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One-Dimensional Aromatic Crystals in Solution. 8. Periodic Arrangement of Naphthyl Chromophores along α-Helical Polypeptides with Varying Spacings and Orientations

Masahiko Sisido*[1a] and Yukio Imanishi[1b]

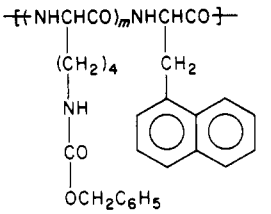
Research Center for Medical Polymers and Biomaterials and Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan. *Received November 25, 1985; Revised Manuscript Received February 13, 1986*

ABSTRACT: Polypeptides having regular sequences of [Lys(Z)$_m$-1-napAla] (m = 1–4) [Lys(Z) = N^ϵ-benzyloxycarbonyl-L-lysine; 1-napAla = L-1-naphthylalanine] were prepared. Infrared spectra of these polymers in trimethyl phosphate solution indicated the occurrence of α-helical main-chain conformation. The polymer solutions showed a strong circular dichroism (CD) at the naphthyl ^1B_b absorption band, indicating a helical arrangement of 1-naphthyl groups along the α-helical main chain. The helical side-chain conformation was analyzed theoretically by the ECEPP conformational energy calculation for poly(Ala$_m$-1-napAla)s assuming α-helical main chains. It was found that the conformational freedom of the 1-naphthylmethyl group is highly restricted and only two regions, i.e., (χ_1, χ_2) = (178 ± 6°, 257 ± 1°) (form A) and (273 ± 6°, 109 ± 2°) (form B), are allowed for the four sequential polypeptides. Theoretical CD curves were computed for the four sequential polypeptides having α-helical main chains with a side-chain conformation in form A or B. The CD curves calculated for form A showed a qualitative agreement with the experimental curves for the four sequential polypeptides.

A one-dimensional chromophoric array is the most basic system on which various aspects of electronic properties of chromophoric assemblies can be studied. The rate of energy transfer and electron transfer will be most simply interpreted in a one-dimensional system in which the complexity arising from the multiple paths of the transfer processes is eliminated. Furthermore, some new electronic interactions that are able to act only in one-dimensional systems have been proposed.[2] For example, Davydov has proposed a soliton state on an α-helical polypeptide chain.[3] Although the Davydov soliton is based on a coupling of an exciton of the amide I vibration with a longitudinal lattice vibration of the α-helix, it is a straightforward extension of the theory to an electronic soliton in which an electronic exciton couples with a longitudinal lattice vibration.[3]

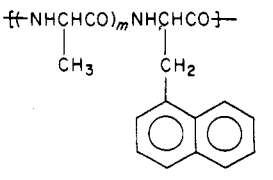
A one-dimensional chromophoric system can be synthesized by covalently attaching chromophores to an α-helical polypeptide chain.[2] A previous papers, we have reported the syntheses and the conformational analyses of poly(L-arylalanine)s which carry 1- and 2-naphthyl and 1-pyrenyl groups as aryl substituents.[4–8] However, these homopolypeptides cannot be considered one-dimensional aromatic systems in a strict sense, since their molecular structure suggests that each aromatic group can interact with more than two neighboring aromatic groups. This multiplicity in the side-chain interaction can be eliminated by inserting spacers between the aromatic amino acid units, keeping the interchromophoric distance between the nearest pair of aromatic groups along the α-helix nearly unchanged.

The present paper describes the synthesis and spectroscopic characterization of a series of sequential polypeptides consisting of *N*-benzyloxycarbonyl-L-lysine [Lys(Z)] and L-1-naphthylalanine (1-napAla) units (I).



p[Lys(Z)$_m$-1-napAla]
I, m = 1–4

The most probable conformations in solution were determined theoretically by empirical energy calculation and theoretical circular circular dichroism (CD) computation on the sequential polypeptides. In the theoretical calculations, the Lys(Z) unit was replaced by Ala unit for simplicity (II).



p(Ala$_m$-1-napAla)
II

Experimental Section

Synthesis of p[Lys(Z)$_m$-1-napAla]. The sequential polypeptides were prepared by a procedure that is known to minimize racemization. However, some racemization can occur during hydrolysis of peptide methyl esters and during polymerization

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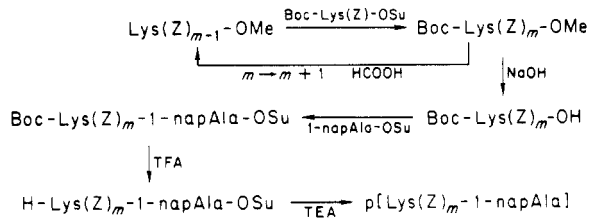
Scheme I



of peptide succinimido esters. The extent of the racemization was not determined in this study, but it should be quite small because very intense CD spectra are observed in some polypeptides. The general procedure employed in this study is shown in Scheme I. L-1-Naphthylalanine was prepared as described previously.[4] Analogous sequential polypeptides carrying L-phenylalanine,[9] L-tyrosine,[10] and L-dihydroxyphenylalanine[11] have been prepared by different procedures.

