On the Molecular Rotations of Polypeptides of Alanine. II.

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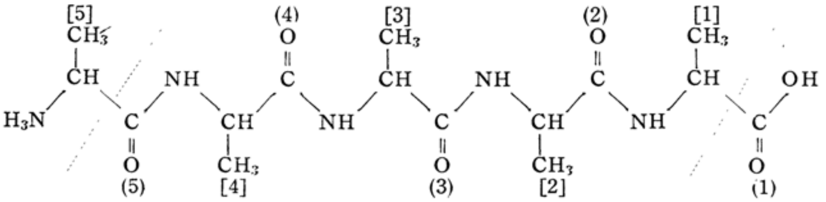
Introduction

In the previous paper, the molecular rotations $[M]_D$ of a series of polypeptides of alanine were calculated theoretically assuming the folded α-type configuration[1]. More precisely, the seven membered ring due to intramolecular hydrogen bond was assumed so as to satisfy Kauzmann and Eyring's suggestion in which the rigid ring structure of polypeptides was required[2]. The recent viewpoint, however, is that one can expect a rather rigid nature even in the extended β-type configuration[3]. Therefore, it seems to be desirable to calculate the molecular rotation for the extended configuration assuming the complete rigidity. As was already shown, the contribution of the one-electron effect is much smaller than that of the dynamical coupling effect. Consequently the calculation will concern only the latter effect.

Method of Calculation

As a molecular model, the extended β-type configuration is used. For example, the configuration of tetra-alanyl-alanine is given by the formula:



Here, one can consider two idealized models. First, the structure completely rigid from one end to the other, $\beta_{(1)}$. Second, the stracture in which only the two terminal groups (COOH and $CH(CH_3)(NH_3)$) are in the state of free rotation and the remaining part being completely rigid, $\beta_{(2)}$.

The method of calculation and the degree of approximation are the same as before* and the following pairs of interactions are taken

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[1] H. Murakami, This Bulletin, 27, 246 (1954).

[2] W. Kauzmann and H. Eyring, *J. Chem.Phys.*, 9, 41 (1941).

[3] M. Laskowski, Jr., and H.A. Scheraga, *J. Am. Chem. Soc.*, 76, 6305 (1954). In this paper, the authors stated as follows: "For rotation in hydrocarbons the potential barriers are quite high compared to *RT* at room temperature. Further, since the potential curves for internal rotation in higher hydrocarbons are, in general, asymmetric and the various potential minima differ appreciably, we can assume that the majority of non-hydrogen bonded molecules are confined to the lowest minimum and that the entropy associated with the distribution among various possible minima is small." (See p. 6308).

* In order to simplify the calculation, the bond angles in the main chain are all assumed to be 120°. This is the only difference from the previous approximation.

into account.*

A: {(1)[1]} {(2)[2]} {(3)[3]} {(4)[4]} {(5)[5]}
B: {(2)[1]} {(3)[2]} {(4)[3]} {(5)[4]}
C: {(3)[1]} {(4)[2]} {(5)[3]}
D: {(1)[2]} {(2)[3]} {(3)[4]} {(4)[5]}

The molecular rotations $[M]_D$ are given for $\beta_{(1)}$ and $\beta_{(2)}$, respectively, as follows:

$\beta_{(1)}$	alanine	A
	alanyl-alanine	$2A+B+D$
	di-alanyl-alanine	$3A+2B+C+2D$
	tri-alanyl-alanine	$4A+3B+2C+3D$
	tetra-alanyl-alanine	$5A+4B+3C+4D$
$\beta_{(2)}$	alanine	0
	alanyl-alanine	B
	di-alanyl-alanine	$A+2B+C$
	tri-alanyl-alanine	$2A+3B+2C+D$
	tetra-alanyl-alanine	$3A+4B+3C+2D$

The numerical results are shown in Tables I and II together with the previous results on the α-type cofiguration and the observed results⁴⁾.

TABLE I

Polypeptides	Calculated values			Observed values
	$[M]_D^{\alpha}$	$[M]_D^{\beta(1)}$	$[M]_D^{\beta(2)}$	$[M]_D$
alanine	0°	− 182°	0°	− 13°
alanyl-alanine	169°	− 521°	− 143°	+ 58°
di-alanyl-alanine	380°	− 823°	− 431°	+179°
tri-alanyl-alanine	609°	−1125°	− 733°	+347°
tetra-alanyl-alanine	837°	−1427°	−1035°	+494°

TABLE II

Polypeptides	Calculated values			Observed values
	$[M]_D^{\alpha}\times 0.591$	$-([M]_D^{\beta(1)}-A)\times 0.382$	$-[M]_D^{\beta(2)}\times 0.491$	$\|[M]_D\|+13°$
alanine	0°	0°	0°	0°
alanyl-alanine	100°	129°	70°	71°
di-alanyl-alanine	225°	245°	212°	192°
tri-alanyl-alanine	360°	360°	360°	360°
tetra-alanyl-alanine	495°	476°	508°	507°

Discussion on the Results

The noticeable features of the theoretical predictions are as follows:

1) The signs of $[M]_D$ for α-and β-type configurations are reverse (see Table I).

2) Except for the sign, the qualitative tendency of the predicted $[M]_D$ agrees relatively well with the observed one for either the configurations of α and β (see Table II).

3) The absolute values of the predicted $[M]_D$ are too great for either the configurations of α and β** (see Table I).

These results may probably require the existence of equilibrium between α-and β-type configurations***. Especially, it is interesting to observe that the predicte values based on $\beta_{(2)}$ agree very well with the experimental results in its qualitative tendency (see Table II). This fact seems to suggest the rather predominant contribution of $\beta_{(2)}$-type configuration in water solution (if this situation is proved to be correct, some statements in the previous paper must be revised within the suitable range). At the present stage, however, it is difficult to give a decisive conclusion about the direction and the degree of shift of equilibrium among various rotational isomers. In order to obtain the detailed knowledge about this equilibrium, further refinement of calculation is necessary and the determination of the absolute configuration of alanine or related amino acid is very desirable. This is a task for future study.

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* Pairs E {(4)[1]}{(5)[2]} are neglected since these pairs correspond to too large separation in case of β-type configuration.

4) P.A. Levene and P.S. Yang, *J. Biol. Chem.*, **99**, 405 (1932). See also E. Abderhalden and W. Gohdes, *Ber.*, **64**, 2070 (1931).

** At the present stage, the values of parameters are not conclusive. Moreover, the degree of rigidity of β-type configuration is still a matter of doubt. Therefore, one should remember that the absolute value of the predicted $[M]_D^{\beta(1)}$ and $[M]_D^{\beta(2)}$ are also inconclusive.

*** Strictly speaking, the contribution of intermediate type configurations—folded and extended configurations are mixed in the one polypeptide chain—should also be considered. In the rough approximation, however, one can replace the intramolecular distribution of α- and β-type configurations by the statistically equivalent intermolecular ones.