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Empirical Conformational Energy Study of the Diastereomeric Dipeptides MeCO-L-Ala-L-Ala-NHMe and MeCO-L-Ala-D-Ala-NHMe: An Approach to the Conformational Analysis of Stereocopolypeptides

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ABSTRACT: A conformational energy study has been carried out with the program ECEPP on the two blocked diastereomeric dipeptides MeCO-L-Ala-L-Ala-NHMe and MeCO-L-Ala-D-Ala-NHMe as models of stereocopolypeptide dyads (CHR–CO–NH–CHR). The results are reported in the form of maps of the space defined by the two internal torsion angles ψ_1 and ϕ_2, whereby only conformers whose energies have been minimized with respect to the other pair of torsion angles (ϕ_1 and ψ_2) are taken into account. A comparison with the low-energy local minima, obtained using all torsion angles as independent variables, indicates the validity of these maps as an approximate representation of the conformational space allowed to the dipeptides. These maps are used to illustrate the conformational preferences of the relevant dyads. An analysis of the periodic conformations so far proposed on the basis of theoretical or experimental evidence for regular stereocopolypeptides shows that the ψ and ϕ values of the component dyads do indeed fall into the low-energy regions of these maps.

Introduction

In recent years various copolypeptides with specific repeating sequences of enantiomeric D and L residues (regular stereocopolypeptides) have been the object of experimental conformational investigations in different laboratories.[1-9] For stereocopolypeptides with the repeating configurational sequences –LD–,[10-14] –LLDD–,[15] and –LDLL–,[2] theoretical studies have also been carried out, whereby the feasibility of specific periodic conformations has been examined by stereochemical or energetic criteria.

In conformity with the procedure used by other authors[16] for vinyl polymers, a different and more general approach to the conformational analysis of regular stereocopolypeptides appears to be a systematic conformational energy study of appropriate models for the configurationally different dyads[17] CHR–CO–NH–CHR (R = substituent) present in these polymers. Since interactions—especially hydrogen bonding—between the dyad peptide group and one or both of its adjacent peptide groups, as well as interactions of the adjacent peptide groups with one another, are important in determining the conformational preferences of a dyad, models that can take into account such interactions are desirable. Blocked diastereomeric dipeptides of the type MeCO-L-X-L-X-NHMe (or MeCO-D-X-D-X-NHMe) and MeCO-L-X-D-X-NHMe (or MeCO-D-X-L-X-NHMe) (X = amino acid residue) fulfill these requirements.

In view of our own interest in the conformational properties of regular stereocooligo-[18-20] and -copolypeptides we have decided to apply this approach, and we have examined two diastereomeric dipeptides of the simplest α-substituted amino acid, namely, MeCO-L-Ala-L-Ala-NHMe and MeCO-L-Ala-D-Ala-NHMe, by using a currently available program[21] to compute conformational energy. In light of the aim of the study, we focused our attention on the dependence of the conformational energy of a dipeptide on the torsion angles ψ_1 and ϕ_2, which describe rotations around the bonds directly connecting the C_α atoms to the central peptide group (the indexes 1 and 2 refer to the first and second residue, respectively, of the dipeptides) (Figure 1). Our results are presented in two-dimensional diagrams where the energy and geometry of those conformers that have locally minimal energy are depicted as functions of these angles. In order to obtain these diagrams we minimized the molecular conformational energy with respect to the two torsion angles ϕ_1 and ψ_2 at fixed, sufficiently close values of ψ_1 and ϕ_2. The validity of these diagrams as an approximative representation of the low-energy region of the four-dimensional conformational energy surface is assessed in a comparison with sets of unconstrained, local low-energy minima for MeCO-L-Ala-L-Ala-NHMe, as obtained by other au-

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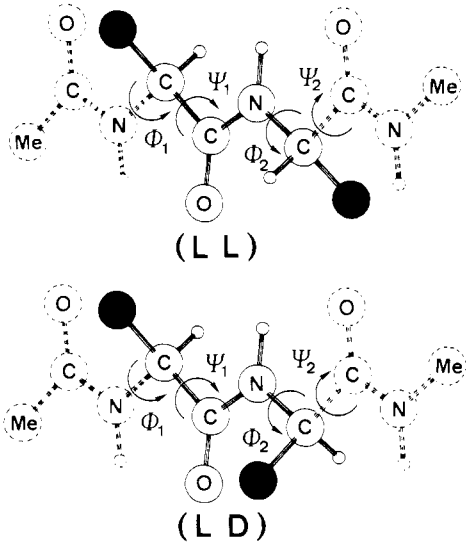

Figure 1. Correspondence between dyads and model dipeptides.

thors,[22,23] and for MeCO-L-Ala-D-Ala-NHMe, as reported in this study. Finally, we consider our results in light of the various kinds of conformations that have been attributed to or envisaged for stereocopolypeptides with different stereosequences.

