$$\alpha_m = \tfrac{1}{3}\left(\bar{\alpha}_{11} + \bar{\alpha}_{22} + \bar{\alpha}_{33}\right) \qquad (30)$$

will be equal to α, which has a value 5.05 Å³.

It will be seen from Table 1 that there is a fairly large variation in the magnitudes of $\bar{\alpha}_{11}$, $\bar{\alpha}_{22}$, $\bar{\alpha}_{33}$ with location, but the trend is always the same namely

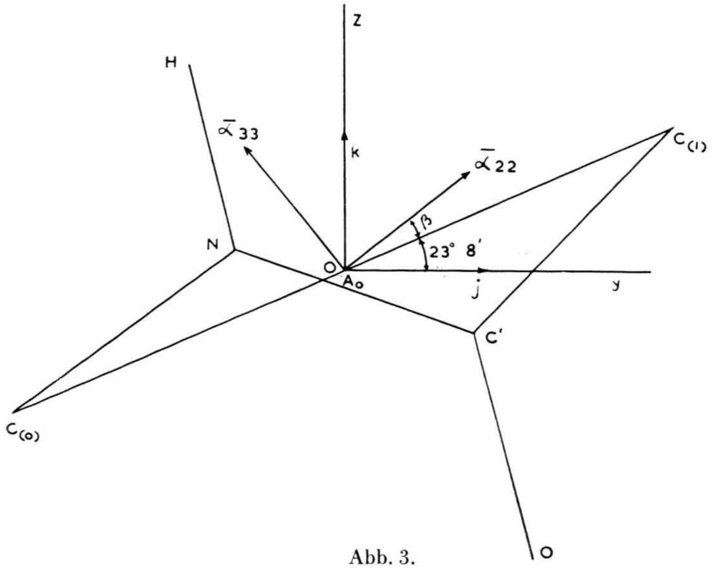
$$\bar{\alpha}_{11} < \alpha_m \,, \quad \bar{\alpha}_{22} > \alpha_m \quad \text{and} \quad \bar{\alpha}_{33} \approx \alpha_m \,. \qquad (31)$$

Also, the orientation of $\bar{\alpha}_{22}$ lies between 8° and 35° from $C_{(0)}C_{(1)}$. Consequently in making the optical activity calculations, emphasis was laid particularly on this trend, rather than the actual magnitudes of $\bar{\alpha}_{11}$, $\bar{\alpha}_{22}$, $\bar{\alpha}_{33}$. Thus typical values chosen for the optical activity calculations were

$(\bar{\alpha}_{11}, \bar{\alpha}_{22}, \bar{\alpha}_{33}) = (4.0,\ 6.0,\ 5.0)$, $(3.5,\ 6.0,\ 5.5)$, $(3.5,\ 7.0,\ 4.5)$, and $(3.0,\ 7.0,\ 5.0)$ with β varying from 0° to 30°. α_m has a value 5.0 for these data, as against the actual value of 5.05 mentioned above, but this difference may be considered to be negligible.

(c) *Calculation of optical activity*

For the calculation of optical activity we have to evaluate the mutual interactions between the residues assuming that their polarisabilities are located on an α-helix. Following PAULING and COREY [10] the structural parameters of the α-helix were taken as 3.6 residues per turn with a residue height 1.50 Å so that the next neighbour to a given residue is obtained by a rotation of 100° and a translation of



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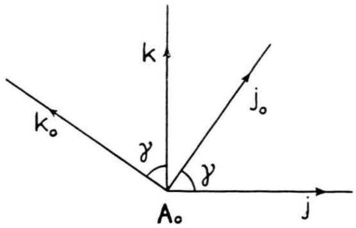

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* It may be mentioned that the designation of the principal axes adopted in this paper differs slightly from that used in a preliminary report read at the Seminar on Collagen held at the Central Leather Research Institute, Madras in November 1960 (under publication).

[9] R. B. COREY and L. PAULING, Proc. Roy. Soc., Lond. B **141**, 10 [1953].

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1.50 Å parallel to the helix axis. The residue was taken to be planar, the peptide plane being parallel to the helix axis with the α-carbon atoms lying at a distance of 2.29 Å from it. Treating each residue as a polarisable group, the optical centre was located at the midpoint of the line joining the α-carbon atoms, so that optically the α-helix was considered to be made up of groups (peptide residues) located on a helix of radius 1.472 Å and pitch 5.40 Å at intervals of 100°.

