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One-Dimensional Aromatic Crystal in Solution. 1. Synthesis, Conformation, and Spectroscopic Properties of Poly(L-1-naphthylalanine)

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Abstract: A novel aromatic poly(α-amino acid), poly(L-1-naphthylalanine), was synthesized and studied by spectroscopy in solution. Polymer solutions in trimethyl phosphate showed a strong exciton splitting in circular dichroism at the ^1B_b absorption band. Theoretical circular dichroism was calculated for six possible main-chain conformations, e.g., right- and left-handed α helices, 3_{10}-helices, and δ helices, with their side-chain conformations being fixed at one of the energy minima in the side-chain energy contour map. Reasonable agreement with the experimental spectrum was attained when the main chain followed a left-handed 3_{10}-helix $(\phi,\psi) = (60°, 30°)$ or a right-handed δ helix $(-75°, -4°)$ with the side-chain conformations at their energy minima. Polymer solutions showed little excimer fluorescence, indicating that side-chain aromatic groups are separated from each other by more than ca. 4 Å. The latter result is consistent with the conformations proposed. The significance of the regularly arranged chromophores along a helical polymer chain is discussed as a possible means for long-distance energy and electron transfer.

Electronic properties of a regular array of chromophores have been extensively studied for organic crystals.[1-3] Exciton state, which is detected as the Davydov splitting in absorption spectrum, delocalizes an electronic excitation energy over a number of chromophores in the crystal, making a coherent and long-distance energy transfer possible. Although the exciton itself does not contribute to electron-transfer processes in crystals, the electronic band structure can transport charges when an excess electron (or a hole) is given. A drawback of organic crystals of aromatic molecules is the fact that their regular structure is mechanically unstable and cannot be maintained in solution. This limits their application as photoelectronic devices and their use as microscopic electron conductors, e.g., "molecular wires".[4,5]

Polymeric chromophores possess a stable structure and can be used as a solid, a film, and a solution. Hence, several vinyl polymers having chromophores have been studied extensively,[6-9] and one of them, poly(vinylcarbazole), has been used practically as a photoconductive film. However, since the main-chain conformations of the vinyl polymers are random, the chromophores are not regularly arranged along the chain and the coherent interaction among them is impossible. Actually, fluorescence spectra of the vinyl polymers having chromophores usually consist of a mixture of monomer fluorescence and multiple excimer emissions, indicating heterogeneous environments of chromophores. Excitation energy given to such heterogeneous systems may migrate among the chromophores by hopping processes but sooner or later will be trapped in excimer-forming sites, from which the energy dissipates as an excimer fluorescence. therefore, the whole chromophores should be placed in an identical environment and arrayed close enough to interact strongly with each other to achieve a long-distance energy transfer through a polymer chain.

Polypeptide chains which can exist as helices even in solution,[10,11] are potential candidates as rigid supports for chromophores to be arranged regularly. A number of aromatic poly(α-amino acid)s have been synthesized, e.g., poly(L-phenylalanine),[12-14] poly(L-tyrosine),[15-17] poly(L-tryptophan),[18,19] and some artificial para-substituted phenylalanines.[20-23] This class of poly(α-amino acid)s, whose aromatic group is separated from the C^α atom by only a methylene group, exhibits an exciton splitting in circular dichroism (CD), indicating that the aromatic chromophores are regularly arranged along the helix. As a typical case, the CD spectrum of poly(L-tryptophan)[18] shows a large positive and a negative peak around the 220-nm absorption band. However, since these aromatic poly(α-amino acid)s carry a small aromatic group, their absorption band lies only in the ultraviolet region and the interaction between chromophores is relatively weak.

Poly(α-amino acid)s having a large aromatic group that is situated more distantly from the C^α atom than the above aromatic poly(α-amino acid)s, e.g., aromatic esters of poly(L-glutamate)s[24-28] and poly(L-aspartate)s,[29,30] exhibit little aromatic CD peaks and show no exciton splitting. The side-chain chro-

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Table I. Electronic Transition Characteristics of Amide and Naphthyl Groups

group	transition	λ, nm	transition dipole moment, $\|\mu\|$, D	direction	location
amide	$\pi\pi^*$	196	3.05	38° from C=O bond in the amide plane	on the O → N line nearest the carbonyl carbon
	$n\pi^*$	225	0		
			$\|m_{n\pi^*}\| = 0.546i\beta$[a]	along the C=O bond	on the oxygen atom
naphthyl	^1B_b	225 (209)[b]	6.78 (7.96)	long axis	center of naphthyl ring
	^1L_a	282 (276)	2.84 (3.91)	short axis	center of naphthyl ring
	^1L_b	– (309)	0 (0)		

[a] β = Bohr magneton = 9.273×10^{-24} m² A. [b] Values in parentheses are the Hückel CI results for naphthalene (ref 47).