In the following, the purity of all intermediates was checked by TLC (ethanol, chloroform, and ethyl acetate) and by IR and ^{1}H NMR spectra. The following abbreviations will be used: Z = benzyloxycarbonyl, Boc = *tert*-butyloxycarbonyl, OMe = methoxy, OSu = *N*-succinimidoxy.

Z-1-napAla. L-1-Naphthylalanine (0.55 g = 2.6 mmol) was dissolved in an ice-cooled alkaline solution ($NaHCO_3$, 0.65 g = 7.8 mmol, in water/tetrahydrofuran, 10 mL/5 mL, mixture) and benzyloxycarbonyl chloride (0.62 mL = 3.8 mmol) was added dropwise with stirring. The stirring was continued overnight, and the aqueous solution was washed with ether and acidified to pH 2 with hydrochloric acid. The oil separated was extracted twice with ether, and the ether extract was dried with anhydrous sodium sulfate. Evaporation gave a crystal, which was washed with hexane: yeild 0.5 g (56%); mp 149–150 °C.

Z-1-napAla-OSu. The Z-1-napAla (0.43 g = 1.2 mmol) and *N*-hydroxysuccinimide (0.14 g = 1.2 mmol) were dissolved in chloroform/dioxane (4 mL/1 mL) mixed solvent and dicyclohexylcarbodiimide (DCC) (0.26 g = 1.2 mmol) was added. The mixture was stirred for 2 h under cooling in an ice bath and kept in a refrigerator overnight. The dicyclohexylurea (DCU) precipitated was filtered off, the filtrate was evaporated, and the residue was redissolved in ethyl acetate. Further DCU precipitated was removed, and the solution was washed with water, 2% aqueous $NaHCO_3$, 10% aqueous citric acid, and water. The organic solution was dried with anhydrous sodium sulfate and evaporated. A crude crystal obtained was recrystallized from an ethyl acetate/ether mixture: yield 0.32 g (58%); mp 83–86 °C. Anal. Calcd for $C_{25}H_{22}N_2O_6$: C, 67.26; H, 4.97; N, 6.27. Found: C, 67.00; H, 4.88; N, 6.34.

1-NapAla-OSu·HBr. The Z-1-napAla-OSu was dissolved in acetic acid saturated with hydrogen bromide at room temperature. After 1 h, excess ether was added and the precipitate was collected, washed with anhydrous ether, and dried under vacuum: yield 90%.

Boc-Lys(Z)$_2$-OMe. Boc-Lys(Z) (2.3 g = 6.1 mmol) and Lys(Z)-OMe·HCl (2.0 g = 6.1 mmol) were dissolved in chloroform (20 mL) containing triethylamine (0.85 mL = 6.1 mmol). After the solution was cooled in an ice bath, DCC (1.25 g = 6.1 mmol) was added and the solution stirred for 3 h at 0 °C. The stirring was continued at room temperature overnight. The DCU precipitated was filtered off, and the filtrate was treated as described above for the synthesis of Z-1-napAla-OSu. A crystal obtained after evaporation was recrystallized from an ethyl acetate/ether mixture: yield 2.3 g (58%); mp 115 °C. Anal. Calcd for $C_{34}H_{48}N_4O_9$: C, 62.08; H, 7.37; N, 8.53. Found: C, 62.09; H, 7.41; N, 8.48.

Boc-Lys(Z)$_3$-OMe. Boc-Lys(Z)$_2$-OMe (3.5 g = 5.3 mmol) was dissolved in formic acid (100 mL) and kept at room temperature for 2 h. The mixture was evaporated under a reduced pressure at room temperature, and ether was added to the residual oil. The crystal precipitated was washed with ether and dried under vacuum to give formic acid salt of Lys(Z)$_2$-OMe. The latter (1 g = 1.7 mmol) and Boc-Lys(Z)-OSu (commercially available, 0.79 g = 1.7 mmol) were dissolved in tetrahydrofuran (10 mL) containing triethylamine (0.25 mL = 1.8 mmol), and the mixture was kept at room temperature for 2 days. The solvent was evaporated, and the residue was redissolved in ethyl acetate. The latter solution was washed with 10% aqueous NaCl, 10% citric acid, 10% NaCl, 4% $NaHCO_3$, and 10% NaCl solution and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crystal, which was washed with ether: yield 0.93 g (61%). The crude crystal was further purified by column chromatography (Sephadex LH-20 in dimethylformamide): mp 100–105 °C. Anal. Calcd for $C_{48}H_{66}N_6O_{12}$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.46; H, 7.24; N, 9.25.

Boc-Lys(Z)$_4$-OMe. The same procedure as above was performed starting with Boc-Lys(Z)$_3$-OMe to yield the protected tetrapeptide: mp 163–166 °C. Anal. Calcd for $C_{62}H_{84}N_8O_{15}$: C, 63.03; H, 7.17; N, 9.48. Found: C, 62.82; H, 7.05; N, 9.66.