The peptide residue $C_{(0)} - NH - C'O - C_{(1)}$ which forms the group 0, is shown in Fig. 3 with the principal axes $\bar{\alpha}_{22}$ and $\bar{\alpha}_{33}$ and the angle β marked on it. The orientation of the residue with respect to the $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ system is also indicated in the figure. The optical centre A_0 is the midpoint of $C_{(0)}C_{(1)}$ which makes an angle 23° 8′ with the axis O y, the origin O of the coordinate system coinciding with A_0. The principal axis $\bar{\alpha}_{11}$ is along the axis O x perpendicular to the peptide plane; $\bar{\alpha}_{22}$ is inclined at an angle $\gamma = 23° \, 8' + \beta$ from O y, and $\bar{\alpha}_{33}$ makes the same angle with O z.

We shall now indicate the method of calculating $[m']^{(\nu)}_{D}$, the contribution to $[m']_D$ by the ν-th neighbour interactions. Let the polarisability tensor of group 0 in the coordinate system of its principal axes $\boldsymbol{i}_0, \boldsymbol{j}_0, \boldsymbol{k}_0$ be designated as $\bar{\alpha}^{(0)}_{sm}$. From Fig. 4, the scheme of direction cosines for transformation to the $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ system may be written as

	$\boldsymbol{i}_0$	$\boldsymbol{j}_0$	$\boldsymbol{k}_0$
$\boldsymbol{i}$	1	0	0
$\boldsymbol{j}$	0	$\cos\gamma$	$-\sin\gamma$
$\boldsymbol{k}$	0	$\sin\gamma$	$\cos\gamma$

The components of the tensor in the $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ system are then given by

$$\alpha^{(0)}_{pq} = \beta_{p1}\,\beta_{q1}\,\bar{\alpha}^{(0)}_{11} + \beta_{p2}\,\beta_{q2}\,\bar{\alpha}^{(0)}_{22} + \beta_{p3}\,\beta_{q3}\,\bar{\alpha}^{(0)}_{33} \quad (32)$$

where β_{pr} is the element of the p-th row r-th column of the scheme of direction cosines. Now let $\boldsymbol{i}_{A_\nu}, \boldsymbol{j}_{A_\nu}, \boldsymbol{k}_{A_\nu}$ denote unit vectors attached to A_ν in the same way as $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ with respect to A_0. Then $\alpha^{(0)}_{pq}$ are also the components of the polarisability tensor of group ν in the $\boldsymbol{i}_{A_\nu}, \boldsymbol{j}_{A_\nu}, \boldsymbol{k}_{A_\nu}$ system. To evaluate the components in the $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ system we require a scheme of direction cosines which may be obtained by reference to Fig. 1:

	$\boldsymbol{i}_{A_\nu}$	$\boldsymbol{j}_{A_\nu}$	$\boldsymbol{k}_{A_\nu}$
$\boldsymbol{i}$	$\cos\nu\varphi$	$-\sin\nu\varphi$	0
$\boldsymbol{j}$	$\sin\nu\varphi$	$\cos\nu\varphi$	0
$\boldsymbol{k}$	0	0	1

The components of the polarisability tensor of group ν in the $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ system are then given by

$$\alpha^{(\nu)}_{pq} = \sum_{r,s=1}^{3} \beta_{pr}\,\beta_{qs}\,\alpha^{(0)}_{rs}. \quad (33)$$

The components of the vector $R_l^{(0\nu)}$ and the tensor $T^{mp}_{(0\nu)}$ may be obtained from (19) and (21) respectively. $L_{(0\nu)}$ may then be calculated by means of (22) and (23), and $[m']^{(\nu)}_{D}$ obtained in accordance with (17). If $[m']^{(\nu)}_{D}$ is evaluated for $\nu = 1, 2, 3, \ldots$ and added up, $[m']_D$ is finally obtained (18).