Table II. Monopole Charges for Amide Transitions and for Its Ground-State Permanent Dipole

center	distance from the amide plane,[a] Å	permanent dipole in the ground state	$\pi\pi^*$
C′	±1.0806	0.5750[b]	−0.4294
O	±0.7737	−0.8057	−0.4390
N	±0.9813	0.2308	0.8683
center	**distance from the O atom, Å[c]**	**$n\pi^*$**	**$n\pi^*\pi\pi^*$**
O	±0.8593	±0.5082	±0.3108

[a] Monopoles are located above and below the amide plane. The charges given are those for each monopole. [b] Monopole charges are given in units of 10^{-10} esu. [c] For $n\pi^*$ and $n\pi^*\pi\pi^*$ transitions there are four transition monopoles which are located in the plane including the O atom and perpendicular to the C=O bond and on the lines ±45° to the amide plane.

mophores in this class of poly(α-amino acid)s are not regularly arranged, at least in solution.

In order to obtain a one-dimensional aromatic crystal in solution, it is assumed essential to attach large aromatic groups to the main chain of poly(α-amino acid)s by a methylene group. In this study, an aromatic poly(α-amino acid), poly(L-1-naphthylalanine) [poly(L-1-NapAla)], was synthesized and studied by spectroscopy in solution. Ueno et al.[30] have synthesized this polymer, but they made no further investigation because of its insolubility. In the present study block copolymers of poly(L-1-NapAla) and soluble polymers were prepared to solubilize poly(L-1-NapAla) without breaking the regular helical structure. The geometry and the electronic structure of a helical array of chromophores may be adequate as a molecular wire which transports energy or electron across biological membranes. Development of this kind of molecular device has been an essential step to construct artificial photosynthetic systems.[31]

The geometry and the electronic properties of helical aromatic polymers are most conveniently studied by CD spectroscopy.[32] The exciton structure in chiral helical polymers can be detected as a splitting of a CD band into a pair of positive and negative peaks with approximately equal intensities. In order to correlate the CD pattern with the geometry of the polymer, a quantum mechanical calculation is necessary, which has been elaborated by Moffitt,[33,34] Tinoco, Jr.,[35] Woody,[36,37] and others.[38] Woody and co-workers[39-41] calculated theoretical CD spectra for some aromatic poly(α-amino acid)s in α-helical or 3_{10}-helical conformation. An extensive review on this subject has been published.[38] In this study, we followed the same procedure as that used for the theoretical CD calculation of poly(L-tyrosine)[39] and poly(L-phenylalanine)[40] and obtained theoretical CD spectra for several

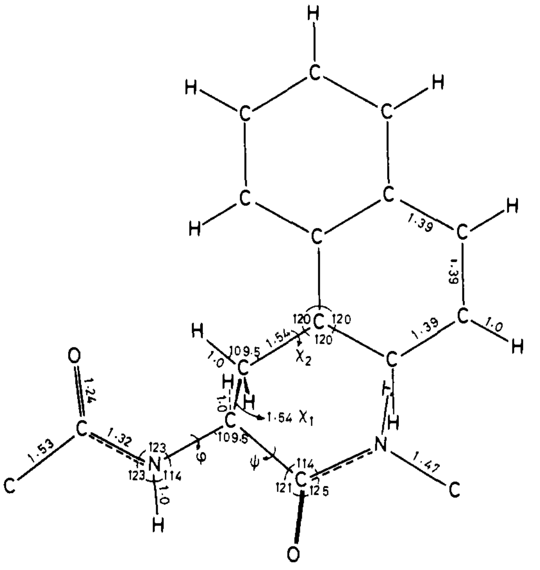

Figure 1. Molecular structure of L-1-NapAla unit.