Method

Molecular coordinates and conformational energies have been calculated with a CDC-adapted version of program ECEPP (QCPE No. 286) and its standard library of covalent geometry for the amino acid residues and end groups.[21] Minima of the conformational energy as a function of two or more variables have been obtained with a "quasi-Newton" nonlinear optimization method provided by the VA10A routine from the Harwell subroutine library.[24] The precision in the determination of minima was set to about 0.5° for any of the variables. Peptide bonds were fixed in the planar, trans configuration (ω = 180°) and methyl groups in one of their torsional minima.

A total of 405 points was used to generate each (ψ_1,ϕ_2) map. These points were chosen by fitting the regions of the (ψ_1,ϕ_2) space with conformational energy lower than 10 kcal/mol (as determined in a coarse-grid preliminary exploration), with a grid of centered squares of 20° per side. Being trapped into a local, high-energy relative minimum was avoided by using a set of three starting points for each of the two independent variables: in the case of MeCO-L-Ala-L-Ala-NHMe ϕ_1 = (−150°, −60°, +60°) and ψ_2 = (+150°, +60°, −60°); in the case of MeCO-L-Ala-D-Ala-NHMe ϕ_1 = (−150°, −60°, +60°) and ψ_2 = (−150°, −60°, +60°). These values are close to those for all known single-residue energy minima.[25] Among the nine local minima so obtained, the lowest one was stored and used for the generation of the (ψ_1,ϕ_2) maps. Contour lines were plotted on the (ψ_1,ϕ_2) plane after transforming the set of unevenly distributed points into a regular lattice of given side using a distance-weighted least-squares fitting.[26]

The unconstrained local energy minima of MeCO-L-Ala-D-Ala-NHMe were obtained with the same devices by using as starting points all of the possible combinations of single-residue minima,[25] as well as all the other states that give rise to low-energy minima for the dipeptides MeCO-L-Ala-L-Ala-NHMe[22,23] and MeCO-L-Ala-Gly-NHMe.[23] All the molecular torsion angles, including those which define the conformation of peptide and methyl groups, were used as independent variables. After a preliminary screening of the high-energy conformers, 64 different structures were minimized, affording a total of 37 local minima with energies less than 3 kcal/mol above the absolute minimum.

The energy values given for any conformer of the two dipeptides are referred to the value of the corresponding lowest minimum. The values obtained by ECEPP for the energies of the two absolute minima are 0.59 kcal/mol for MeCO-L-Ala-L-Ala-NHMe and 0.20 kcal/mol for MeCO-L-Ala-D-Ala-NHMe. For MeCO-L-Ala-L-Ala-NHMe Zimmerman and Scheraga[23] report 0.60 kcal/mol, in good agreement with our result.

Results and Discussion

A. Representation of Local Minima of the Conformational Energy of the Dipeptides. The results of our conformational energy calculation for MeCO-L-Ala-L-Ala-NHMe and for MeCO-L-Ala-D-Ala-NHMe are illustrated on the left and the right, respectively, of Figure 2. The upper two maps correlate directly, through isoenergy contour lines, local minima energies and torsion angles ψ_1 and ϕ_2. The central and lower maps give, by means of isoclines, the values of ϕ_1 and ψ_2 that minimize the conformational energy of a dipeptide for any given pair of ψ_1 and ϕ_2 values. Thus, within the set of local, constrained minima used to approximate the molecular energy surface, each set of three maps gives a complete description of the molecular conformation of the pertinent dipeptide. To complement this description the conformational letter code introduced by Zimmerman et al.[25] is used: the letter-coded regions delineated by thick lines in the central and lower maps define the conformational states of the first and of the second residue of the dipeptides, respectively.

Figure 2 offers direct evidence for the influence of interresidue interactions on the conformational properties of the dipeptides studied. If molecular energy were precisely representable as the sum of single-residue contributions, the two energy maps would be mirror images of each other, with a reflection plane passing through the (ϕ_2 = 0) line, perpendicular to the plane of Figure 2. Clearly, this is not the case. However, the deviations from such a relationship are not very large, and this is in agreement with the observation by the group of Scheraga[22,23] that conformational properties of dipeptides are determined primarily by intraresidue interactions. The influence of interresidue interactions is shown also by the ϕ_1 and ψ_2 isoclines (Figure 2) that are not horizontal and vertical straight lines, as they would be if the residues were completely conformationally independent. The interaction is reflected by the ψ_2 isoclines (lower maps) more than it is by the ϕ_1 isoclines (central maps).