$[m']^{(1)}_{D}$ was calculated for various values of the anisotropy, but the successive contributions $[m']^{(\nu)}_{D}$ were calculated up to $\nu = 7$ only in the few cases mentioned in Section 4(b). The results are summarised in Tables 2 and 3 respectively. It will be seen that the individual contributions from beyond the seventh neighbours are not likely to come to more than 10% of the value given for $[m']_D$ while the sum from all neighbours beyond the seventh is likely to be even less owing to alternations in sign.

Anisotropy	β (in deg.)	$[m']^{(1)}_{D}$
4.0 : 6.0 : 5.0	0	+ 94
4.0 : 6.0 : 5.0	15	+172
4.0 : 6.0 : 5.0	30	+213
3.5 : 6.0 : 5.5	0	+286
3.5 : 6.0 : 5.5	30	+364
3.5 : 7.0 : 4.5	0	+138
3.0 : 7.0 : 5.0	0	+377
2.5 : 7.5 : 5.0	0	+588
2.0 : 8.0 : 5.0	0	+846
3.0 : 6.0 : 6.0	0	+575
3.0 : 8.0 : 4.0	0	+183
3.0 : 9.0 : 3.0	0	0
3.5 : 8.0 : 3.5	0	0
3.5 : 7.5 : 4.0	0	+ 68
4.0 : 7.0 : 4.0	0	0
4.0 : 7.0 : 4.0	15	+419
4.0 : 7.0 : 4.0	30	+493
4.0 : 7.0 : 4.0	45	+254

Table 2. Contribution to $[m']_D$ by the first neighbour interactions for various values of the anisotropy.

(d) *Results*

(i) Magnitude of Residue Rotation

It will be seen from Table 3 that the residue rotation is positive throughout for all the possibilities

Anisotropy	ν	$[m']_{\mathrm{D}}^{(\nu)}$							$[m']_{\mathrm{D}}$
	β	1	2	3	4	5	6	7	
4.0 : 6.0 : 5.0	0°	+ 94	+ 55	− 67	+25	−10	+13	− 8	+102
4.0 : 6.0 : 5.0	15°	+172	+ 59	− 58	+14	− 2	+13	− 6	+192
4.0 : 6.0 : 5.0	30°	+213	+ 47	− 42	+ 9	+ 4	+11	− 4	+238
3.5 : 6.0 : 5.5	0°	+286	+ 21	−107	+58	−17	+18	−14	+245
3.5 : 6.0 : 5.5	30°	+364	+ 19	− 97	+46	− 8	+15	−11	+328
3.5 : 7.0 : 4.5	0°	+138	+236	−200	+43	−35	+44	−21	+205
3.0 : 7.0 : 5.0	0°	+377	+219	−268	+98	−40	+54	−32	+408

Table 3. Variation of $[m']_{\mathrm{D}}$ with changes in the polarisability tensor.

tried for the polarisability tensor. The magnitude also lies in the region of $+100^\circ$ for the anisotropy 4:6:5 with β between 0° and 15°. Since this range is roughly in agreement with the tensor calculated from the configuration of the peptide residue and the mean polarisability of its constituent groups, we may give it as a result from theory that the residue rotation for the α-helical structure is about $+100^\circ$. This is in excellent agreement with observations[2−4] which generally yield values lying between 65° and 110°. In this connection it may be mentioned that the quantity that has been determined experimentally is the residue rotation of a meso-polypeptide containing an equal number of D and L residues, but having a single helical sense namely that of the L polypeptide. This need not necessarily be equal to the residue rotation of an α-helix shorn of its side groups. We however believe that the experimental value gives correctly the order of magnitude of the residue rotation of such an unadorned α-helix.

(ii) Sense of the α-Helix

The calculations listed here were made for a right handed α-helix, and they all lead to a positive contribution to the residue rotation. Since this agrees with the sense of the rotation observed experimentally for most L polypeptides, we may say that the α-helix in these cases must be right handed. It should be mentioned that slight changes in the magnitudes of $\bar{a}_{pq}$ used in the calculations do not affect the sign and so the sense of the α-helix is quite definite. It is reassuring to note that the sense is in agreement with the conclusions reached from stereochemical considerations by SASISEKHARAN[11]. It agrees also with the sense of the α-helix in crystals established by ELLIOTT and MALCOLM[12] from x-ray data. It may be mentioned that the case of poly-β-benzyl-L-aspartate is rather special and the stereochemistry in this case requires further examination.

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