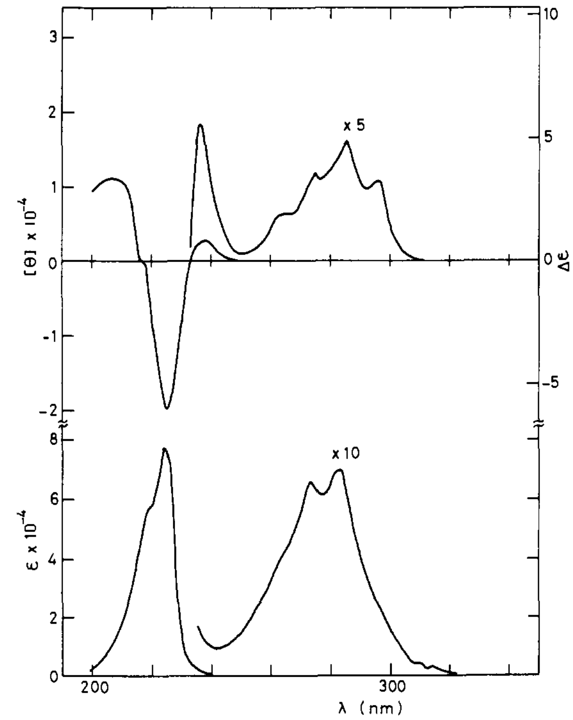

Figure 2. Absorption (lower curve) and CD (upper curve) spectra of *N*-acetyl-L-1-naphthylalanine ethyl ester in trimethyl phosphate.

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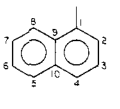
Table III. Monopole Charges for Naphthyl Transitions[b]

center[a]	ground state permanent dipole moment	^1B_b[c]	^1L_a[c]	^1L_b[d]	$^1L_b{}^1L_a$[d]	$^1L_b{}^1B_b$[d]	$^1L_a{}^1B_b$[d]
C_1[e]	0	0.00396	0.3981	0	−0.0460	−0.4182	0
C_2	0	−0.3517	−0.2481	0	0.2348	0.1603	0
C_3	0	−0.3517	0.2481	0	−0.2348	0.1603	0
C_4	0	0.00396	−0.3981	0	0.0460	−0.4182	0
C_5	0	−0.00396	−0.3981	0	−0.0460	−0.4182	0
C_6	0	0.3517	0.2481	0	0.2348	0.1603	0
C_7	0	0.3517	−0.2481	0	−0.2348	0.1603	0
C_8	0	−0.00396	0.3981	0	0.0460	−0.4182	0
C_9	0	0	−0.0840	0	0	0.5159	0
C_{10}	0	0	0.0840	0	0	0.5159	0

[a] Monopoles are located 1.0806 Å above and below the aromatic ring. Charges given are those for each monopole. [b] Charges are given in units of 10^{-10} esu. [c] Results of Hückel CI calculation for naphthalene were normalized to reproduce the observed oscillator strength. [d] Results of Hückel CI calculation (ref 47). [e] Numbering of the carbon atoms:



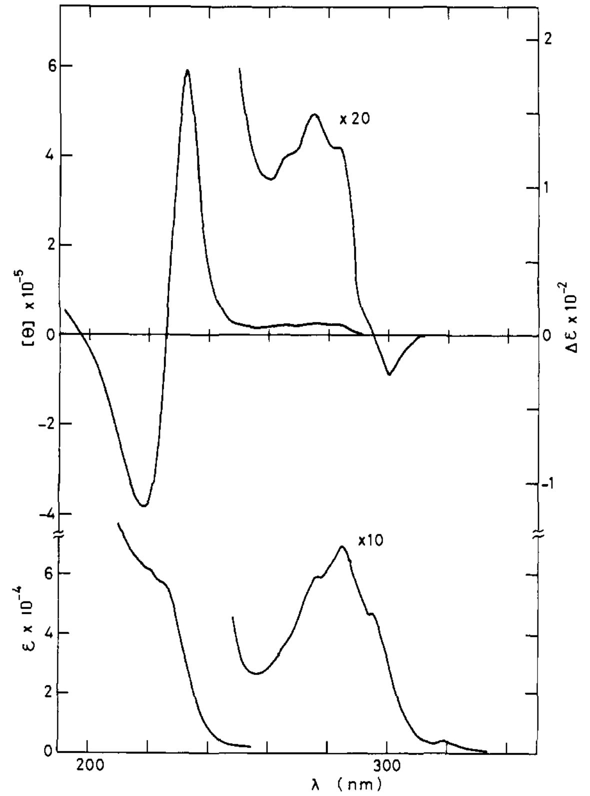


Figure 3. Absorption (lower curve) and CD (upper curve) spectra of poly(L-1-NapAla) in trimethyl phosphate.

possible conformations of poly(L-1-NapAla). By comparison with the experimental spectrum, possible conformations of poly(L-1-NapAla) in solution were proposed.