Using the criterion of Zimmerman et al.,[27] we can classify the conformations of blocked dipeptides such as those studied in this work as either folded or extended. The distance R between the carbon atoms of the two terminal methyl groups is the discriminating parameter: conformations with $R \leq 7$ Å are defined as folded and those with $R > 7$ Å as extended. The folded or extended character of the minimum-energy conformations considered in Figure 2 can be deduced from maps of distance R such as those shown in Figure 3. An inspection of this figure shows that folded conformations are confined to the (−,−) and (+,+) quadrants of the (ψ_1,ϕ_2) plane for both dipeptides. These conformations can be identified by using the code letters given in the central and lower maps of Figure 2. In the case of MeCO-L-Ala-L-Ala-NHMe, in the (−,−) quadrant, there are the conformations AA, AC, GC, and AD that represent β turns of type III, I, IV, and VIII, respectively, according to the classification of Lewis et al.[28] Conformation CA*, an example of β turn type II, is contained in the (+,+) quadrant. In the case of MeCO-L-

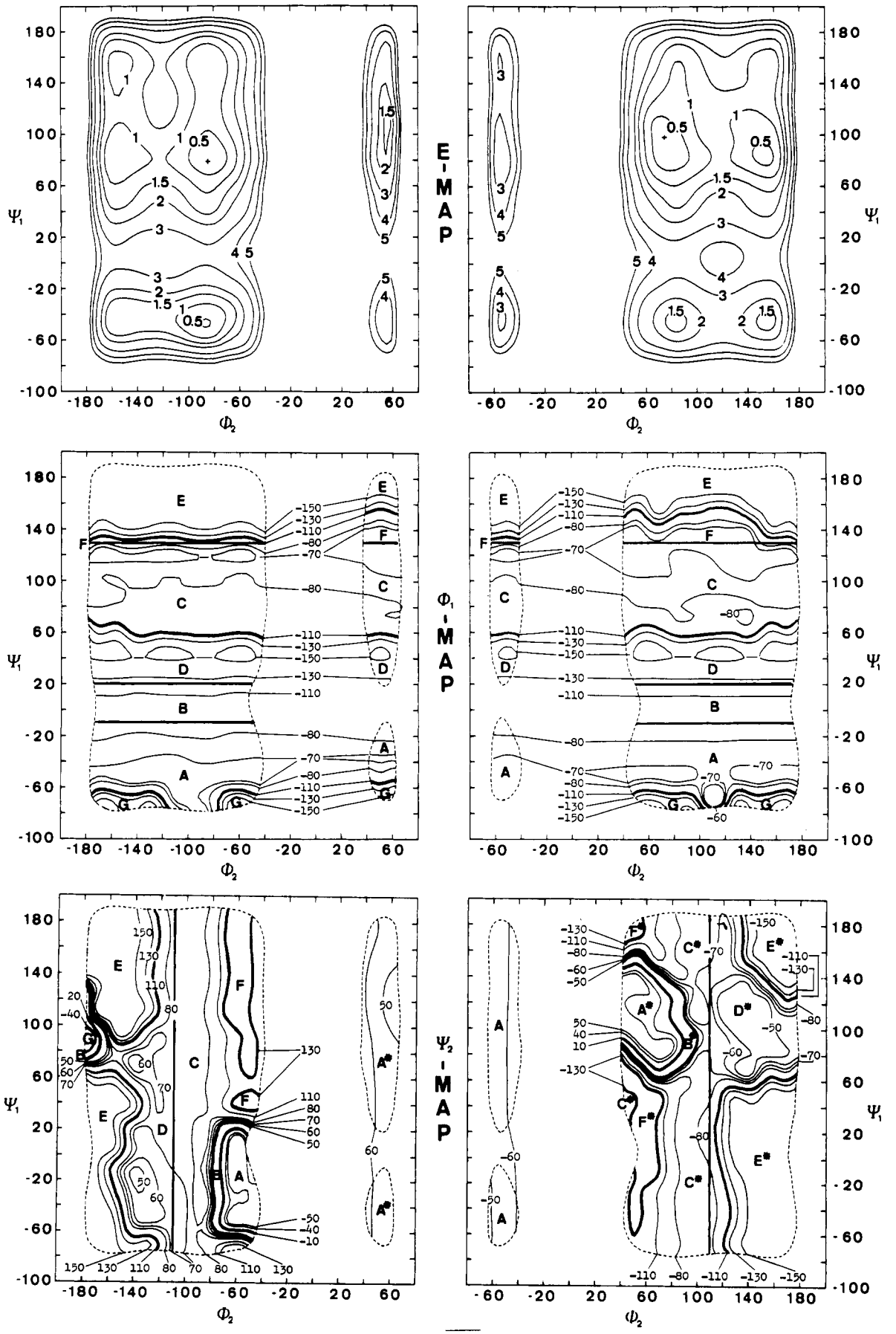

Figure 2. Conformational maps of MeCO-L-Ala-L-Ala-NHMe (left) and MeCO-L-Ala-D-Ala-NHMe (right). The upper diagrams report constant conformational energy (in kcal/mol) curves, obtained for a set of local (ψ_1,ϕ_2)-constrained energy minima (see text for explanation). The energy values are referred to that of the absolute minimum (indicated in each diagram with a cross). The central and lower diagrams represent isoclines for ϕ_1 and ψ_2, respectively, for the same set of constrained minima. The thickened isoclines and the thick straight lines delineate letter-coded[25] conformational regions for residue 1 (central diagram) and residue 2 (lower diagram).

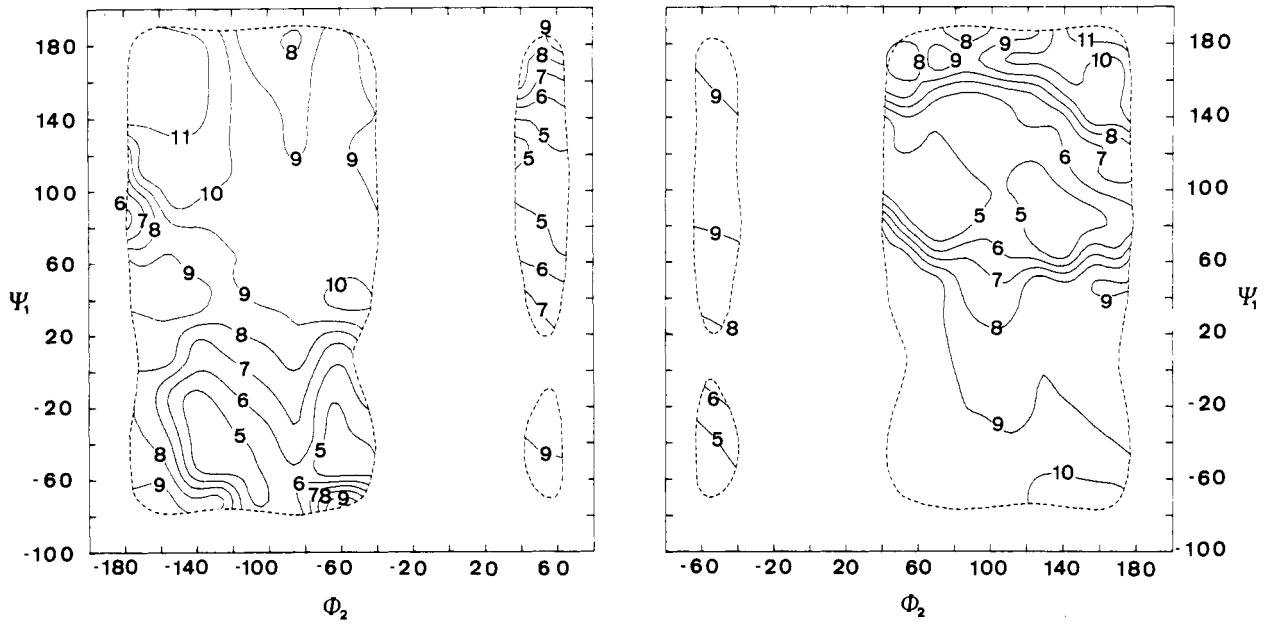

Figure 3. Lines of constant R in the (ψ_1,ϕ_2) conformational map of MeCO-L-Ala-L-Ala-NHMe (left) and of MeCO-L-Ala-D-Ala-NHMe (right). R is the distance (in Å) between the carbon atoms of the terminal methyl groups of the dipeptide. The conformers used to generate these diagrams are the constrained local minima of Figure 2. Dashed lines enclose those areas that are within 5 kcal/mol of the lowest minimum.