Boc-Lys(Z)-1-napAla-OSu. Boc-Lys(Z) (0.65 g = 1.7 mmol) was dissolved in tetrahydrofuran (0.4 mL) containing *N*-methylmorpholine (0.19 mL = 1.7 mmol) and cooled to −4 °C. Isobutyl chloroformate (0.23 mL = 1.7 mmol) was added, and the mixture was stirred for 6 min. Then 1-napAla-OSu·HBr (0.67 g = 1.7 mmol) in dimethylformamide (2 mL) was added, and *N*-methylmorpholine (0.19 mL = 1.7 mmol) was further added. The mixture was stirred at −4 °C for 10 min and stored in a refrigerator overnight. The mixture was poured into ethyl acetate (100 mL) and the solution was washed with 2% aqueous $NaHCO_3$, 10% citric acid, and water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crystal, which was recrystallized from ethyl acetate/hexane mixture: yield 0.21 g (18%); mp 158–160 °C. Anal. Calcd for $C_{36}H_{42}N_4O_9$: C, 64.08; H, 6.27; N, 8.30. Found: C, 63.91; H, 6.30; N, 8.14.

Boc-Lys(Z)$_m$-1-napAla-OSu (m = 2, 3, and 4). Boc-Lys(Z)$_m$-OMe (m = 2, 3, and 4) was treated with a 1.5-fold excess mole of NaOH in dioxane/ethanol mixture. The mixture was left standing for 3 h at room temperature, and an excess amount of 1 M aqueous citric acid solution was added. The organic solvent was evaporated, and the residue was dissolved in ethyl acetate and washed with 10% citric acid and water. The mixture was dried over anhydrous sodium sulfate, and the solvent was evaporated. The residual oil was treated with ether and hexane to obtain a solid product. The peptide having a free carboxyl group was reacted with 1-napAla-OSu as described above. Boc-Lys(Z)$_m$-1-napAla-OSu obtained was purified by a Sephadex column (LH-20 in dimethylformamide): yield 40–60%; mp 133–135 °C (m = 2), 155–158 °C (m = 3), 138–140 °C (m = 4). Anal. Calcd for $C_{50}H_{60}N_6O_{12}$ (m = 2): C, 64.09; H, 6.45; N, 8.97. Found: C, 64.16; H, 6.51; N, 8.81. Anal. Calcd for $C_{64}H_{78}N_8O_{15}$ (m = 3); C, 64.09; H, 6.55; N, 9.34. Found: C, 63.45; H, 6.53; N, 9.30. Anal. Calcd for $C_{78}H_{96}N_{10}O_{18}$ (m = 4): C, 64.10; H, 6.62; N, 9.58. Found: C, 63.71; H, 6.88; N, 9.91.

P[Lys(Z)$_m$-1-napAla] (m = 1–4). Boc-Lys(Z)$_m$-1-napAla-OSu was dissolved in cooled trifluoroacetic acid, and the solution was kept at 0 °C for 1 h. Excess ether was added to precipitate the peptide deblocked at the N-terminal, which was washed with ether and dried under vacuum. The N-deblocked peptide was dissolved in a least amount of dimethylformamide, and a 1.5-fold molar triethylamine was added. The mixture was kept at room temperature for 3–7 days. A viscous solution of polypeptide was diluted with dimethylformamide and poured into methanol. The precipitate was repeatedly washed with methanol/water (1/1) mixture and finally with ether. The polymer was redissolved in dimethylformamide and subjected to gel permeation chromatography (Sephadex LH-60 in dimethylformamide). The fraction eluted at the elution limit of the LH-60 gel (mol wt > 10 000) was collected.

Measurements. The following instruments were used: UV absorption, Jasco UVIDEC II and Hitachi EPS-3T; fluorescence, Hitachi MPF-4; circular dichroism (CD), Jasco J-20; infrared, Digilab FTS-15E. Fluorescence-detected circular dichroism (FDCD) was measured on a Jasco J-20 instrument equipped with a cutoff filter for exciting light, a photomultiplier tube (Hamamatsu R-268), and a preamplifier.[7]

The spectroscopic measurements were made in trimethyl phosphate (TMP) solution. Nitrogen gas was passed for 15 min before the fluorescence and FDCD spectra were measured.

Experimental Results and Discussion

Infrared Spectra in the Solid State and in Solution. IR spectra of the four sequential polypeptides were re-

Table I
Peak Positions of Amide I and II Infrared Absorption Bands of Poly[Lys(Z)$_m$-1-napAla] in the Solid State and in Solution[a]

	solid state (KBr)		solution (TMP)	
m	amide I	amide II	amide I	amide II
1	1635	1515	1653	1546
2	1645	1520	1653	1545
3	1640	1520	1655	1543
4	1624	1528	1657	1537

[a] In cm^{-1}.

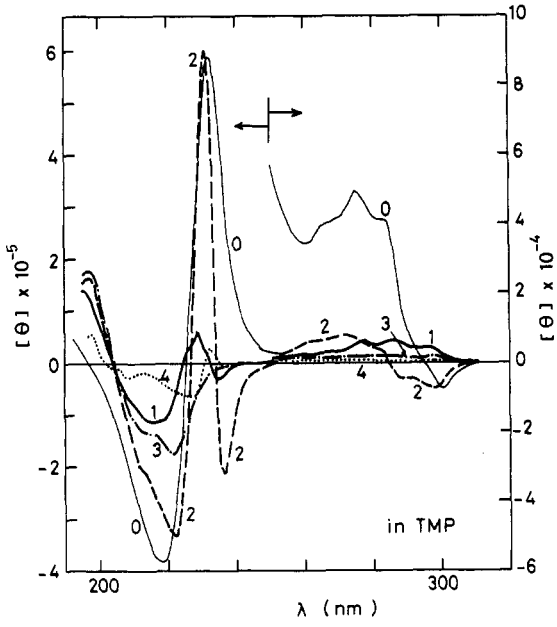


Figure 1. Experimental CD spectra of p[Lys(Z)$_m$-1-napAla] in trimethyl phosphate at room temperature: m = 0 (—); m = 1 (—); m = 2 (- - -); m = 3 (-·-); m = 4 (···). [1-napAla] = 2 × 10^{-4} mol L^{-1}; cell length = 0.1 cm (<250 nm), 1.0 cm (>250 nm). The CD spectrum of m = 0 is taken from ref 4.