Experimental Section

Materials. Polymer Samples. The amino acid, L-1-NapAla, was prepared by the method reported for the synthesis of 2-naphthylalanine.[42] The optical resolution was performed by the selective hydrolysis of the *N*-acetyl-L-1-naphthylalanine with acylase.[43] Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.15; H, 6.05; N, 6.45.

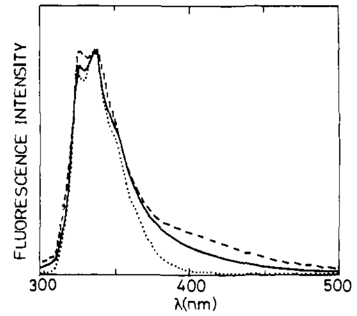
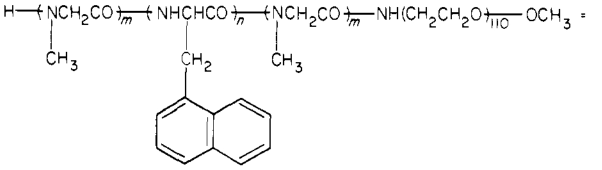


Figure 4. Fluorescence spectra of *N*-acetyl-L-1-naphthylalanine ethyl ester (···), poly(L-1-NapAla) (–), and poly(DL-1-NapAla) (--) in trimethyl phosphate. [Nap] = 1 × 10^{-5} mol L^{-1}, excitation wavelength = 285 nm.

The optical purity of L-1-naphthylalanine methyl ester was checked with ^1H NMR spectroscopy in the presence of 0.4 mol of tris[3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato]europium(III) in deuteriochloroform. Under these conditions, a racemic mixture gives two $O\text{-}CH_3$ signals with a chemical shift difference of ca. 0.07 ppm. However, no D isomer was detected in the optically resolved sample, indicating that the optical purity of the ester of the original amino acid is better than 95%.

The L-1-naphthylalanine was treated with trichloromethyl chloroformate (phosgene dimer) to give the corresponding *N*-carboxyanhydride (NCA). Since the homopolymer of L-1-NapAla was insoluble in all organic solvents examined, the following tetrablock copolymer was synthesized by the stepwise addition of NCA's.



$$H\!-\!(NCH_2CO)_m\!-\!(NHCHCO)_n\!-\!(NCH_2CO)_m\!-\!NH(CH_2CH_2O)_{110}\!-\!OCH_3 =$$

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$$(Sar)_m(L\text{-}1\text{-}NapAla)_n(Sar)_m(EO)_{110}$$

The block copolymer was prepared from right to left. First, the amine-terminated polyethylene oxide (degree of polymerization = ca. 110) was used as an initiator for the polymerization of sarcosine NCA in dimethylformamide. After the completion of the first polymerization, L-1-NapAla NCA was added and at the end of the second polymerization sarcosine NCA was added succeedingly. The degree of polymerization of each polymer unit (*m* or *n*) was adjusted by the NCA/amine molar ratio to be *m* = 160 and *n* = 40. Since no polymer precipitated during the polymerization, the product polymer should not contain the homopolymer of L-1-NapAla. The polymer solution was poured into ether and the precipitate was collected and washed with ether. The crude polymer was fractionated with a gel chromatography (Merckogel OR-PVA

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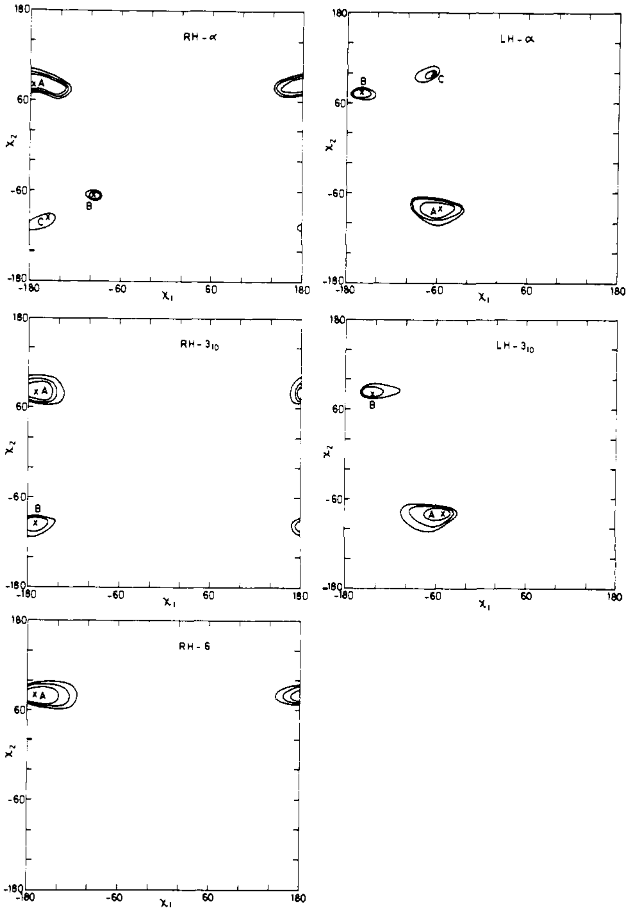