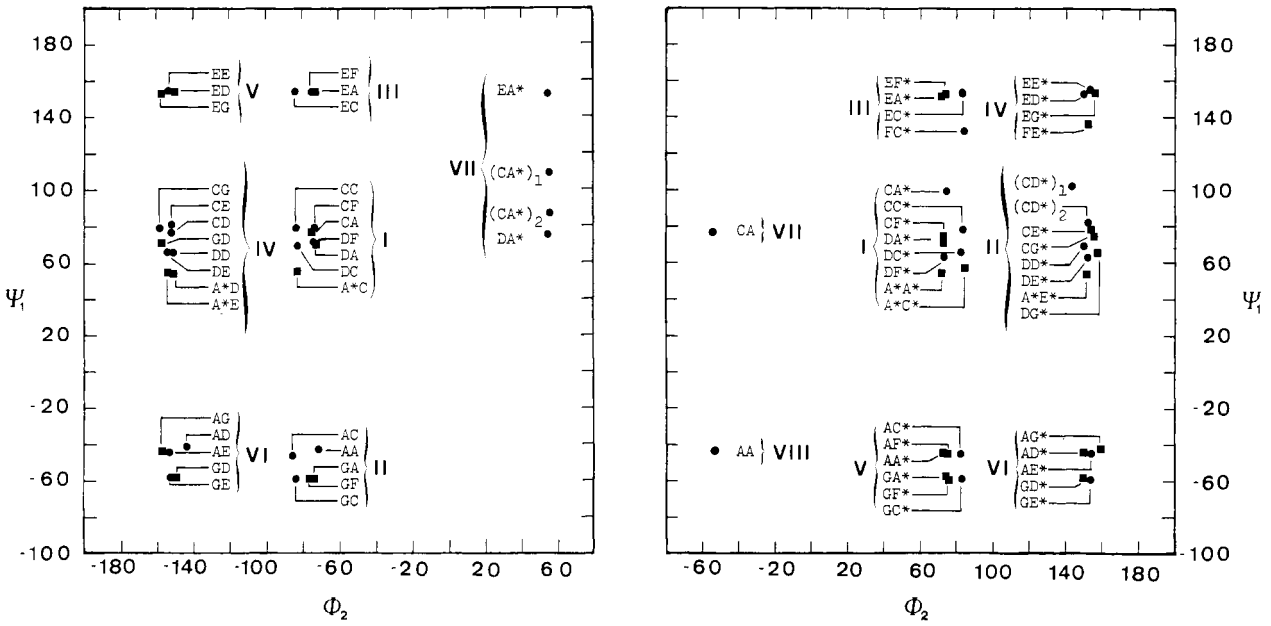

Figure 4. Projection of the unconstrained local minima of MeCO-L-Ala-L-Ala-NHMe (left) and MeCO-L-Ala-D-Ala-NHMe (right) on the (ψ_1,ϕ_2) plane. Minima indicated with filled circles correspond (within ±15° for each torsion angle) to conformers that can be identified in Figure 2. The other minima are indicated with filled squares. Roman numerals label groups of minima according to the increasing energy of the lowest energy member.

Ala-D-Ala-NHMe, only the AA conformer (β turn of type III) is contained in the (−,−) quadrant; conformations typical of β turns of type II (CA*), V (CC*), and IV (CD*, DD*, and DC*) occur for this dipeptide in the (+,+) quadrant. That the two dipeptides have different distributions of the allowed conformational space in terms of folded and extended conformations is immediately evident from a comparison of the energy maps of Figure 2 with the maps of Figure 3. The extended conformers of MeCO-L-Ala-L-Ala-NHMe fill the largest sector of the low-energy part of the (ψ_1,ϕ_2) map. This role is played by the folded conformers in the case of MeCO-L-Ala-D-Ala-NHMe. This observation is in good agreement with a previous analysis,[29] which indicated that folded conformers (turns) should be more stable and flexible for L,D dipeptides than they are for L,L dipeptides.

B. Validity and Limitations of the Representation Used. The main limitation of the representation given in Figure 2 is its incompleteness: in a series of relative minima that differ only in the values of ϕ_1 and ψ_2, only one conformer (in principle, the one with lowest energy) can be located. The importance of this limitation as well as the validity of our approach can readily be assessed by comparison with a set of unconstrained local energy minima (up to a given value) for the two dipeptides. We have used for MeCO-L-Ala-L-Ala-NHMe the minima (up to 3 kcal/mol from the lowest one) reported by Zimmerman et al.[23] For MeCO-L-Ala-D-Ala-NHMe an analogous set of minima was not available from the literature. We have calculated such a set using a procedure very similar to that