corded in the solid state by a KBr pellet technique and in TMP solution. The wavenumbers of the amide I and II peaks are listed in Table I. Two of the four sequential polypeptides (m = 1 and 4) show typical IR peaks characteristic of β-structure (1630 cm^{-1})[12] in the solid state. In TMP solution, however, all the polypeptides show IR spectra characteristic of an α-helical conformation, and no residual peak was detected at the peak position for the β-structure.

Circular Dichroism. CD spectra of the four sequential polypeptides and poly(1-napAla) (m = 0)[4] are shown in Figure 1. The sequential polypeptide with m = 2 shows an intense exciton splitting at the ^1B_b absorption band (230 nm), indicating that the naphthyl groups are arranged regularly along a helical main chain. In other sequential polypeptides (m = 1, 3, and 4), the molar ellipticities are not very large, but the contribution of the naphthyl ^1B_b absorption is evident in the CD spectra. The weak CD, however, does not necessarily indicate a random orientation of naphthyl groups, since the CD pattern depends not only on the regularity in the chromophore arrangement but also on the interchromophoric distance and the relative orientation of chromophores in the regular array. By the theoretical computation below it will be shown that the different CD patterns for the sequential polypeptides with different m are explained in terms of different geometrical arrangements of naphthyl groups along the helical main chain.

Fluorescence Spectra and Fluorescence-Detected Circular Dichroism. Fluorescence spectra of the four

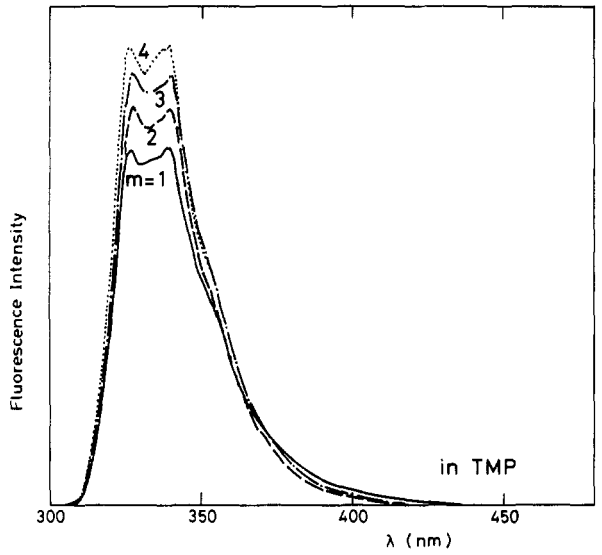


Figure 2. Fluorescence spectra of p[Lys(Z)$_m$-1-napAla] in trimethyl phosphate at room temperature: m = 1 (—), m = 2 (- - -); m = 3 (-·-); m = 4 (···). [1-napAla] = 5.0 × 10^{-5} mol L^{-1}; λ_{ex} = 295 nm.

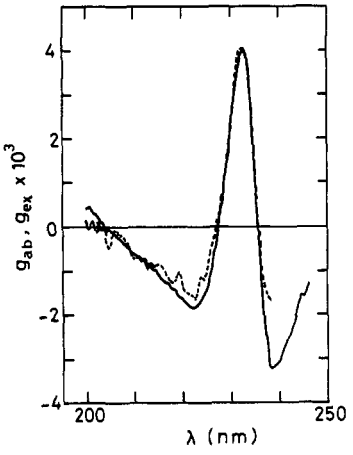


Figure 3. Circular dichroism (g_{ab}) (—) and fluorescence-detected circular dichroism (g_{ex}) (- - -) of p[Lys(Z)$_2$-1-napAla] in trimethyl phosphate at room temperature. [1-napAla] = 2.0 × 10^{-5} mol L^{-1}. Monitor wavelength for FDCD spectrum >310 nm.

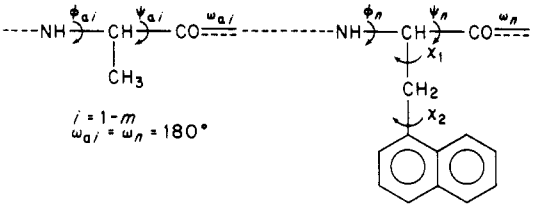
sequential polypeptides are shown in Figure 2. No excimer emission is detected in the fluorescence spectra, indicating that the naphthyl groups cannot approach each other within the critical distance to form excimers (about 3.5 Å). No excimer has been observed in p(1-napAla) in TMP, either.[5] Polypeptide chains in α-helical conformation may be too stiff to cause local deformations required for the intramolecular excimer formation. Incidentally, a small but definite excimer was observed in a random copolymer of D- and L-1-napAla's.[4] Therefore, the importance of the regular conformation in the electronic properties of chromophoric polymers is evident.