Figure 5. Energy contour maps for side-chain conformations of helical poly(L-1-NapAla). Main-chain conformations are fixed to right- and left-handed α, δ, and 3_{10}-helices. The contour lines represent the energies higher by 2.5, 5.0, and 7.5 kcal mol^{-1} than the minimum indicated by "A" in the map.

80 000,1.4 cm o.d. × 40 cm) in dimethylformamide and the highest molecular weight fraction of $M_r \simeq 80\,000$ was collected for the following spectroscopic measurements. The molecular weight of the fractionated sample is higher than the average (35 500) calculated from $m = 160$ and $n = 40$. Since the polymer blocks to solubilize the poly(L-1-NapAla) part do not affect CD and fluorescence spectra, the tetrablock copolymer will be refered to as poly(L-1-NapAla) hereafter.

A racemic poly(L-1-NapAla) was prepared in a similar way. Since it is soluble in some organic solvents, no polysarcosine unit was attached to solubilize it. The structure is represented as $(\text{DL-NapAla})_{40}(\text{EO})_{68}$ (II).

Model Compound and Solvent. *N*-Acetyl-L-1-naphthylalanine ethyl ester was prepared by the acetylation of L-1-naphthylalanine ethyl ester. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.82; H, 6.83; N, 4.69.

Commercially available trimethyl phosphate was found to contain some fluorescent impurity, which was removed by the treatment with activated charcoal and subsequent vacuum distillation.

Measurements. UV-visible absorption spectra were measured on a Hitachi EPS-3T instrument. CD spectra were recorded on a JASCO J-20 spectropolarimeter. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrofluorometer with an automatic correction attachment. All measurements were performed under aerated conditions.

Methods. Construction of Helical Conformations and Calculation of Conformational Energies. The geometry used to determine the atomic coordinates of poly(L-1-NapAla) is shown in Figure 1. The helix conformation is characterized by four dihedral angles, ϕ, ψ, χ_1, χ_2; the former two determine the main-chain and the latter two determine the side-chain conformation.[44] The helix parameters, i.e., the translation along the helix axis h, the angle of rotation about the axis per repeating unit t, and the distance of the C$^\alpha$ atom from the helix axis ρ, were calculated from the main-chain dihedral angles by the procedure reported by Sugeta and Miyazawa.[45] For each set of the dihedral angles, the atomic coordinates of monomeric L-1-naphthylalanine unit were calculated. The monomer coordinates were then subjected to a helix transformation along the helix axis according to the helix parameters, and all atomic coordinates in the helix were obtained. Examples of the helical structure will be shown later (Figure 9).

An empirical conformation energy calculation was carried out for a helical heptamer of poly(L-1-NapAla). All nonbonded atom pairs in the heptamer were considered. Empirical potential functions reported by Momany et al.[46] were employed, which include electrostatic, nonbonded van der Waals, general hydrogen-bond interactions, and intrinsic rotational energies. The calculation was started by fixing the main-chain

Table IV. Stable Side-Chain Conformations of Poly(L-1-NapAla)

main-chain conformation[a]	screw sense[b]	side-chain conformation	χ_1, deg	χ_2, deg	E,[c] kcal mol^{-1}
α helix	R	A	−175	80	5.7
($\phi = -50°$,		B	−95	−65	10.0
$\psi = -56°$,		C	−155	−95	11.1
$t = 99°$,					
$h = 1.47$ Å)					
α helix	L	A	−55	−80	3.2
($\phi = 49°$,		B	−160	75	6.0
$\psi = 57°$,		C	−65	100	8.1
$t = -99°$,					
$h = 1.47$ Å)					
3_{10} helix	R	A	−170	80	6.5
($\phi = -60°$,		B	−170	−95	9.2
$\psi = -30°$,					
$t = 111°$,					
$h = 1.75$ Å)					
3_{10} helix	L	A	−50	−80	4.7
($\phi = 60°$,		B	−145	80	7.4
$\psi = 30°$,					
$t = -111°$,					
$h = 1.75$ Å)					
δ helix	R	A	−170	80	9.3
($\phi = -75°$,					
$\psi = -4°$,					
$t = 121°$,					
$h = 2.00$ Å)					

[a] Values in the parentheses are the main-chain rotational angles (ϕ,ψ), the rotational angle per residue about the helix axis, t, and the translation per residue along the helix axis, h. [b] R = right-handed helix, L = left-handed helix. [c] (Empirical potential energy for the heptamer)/7.