Table I
Minimum-Energy Conformations[a] of MeCO-L-Ala-D-Ala-NHMe

conformation letter code[b]	ΔE[c]	ϕ_1	ψ_1	ϕ_2	ψ_2	conformation letter code[b]	ΔE[c]	ϕ_1	ψ_1	ϕ_2	ψ_2
CA*	0.00	−72	99	74	37	AF*	1.82	−73	−44	76	−137
CC*	0.26	−83	79	85	−78	EA*	1.86	−153	152	73	45
$(CD^*)_1$	0.42	−70	102	145	−39	GC*	1.89	−158	−58	84	−80
$(CD^*)_2$	0.45	−80	83	152	−48	DD*	1.92	−150	70	151	−68
FC*	0.82	−70	133	85	−75	DA*	2.02	−147	73	74	44
CF*	0.85	−84	76	74	−143	AD*	2.07	−72	−44	150	−74
EC*	0.93	−154	154	84	−79	GE*	2.11	−158	−59	154	−154
CE*	1.10	−85	78	154	−151	CA	2.41	−83	79	−54	−57
DC*	1.13	−151	67	84	−80	EG*	2.44	−154	153	158	58
EE*	1.22	−154	155	154	−153	GF*	2.47	−158	−59	76	−139
AC*	1.30	−73	−44	84	−81	DG*	2.58	−149	65	158	58
CG*	1.35	−83	75	157	57	GD*	2.60	−158	−58	150	−73
AE*	1.43	−72	−44	154	−155	AA*	2.62	−73	−44	75	45
DF*	1.53	−152	63	74	−143	AG*	2.70	−71	−42	159	58
ED*	1.55	−153	154	151	−73	A*A*	2.70	54	55	73	44
DE*	1.55	−152	63	153	−155	A*E*	2.82	54	55	153	−152
FE*	1.55	−75	138	154	−151	AA	2.86	−69	−43	−53	−52
EF*	1.60	−154	153	75	−134	GA*	3.00	−158	−58	74	44
A*C*	1.68	54	58	85	−75						

[a] All minimum-energy conformations with $\Delta E \leq 3$ kcal/mol are listed. [b] For a definition of letter-coded conformational areas of single residues, see ref 25. [c] Energies, in kcal/mol, relative to the lowest minimum ($E_0 = +0.20$ kcal/mol).

of Zimmerman et al.[23] These local energy minima for MeCO-L-Ala-D-Ala-NHMe are reported in Table I. A comparison with results of studies[30,31] conducted with other methods is less indicative, because the values of torsion angles at local minima are dependent on the method used for the calculation of conformational energy.[23]

When the unconstrained minima of the two dipeptides are projected on the (ψ_1,ϕ_2) plane as points, most of them cluster into groups (Figure 4). These groups have been labeled with Roman numerals according to the increasing energy of the lowest energy member. A comparison with the energy maps of Figure 2 shows that clusters of minima correspond to regions of low energy. However, as indicated in Figure 4, part of the local unconstrained minima do not correspond to conformations that can be located in the set of maps reported in Figure 2. Missing conformations are generally the higher energy members of each group. Possibly they have been obscured in the maps of Figure 2 by the neighboring lower energy minima due to the relatively coarse grid used to fit the (ψ_1,ϕ_2) plane. In this regard we notice that a finer grid would have probably allowed us to locate a greater number of conformers in Figure 2. However, in this case the isocline maps would have lost much of their meaning. In fact, minima with different energies in the same group often differ drastically in their ϕ_1 or ψ_2 values. Since the maps are generated by fitting continuous functions, these abrupt changes would be shown as a series of closely spaced contour lines, making the maps almost unreadable. An example of a problematic region can be observed in the ψ_2 map of MeCO-L-Ala-L-Ala-NHMe (Figure 2) at the position of group IV minima (Figure 4). This is also the only case where the lowest minimum in a group (CG) corresponds to a marginal, relatively unfavorable area in the maps of Figure 2.

Within the limits outlined above, the maps of Figure 2 appear to be a valid, although approximate, projection of the local minima of the four-dimensional energy function, $E_{con}(\phi_1,\psi_1,\phi_2,\psi_2)$ on the (ψ_1,ϕ_2) plane. As noted above, most of the inherent imperfections in the isocline maps are a result from the necessary compromise between resolution and readability.

C. Conformational Preferences of the L,L and L,D Dyads. Within the limits of validity of the dipeptides as conformational models of the different stereocopolypeptide dyads, CHR–CO–NH–CHR, the (ψ_1,ϕ_2) energy maps of Figure 2 define the regions where the torsion angles ψ and ϕ of energetically favorable conformations of the L,L and L,D dyads should fall. For convenience, these regions will be indicated henceforth with the Roman numerals denoting the clusters of minima in Figure 4. Likewise, maps with ψ_1 and ϕ_2 of opposite sign with respect to Figure 2 would define the analogous regions for the D,D and D,L dyads.