FDCD is an excellent technique to detect inhomogeneity in a solution of chiral fluorophores.[13] If a sample consists of a mixture of fluorescent species having different fluorescence quantum yields, the FDCD spectrum represents an average of the CD spectra, each spectrum being weighted by the population and the quantum yield of the corresponding species. Conventional CD spectrum represents an average of the CD spectra, each of which is weighted only by the population of the species. Therefore, if a polypeptide takes several different conformations in solution, an FDCD spectrum should differ from the conventional CD spectrum.

Table II
Results of Total Energy Minimization of (1-napAla-Ala$_m$)$_n$ in Right-Handed α-Helical Main-Chain Conformation

m	form[a]	ϕ_n[c]	ψ_n[c]	χ_1[c]	χ_2[c]	ϕ_{a1}, ϕ_{a3}[c]	ψ_{a1}, ψ_{a3}[c]	ϕ_{a2}, ϕ_{a4}[c]	ψ_{a2}, ψ_{a4}[c]	V,[b] kcal/unit
0	A	−67	−41	177	257					0.8
	B	−54	−50	267	111					5.6
1	A	−65	−34	180	258	−69	−44			8.1
	B	−60	−42	272	110	−54	−53			12.1
2	A	−66	−33	172	256	−66	−38	−73	−37	13.3
	B	−58	−38	279	110	−64	−37	−64	−49	17.5
3	A	−67	−27	184	258	−75	−32	−76	−35	19.1
						−74	−37			
	B	−63	−34	279	107	−68	−37	−70	−36	21.0
						−64	−46			
4	A	−62	−35	176	257	−70	−35	−71	−33	25.6
						−72	−38	−67	−43	
	B	−60	−35	273	110	−67	−44	−63	−36	30.0
						−68	−36	−64	−49	

[a] Type of side-chain conformation indicated in the (χ_1, χ_2) energy contour map. [b] Total energy/n, n = 12 (m = 0), 8 (m = 1), 7 (m = 2), 6 (m = 3), and 4 (m = 4). [c] The definition of the rotational angles is as below:



CD and FDCD spectra of p[Lys(Z)$_2$-1-napAla] in TMP are compared in Figure 3. In this figure the two spectra are represented by the Kuhn's absorption (g_{ab}) and excitation (g_{ex}) dissymmetry factors.

$$g_{ab} = 2(\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R) \quad (1)$$

$$g_{ex} = 2(I_L^{ex} - I_R^{ex})/(I_L^{ex} + I_R^{ex}) \quad (2)$$

The two dissymmetry factors coincided within the experimental accuracy, indicating conformational homogeneity of the chromophoric assembly in p[Lys(Z)$_2$-1-napAla]. Therefore, it can be concluded that p[Lys(Z)$_2$-1-napAla] is exclusively in an α-helical conformation in solution and its chromophoric array contains no defect, which would fluoresce with different quantum yields and/or at different wavelengths. The observation is consistent with the absence of excimer in the fluorescence spectrum. Similar results were obtained with other sequential polypeptides.

It is concluded from the above spectroscopic results that the naphthyl groups in p[Lys(Z)$_m$-1-napAla] are arranged regularly along the helical main chain.

Results of Theoretical Computations

Conformational Energy Calculation. Empirical energy calculations were performed on p(Ala$_m$-napAla) (m = 0–4) (II) in right-handed α-helical conformations. The calculation was performed by assuming a helical symmetry in the main chain and in the side chain. Thus, the main-chain and the side-chain rotational angles in every Ala$_m$-1-napAla unit were taken to be the same. The structural and energy parameters were taken from the ECEPP system.[14] The parameters for the 1-napAla unit were the same as those used for the homopolymer of 1-napAla.[4] The procedure adopted is essentially the same as those for p(1-napAla),[4] p(2-napAla),[5] and poly(1-pyrenylalanine) [p(1-pyrAla)].[8] First, the main-chain conformation was fixed to a right-handed α-helix (ϕ = −57° and ψ = −47° for all amino acid residues), and the side-chain rotational angles (χ_1, χ_2) of all 1-napAla residues were varied simultaneously from 0° to 360° with an interval of 10°. The side-chain energy contour maps for helical p[Ala$_m$-1-napAla] (m = 1–4) are shown in Figure 4. The four maps are very similar to each other and also to that for p(1-napAla) reported previously.[4] (It is noted that the definition of χ_2 in the previous paper[4] differs from the present one by 180°.) It is evident that the rotational angles of the side chain of 1-napAla residue are virtually restricted in two regions, (χ_1, χ_2) = (178 ± 6°, 257 ± 1°) (form A) and (273 ± 6°, 109 ± 2°) (form B). Form A has lower energy and a wider allowed region in the contour map, making it much more probable than form B.