Table V. Results of Energy Minimization for Poly(L-1-NapAla)

starting conformation[a]	screw sense	ϕ, deg	ψ, deg	χ_1, deg	χ_2, deg	E, kcal mol^{-1}
α-A (R) 3_{10}-A (R) δ-A (R)	R	−69	−39	−177	80	3.4
α-B (R)	R	−57	−47	−96	−73	7.0
α-C (R) 3_{10}-B (R)	R	−74	−34	−178	−96	6.1
α-A (L) 3_{10}-A (L)	L	54	50	−51	−79	2.7
α-B (L) 3_{10}-B (L)	L	54	50	−150	76	4.8
α-C (L)	L	43	62	−62	98	7.3

[a] Starting conformations for the energy minimization step were written in an abbreviated form, i.e., α-A (R) indicates right-handed α helix with side-chain conformation of A form. [b] For other notations, see Table IV.

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(44) Throughout this paper the IUPAC-IUB recommendation was followed for the definitions and notations of the rotational angles. See: *Biochemistry* **1970**, *9*, 3471.

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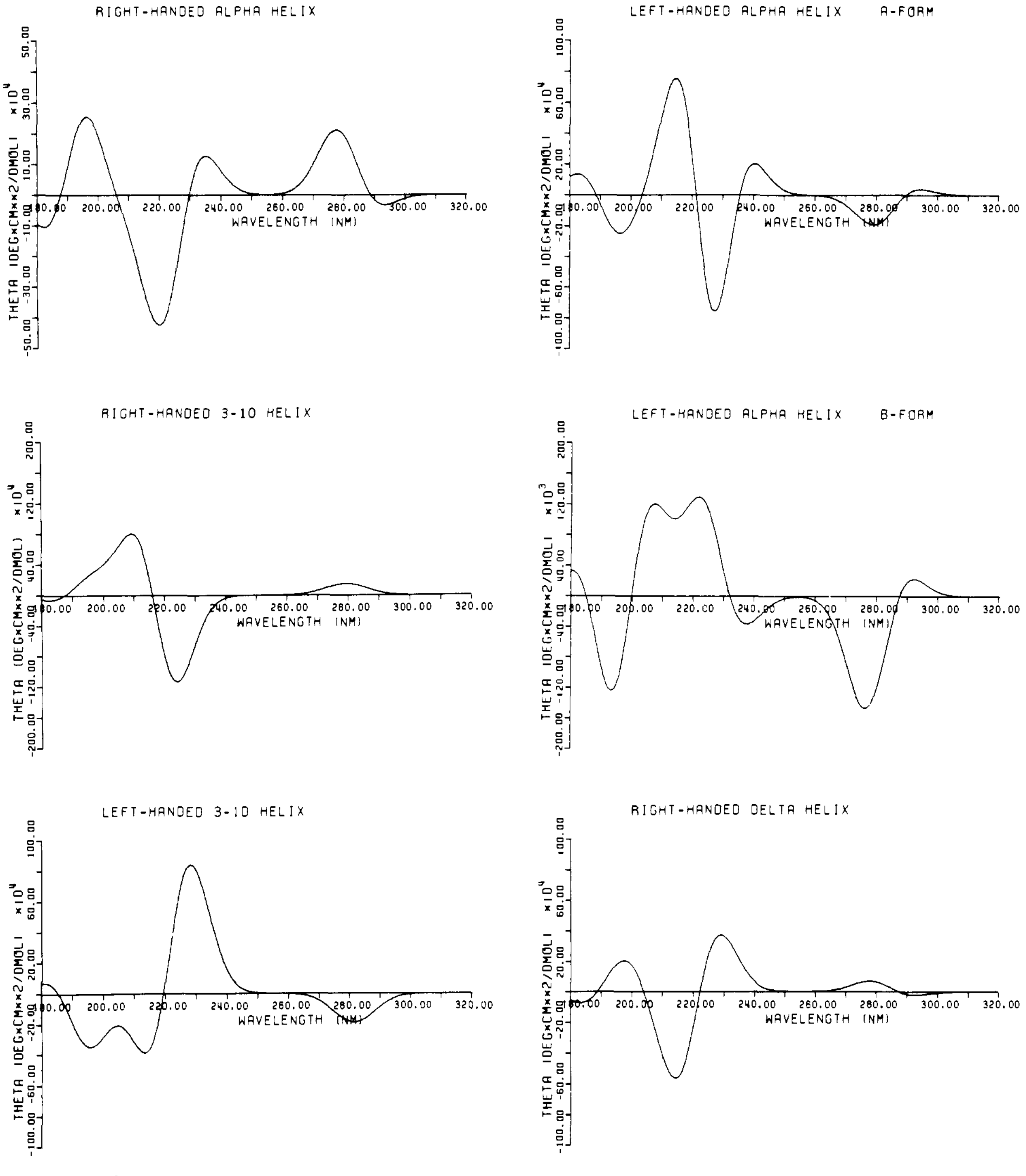
RIGHT-HANDED ALPHA HELIX