As a rough approximation, the conformational energy of a stereocopolypeptide can be considered to be the sum of the energies of the component dyads. This approximation does not take into account either long-range intramolecular interactions or intermolecular interactions; therefore, it is expected to be valid only for the unperturbed random coil state, where the values of ψ and ϕ of the component dyads should be distributed in the different regions of the (ψ_1,ϕ_2) maps, relative to their energies, according to Boltzmann statistics. Based on the qualitative observation (see section A) that a different conformational space is available to the extended and folded conformers of the diastereomeric alanine dipeptides, one expects smaller average coil dimensions for a stereocopolypeptide than for a homo-L-(or D)polypeptide; this is agreement with the results of a theoretical and experimental study.[32]

In general, however, long-range intramolecular interactions and intermolecular interactions do play a role in determining the conformation of a polymer, so that it is not valid to use the (ψ_1,ϕ_2) maps to predict the actual conformation that a stereocopolypeptide may adopt. In the presence of these interactions the dyads of a regular stereocopolypeptide may assume one or a few different, low-energy conformations, possibly resulting in a periodic chain conformation. The different types of periodic conformations proposed so far for regular stereocopolypeptides on the basis of theoretical or experimental evidence are reported in Table II. It is interesting to establish the extent to which these periodic conformations are compatible with our results. Table II shows that in most cases the values of the torsion angles for the L,L and L,D dyads fall in low-energy regions of the maps of Figure 2.

A few cases deserve some comments. For a right-handed α helix, only a small area (VIII) of moderately high energy is available in the maps pertinent to the L,D dyad. An identical situation would result for a left-handed α helix in the maps pertinent to the D,L dyad. This result would

Table II
Correlation between Types of Periodic Conformations Proposed in the Literature for Regular Stereocopolypeptides and Low-Energy Regions of the (ψ_1,ϕ_2) Maps

repeating unit of the polypeptide	periodic chain conformation		regions of the (ψ_1,ϕ_2) maps[a,b]	
	type	handedness	L,L dyads	L,D dyads
-DL- or -LD-	extended α[12,33]			V(AA*)
	cross β[5,8]			none(*EE*) or IV(*E*E**) + I(CA*)
	LD and DL ribbon[10,11]	right		I(CA* respectively DC*)
		left		II(CD*) respectively V(AC*)
	helical α[3,4,10-12,14]	right		VIII(AA)
		left		I(A*A*)
	helical β[4,6,10-14]			
	single	right		II(CD* or CE*) or IV(EE*)[c,d]
		left		I(DC*) or III(EC*) or IV(EE*)[c,d]
	double ↑↓	right		IV(ED* or EE*)[c,e]
		left		II(DE*) or IV(EE*)[c,e]
	double ↑↑	right		IV(ED*)[e]
		left		II(DE*)[e]
	others[12]			III(EA*) or VI(AE*)
-DDL-	helical α[3]	left		I(A*A*)
	cross β[3]			II(CE*)
-LLD-	extended β[9]		V(EE)	none(*EE*)
-LLDD-	extended β[9]		V(EE) or none(*E*E**)	none(*EE*) or IV(*E*E**)
	helical α[15]	right	II(AA)	VIII(AA)
		left	VII(*A*A**)	I(A*A*)
	others[15]		II(AA)	V(AA*)
			VII(*A*A**)	VII(*A*A*)
			I(CC)	I(CC*)
			V(EE)	IV(EE*)
-DDDL-	helical α[3]	left		I(A*A*)
	cross β[3]			II(CE*)
-LLLD-	extended β[9]		V(EE)	none(*EE*)
-LDLL-	helical α[2]	right	II(AA)	VIII(AA)
		left	VII(*A*A**)	I(A*A*)
-DDDDL-	helical α[3]	left		I(A*A*)
	cross β[3]			II(CE*)

[a] For the classification of the low-energy regions I-VIII of the (ψ_1,ϕ_2) maps see Figure 4. "none" indicates that none of the low-energy regions of Figure 4 comprises the set of ψ and ϕ values of this particular conformation of the dyad. [b] The code letters in parentheses (see Figure 1 in ref 25 for definition) indicate the conformational state(s) of the model dipeptides that correspond(s) to the periodic chain conformation. The code letters of conformational states with $\Delta E > 3$ kcal/mol are italic. [c] Depending on the number of residues per turn. [d] The torsion angles considered are those of Ramachandran and Chandrasekaran[10] for their lowest energy helices. [e] The torsion angles considered are those given by Venkatram Prasad and Chandrasekaran[13] for their lowest energy helices.