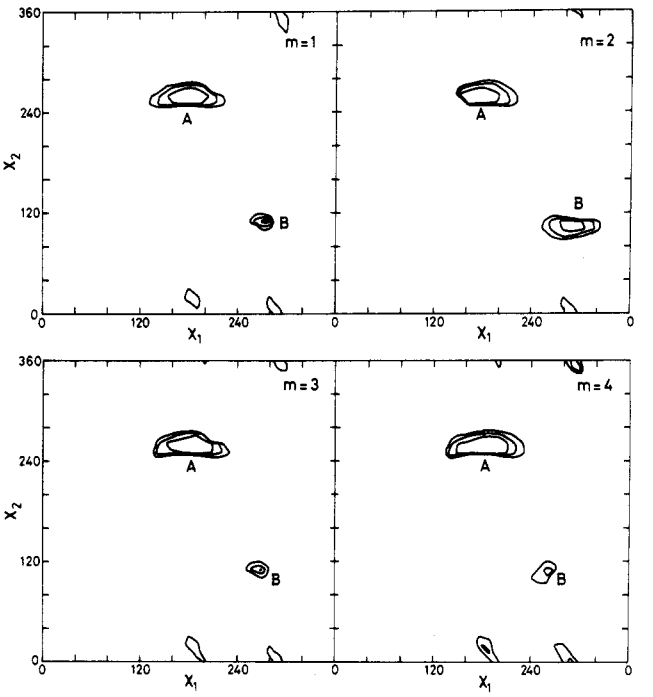


Figure 4. Energy contour maps for side-chain conformations of p[Ala$_m$-1-napAla]s in right-handed α-helical main-chain conformation (ϕ = −57°, ψ = −47°). The contour lines represent the energies higher by 2.5, 5.0, and 7.5 kcal/(1 mol of Lys(Z)$_m$-1-napAla unit) than the minimum at A.

Simplex energy minimizations were performed by starting from an α-helical main-chain conformation with side chains in forms A and B and varying all main-chain rotational angles [ϕ_{ai}, ψ_{ai} (i = 1–m), ϕ_n, and ψ_n] and the

Table III
Oscillator Strengths and Peak Positions of the Vibronic Peaks of 1-Methylnaphthalene in Trimethyl Phosphate[a]

electronic transition	peak position cm^{-1}	oscillator strength
^1L_b	31 378	0
	32 728	0
	34 078	0
	35 428	0
	36 778	0
^1L_a	34 023	0.0306
	35 373	0.0491
	36 723	0.0424
	38 073	0.0278
	39 423	0.0178
^1B_b	44 484	0.757
	45 783	0.483
	47 083	0.284

[a] Refractive index = 1.40.

side-chain angles (χ_1 and χ_2). Table II collects the results of the energy minimizations. It should be noted that the main-chain rotational angles of the minimum-energy (ME) conformations deviated considerably from those of the standard α-helical conformation ($\phi = -57°, \psi = -47°$). The deviation is not due to the introduction of the bulky 1-napAla residue into the polypeptide chain but represents a common feature of the ECEPP system.[15,16] The effect of the attachement of a naphthyl group at C$^\beta$ position on the main-chain rotational angles is not large, suggesting that the bulkiness of the naphthyl groups does not alter the main-chain conformation significantly.

Theoretical CD Computation. Theoretical CD curves for the sequential polypeptides were computed on the basis of the exciton theory,[17] taking amide nπ^* and $\pi\pi^*$ and naphthyl ^1L_b, ^1L_a, and ^1B_b transitions into account. The procedure employed was essentially the same as that used previously for p(2-napAla)[5] and p(1-pyrAla).[8]

Two amide transitions (nπ^* and $\pi\pi^*$) and 13 naphthyl vibronic transitions (five for ^1L_b, five for ^1L_a, and three for ^1B_b) were considered. The transition dipoles and monopoles for the amide transitions were taken from Woody's paper.[18] The parameters for the naphthyl groups were taken from the results of Hückel-CI calculation.[19] The transition dipoles and monopoles for ^1L_a and ^1B_b transitions were, however, normalized to reproduce the oscillator strengths calculated from an experimental absorption spectrum of 1-methylnaphthalene in TMP. The peak positions and the partial oscillator strengths of the vibronic peaks employed are listed in Table III.

The transition dipoles and the monopoles for the ^1L_b band were assumed to be zero. Those for the transitions between excited states, i.e., ^1L_b–^1L_a and ^1L_b–^1B_b, were taken directly from the Hückel-CI result.

Each vibronic peak in the ^1L_b, ^1L_a, and ^1B_b bands of the naphthyl group was treated as a single independent transition. The direction of the transition moment and the mode of the distribution of monopole charges for each vibronic transition were assumed to be the same within vibronic peaks that belong to the same band.[5]

Since the total number of local excited states for [Ala$_m$-1-napAla]$_n$ is $(2m + 15)n$, the Hamiltonian matrix of that order was constructed and diagonalized to obtain the wave functions and the energies of the polypeptide. The numbers of Ala$_m$-1-napAla units n considered were 15 (m = 0), 10 (m = 1,2,3), and 8 (m = 4). A Gaussian bandshape with a half width of 10 nm was assigned to each rotational strength, and a theoretical CD curve was drawn.