LEFT-HANDED ALPHA HELIX A-FORM

RIGHT-HANDED 3-10 HELIX

LEFT-HANDED ALPHA HELIX B-FORM

LEFT-HANDED 3-10 HELIX

RIGHT-HANDED DELTA HELIX

Figure 6. Theoretical CD curves for the standard helical conformations listed in Table IV. The side-chain conformations are in the A form, unless otherwise indicated.

conformation to one of the standard helical conformations typical for poly(α-amino acid)s, and the energy contour map was obtained for the side-chain conformations. Starting from each energy minimum in the contour map, we performed the total energy minimization, varying all rotational angles (ϕ, ψ, χ_1, χ_2) and excluding that for the amide bond (ω). Since the energy minimization gave considerably different conformations from the starting ones, the theoretical CD calculations were carried out both for the standard conformations and for the energy minimum conformations.

Calculation of Theoretical CD Spectra. Following the procedure reported by Woody,[39,40] theoretical CD was calculated for an eicosamer ($n = 20$) of helical poly(L-1-NapAla). The electronic structure, the monopole positions, the monopole charges, the electronic trnsition moments, and the magnetic transition moments for the two amide transitions, i.e., $\pi\pi^*$ and $n\pi^*$ were also taken from the Woody's paper.[37] The electronic parameters for the naphthyl group were obtained from the result of Hückel CI calculation for naphthalene reported by Pariser.[47] However, the transition wavelengths and the transition dipole moments for ^1L_a and ^1B_b transitions were corrected to reproduce the absorption spectrum of *N*-acetyl-L-1-naphthylalanine ethyl ester in trimethyl phosphate. The monopole charges for the ^1L_a and ^1B_b transitions were also normalized to reproduce the observed transition dipole moment of the model compound. The correction factor was 0.726 for the ^1L_a and 0.696 for the ^1B_b band. In this calculation only the three low-energy transitions, ^1L_b, ^1L_a, and ^1B_b, were taken into consideration. The ground-state dipole moment for the substituted naphthyl group was ignored. The electronic properties are collected in Table I and the monopole charges for amide and naphthyl groups are tabulated in Tables II and III, respectively.

Since five excited states are considered for each monomer unit, there

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[47] Pariser, R. *J. Chem. Phys.* **1956**, *24*, 250.