suggest that α helices of either sense of twist are less stable than other periodic conformations for stereocopolypeptides. However, studies[2,14] on D,L-alternating stereocopolypeptides indicate that α helices can be stabilized by long-range interactions. The extended-β conformation proposed[9] for polyalanines with the sequence -LLD-, -LLDD-, or -LLLD- and the cross-β conformation proposed for D,L-alternating polymethionine[5] and, though with some reservations, for D,L-alternating polyalanine[8] are difficult to reconcile with our results. In fact, such conformations appear in the maps of the L,D dyad above the 3 kcal/mol limit. It is worth noting that the ψ and ϕ values of the L,D dyads of alternating stereocopolypeptides in single- and double-stranded β-helical conformations of different senses of twist (Table II) lie in a rather flat, low-energy basin (Figure 2). Therefore, for this kind of regular stereocopolypeptides, it is conceivable that there are β helices having different geometries and differing only slightly in energy. This result is in keeping with other authors' theoretical findings for single-[10] and double-stranded[13] β helices.

In the case of the regularly alternating stereocopolypeptides, all low-energy regions of the (ψ_1,ϕ_2) map of MeCO-L-Ala-D-Ala-NHMe, with the single exception of region VII, are present in the periodic conformations proposed. On the contrary, the regions of low energy in the (ψ_1,ϕ_2) maps are not so well represented for stereocopolypeptides with other stereosequences, and some of them (III, IV, and VI for the L,L dyads and III, VI, and VII for the L,D dyads) have no correspondence with periodic conformations considered so far. Whereas some of the combinations of ψ and ϕ values from these regions possibly generate cyclic structures[11,32] and thus must be discarded, others may be feasible. At present, we are investigating the possibility that there are other periodic conformations for regular stereocopolypeptides that would fit into these regions.

Conclusions

The approximate representation proposed for the conformational space of diastereomeric alanine dipeptides provides a useful visualization of their conformational differences. We believe that the advantages of a map with respect to a numerical tabulation of minima outweigh the necessary incompleteness and low resolution that are inherent in the representation. An example of the illustrative power of the method is the simple distinction of folded and extended conformers evident in Figure 3.

The conformational preferences of the L,L and L,D dyads, as resulting from these maps, are in reasonable agreement with the periodic conformations proposed in the literature for stereocopolypeptides. It appears, however, that some low-energy conformational regions for the dyads have not been investigated as to their ability to give rise to stable periodic conformations.

It is in the sense of a simple source of initial values of ψ and ϕ torsion angles that can be tested in combination with other experimental and theoretical methods that we

plan to use the (ψ_1,ϕ_2) maps for the study of conformational properties of stereocooligo- and stereocopolypeptides.

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Registry No. MeCO-L-Ala-L-Ala-NHMe, 27482-45-7; MeCO-L-Ala-D-Ala-NHMe, 37460-17-6.

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Studies of Elastic Properties of Stretched Films of Polycarbonate by Brillouin Scattering

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ABSTRACT: Results of the Brillouin scattering study of polycarbonate (PC) films stretched at a temperature slightly above T_g are reported. The elastic constants C_{11}, C_{13}, C_{33}, and C_{44} are determined as a function of stretch ratio. By use of the affine orientational model recently developed by Wang and Cavanaugh, the orientation parameter is obtained as a function of stretch ratio. The changes in the elastic constants and the orientation parameter are discussed in terms of chain morphology. The results in PC films are found to be significantly different from those in other polymer films, such as poly(ethylene terephthalate) and isotactic polypropylene, recently investigated in this laboratory. The reason for the difference is discussed.

Introduction

Viscoelastic properties of polymers are affected by externally applied perturbations. The external perturbations, such as stretching or extrusion, induce a preferred orientation of polymer chain segments along the deformation axis. The increased chain orientation occurs in both the crystalline and amorphous regions. In some cases, reorganization of the semicrystalline structure with replacement of lamellae by fibrous elements may also occur. One manifestation of this is an increase in the elastic (stiffness) constant along the axis of stretching, but Young's modulus perpendicular to the stretching axis or shear modulus about the axis may not be significantly affected. However, in polymers, such as poly(ethylene terephthalate),[1] polyethylene,[2] polyamides (Nylon 6-6),[1] and other semicrystalline polymers,[3] an increase in Young's modulus with orientation has been found. These studies are carried out by using low-frequency acoustic or ultrasonic techniques. The results may be due in part to the reorganization of the crystal structure and in part to the stretching of many of the intercrystalline tie molecules. In any case, a full description of the anisotropic elastic property of the solid polymer will require separate specification of the orientation of crystalline and amorphous regions.[4]

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