The theoretical CD curves for the ME conformations listed in Table II are shown in Figure 5 (side-chain conformation, form A) and Figure 6 (form B). The theoretical spectra should be compared with the experimental spectra shown in Figure 1. Theoretical spectra for m = 0–4 in form A agree qualitatively with the experimental ones. An exceptionally large exciton splitting at the ^1B_b band of p[Lys(Z)$_2$-1-napAla] is correctly reproduced in the theoretical CD curve for p[Ala$_2$-1-napAla]. In the case of m = 2, the theoretical CD curve at the ^1L_a band (260–310 nm) is also consistent with the experimental spectrum. Fairly good agreement is seen in the cases of m = 1, 3, and 4 as well. For all m, the agreement of the CD pattern at the ^1L_a band is satisfactory.

It should be noted that in the previous calculation on p(1-napAla) the most likely conformation was proposed to be a right-handed δ-helix.[4,5] However, the result of the present calculation, which took vibronic transitions into account, shows that the right-handed α-helix with side-

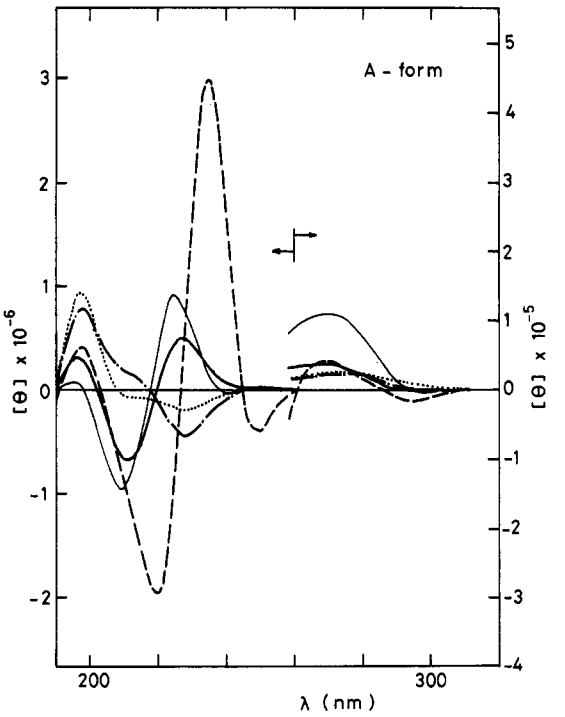


Figure 5. Theoretical CD spectra of p[Ala$_m$-1-napAla] in α-helical main-chain conformation with side-chain conformation in form A: m = 0 (—); m = 1 (—); m = 2 (- - -); m = 3 (-·-); m = 4 (···).

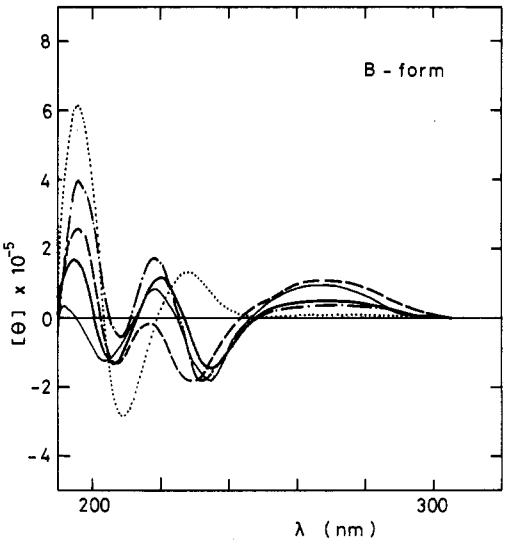


Figure 6. Theoretical CD spectra of p[Ala$_m$-1-napAla] in α-helical main-chain conformation with side-chain conformation in form B: m = 0 (—); m = 1 (—); m = 2 (- - -); m = 3 (-·-); m = 4 (···).

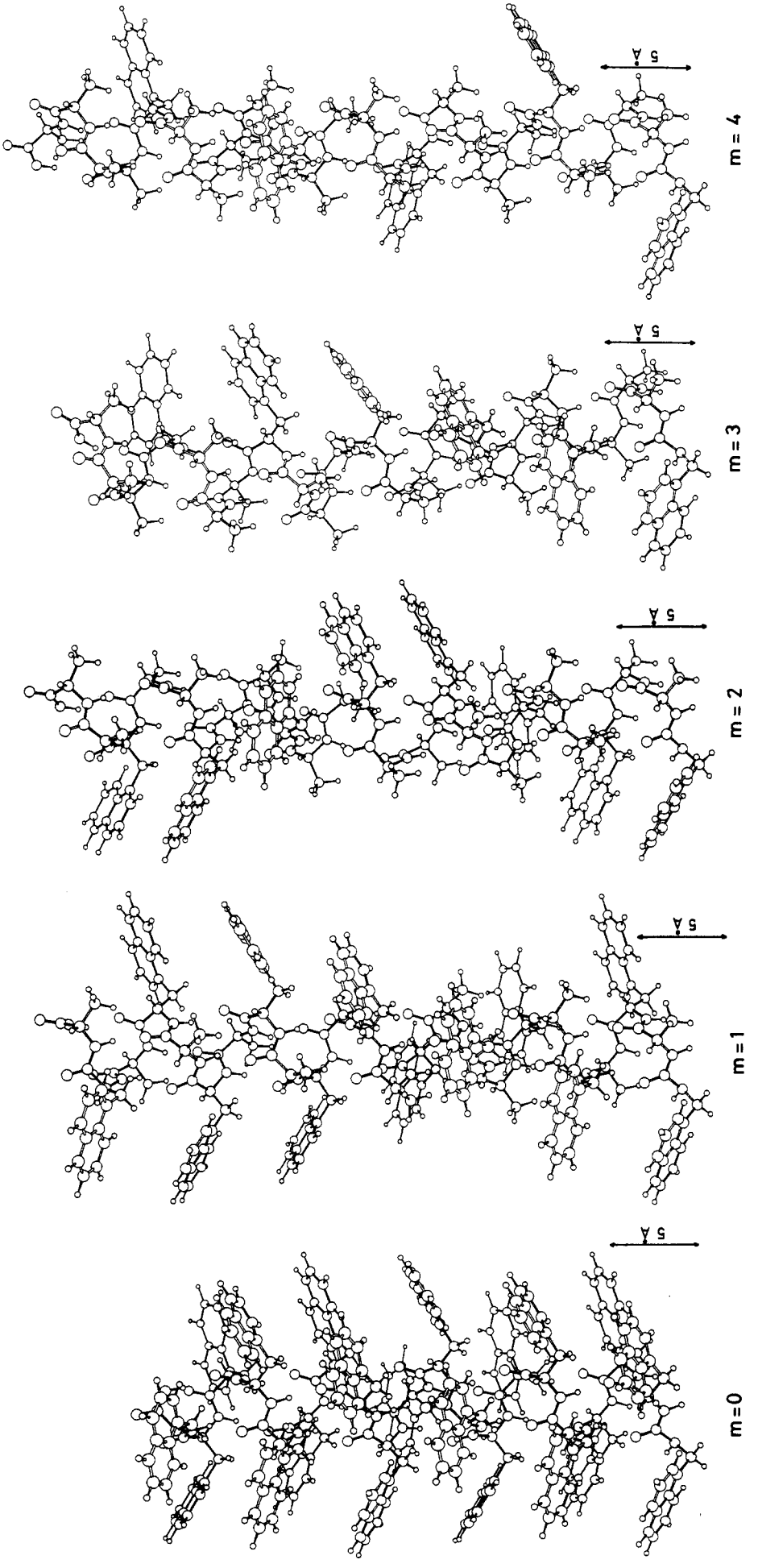


Figure 7. NAMOD (version 3) molecular display of p[Ala_m-1-napAla] in right-handed α-helical main-chain conformation with side-chain conformation in form A.

chain conformation in form A is more probable for p(1-napAla). Although peak positions of the theoretical CD spectra in the ^1B_b region deviated to shorter wavelengths than those in the experimental spectrum, no other conformation gave a more reasonable CD pattern than the α-helical conformation with the side-chain conformation in form A.

The molar ellipticities of the theoretical CD spectra are about 5 times larger than the experimental ones except for the case of $m = 0$. This is partly due to the fact that the experimental spectra are an average of the CD spectra for thermally fluctuating conformations, especially of the side chains. In the case of $m = 0$, however, the intensity of the experimental CD is almost correctly reproduced by the theoretical calculation. Possibly, the side-chain fluctuations in the homopolymer of 1-napAla are severely suppressed due to the steric crowdings of the side chains.

Contrary to the theoretical CD spectra for the side-chain conformations in form A, those for form B are quite different from the experimental ones (Figure 6). Therefore, it is concluded that the sequential polypeptides take a right-handed α-helical conformation with the side-chain conformation in form A. This conclusion is consistent with the results of conformational energy calculations, which predicted higher conformational energy and smaller conformational entropy for form B.

Theoretical CD calculations were also performed for the standard α-helical main-chain conformations with side-chain conformations in forms A and B. However, no qualitative difference was observed between the spectra for the standard ($\phi = -57°, \psi = -47°$) and the ECEPP ($-65 \sim -75°, -33 \sim -43°$) α-helical conformations, provided that the side-chain conformations are in the same form. The insensitiveness of the theoretical CD spectra to the main-chain conformation reflects the fact that the relative positions and orientations of naphthyl groups along the polypeptide chain are not much different in the two α-helical main-chain conformations.

Figure 7 illustrates "NAMOD (version 3)" molecular display drawings[20] for the four sequential polypeptides and p(1-napAla) in the ECEPP α-helical conformation with the side-chain conformation in form A. The center-to-center distance between the nearest-neighbor naphthyl groups is 6.7 [(1,5), $m = 0$], 7.1 [(1,5), $m = 1$], 6.7 [(1,4), $m = 2$], 6.7 [(1,5), $m = 3$], and 13.4 [(1,6), $m = 4$] Å. The numbers in the parentheses indicate the pair of amino acid units carrying the nearest pair of naphthyl groups. Although the spacings of the naphthyl groups for $m = 0$–3 are not much different, the relative orientations between the neighboring pair of naphthyl groups differ significantly, which is reflected in the CD spectra of the sequential polypeptides. The differences in the spacings and the orientations will aslo affect the electronic properties of these polypeptides. Studies on the efficiency and the rate of intramolecular energy migration along these polypeptide chains are in progress.

Acknowledgment. This work is supported by a Grant-in-Aid for Scientific Research, No. 59550626, from the Ministry of Education, Science, and Culture, Japan.

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