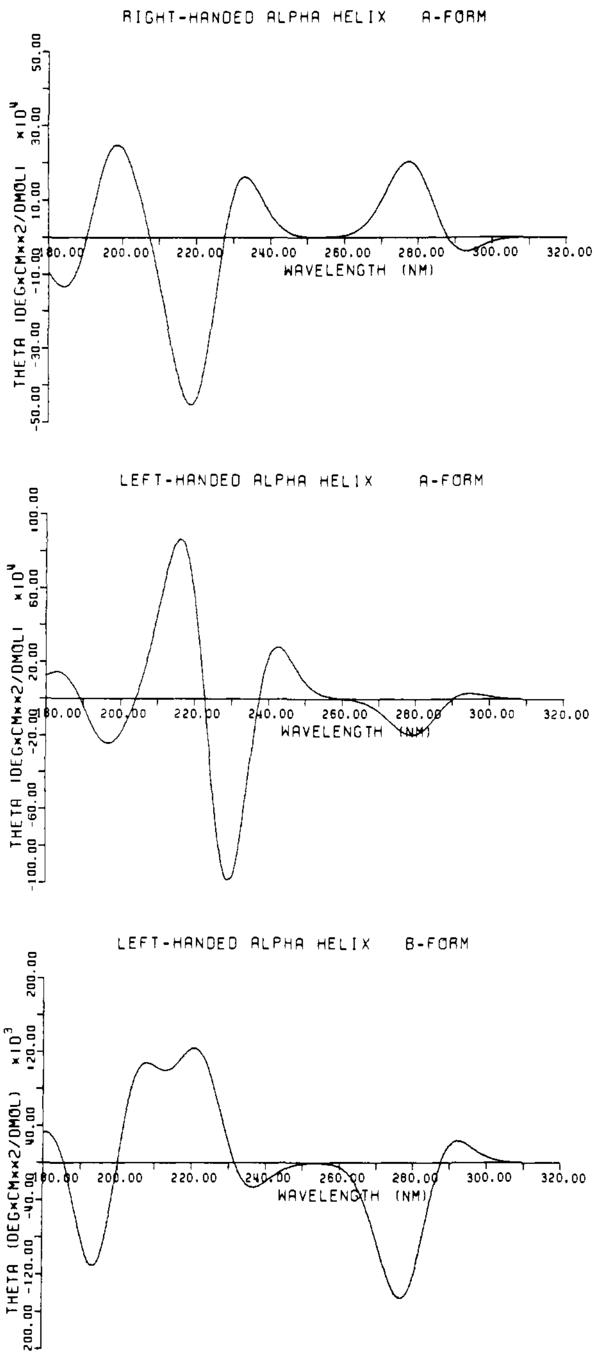

Figure 7. Theoretical CD curves for the energy minimum conformations listed in Table V. The starting conformations for the energy minimization are indicated.

are 100 locally excited wave functions for the eicosamer. The Hamiltonian matrix of the dimensions 100 × 100, whose elements were evaluated by the monopole–monopole interaction approximation, was diagonalized to yield the energies and the coefficients for the polymeric wavefunctions. The oscillator and the rotational strengths were calculated from the coefficients in a usual manner. A Gaussian broadening was assigned to each rotational strength with a half-width of 10 nm to compare the calculated rotational strengths with the experimental CD curve.[39,40] A test calculation for a polymer without the naphthyl group reproduced essentially the same oscillator and rotational strengths reported by Woody.[37]

Results and Discussion

Absorption and CD Spectra. Figures 2 and 3 show absorption and CD spectra of *N*-acetyl-L-1-naphthylalanine ethyl ester and poly(L-1-NapAla) in trimethyl phosphate solution, respectively. In the absorption spectrum of the polymer, the ^1B_b band (225 nm) exhibits a marked hypochromicity as compared with the model compound, although its quantitative evaluation is impossible due to the overlapping of the amide absorption band of polysarcosine chains. The hypochromicity reflects the interaction among the fully allowed ^1B_b transitions in the polymer.

The CD spectrum of the polymer exhibits a marked exciton splitting in the ^1B_b band. The molar ellipticity reaches a value as large as 5.9×10^5 deg cm^2 dmol^{-1} at 233 nm and -3.8×10^5 at 218 nm. Undoubtedly the large molar ellipticity results from the strong electronic interactions among the helically arranged electronic dipole moments of the allowed ^1B_b transitions of the naphthyl groups. The large exciton splitting in poly(L-1-NapAla) contrasts with the observation that poly(naphthylmethyl L-glutamate)[25] and poly(napthylmethyl L-aspartate)[29] showed smaller CD peaks at the ^1B_b band by an order of magnitude without a significant splitting. In the latter two polymers, the naphthyl groups, which are linked to polypeptide main chain by a flexible ester linkage, may not be regularly arranged. Furthermore, longer spacer chains in the latter two polymers will make the interchromophore distance longer to weaken the interaction. In any case, it was demonstrated that in order to achieve an exciton state of aromatic poly(α-amino acid), the chromophores should be linked to the C^α atom with the shortest possible spacer chains.

As for the partially allowed ^1L_a band around 280 nm, the exciton splitting is less marked. But the molar ellipticity of the polymer is about 5 times larger than that of the model and a small negative peak at 300 nm is noticeable. It is therefore concluded that the polymeric ^1B_b state is classified as a strong interaction case and forms an exciton band, whereas the ^1L_a band is an intermediate or weak interaction case and the interaction occurs only within the corresponding vibronic levels of the naphthyl group.[48]

Interestingly, the CD curve of poly(L-1-NapAla) closely resembles that of poly(L-tryptophan).[18] In the latter a large positive peak appears at 226 nm ($[\theta] = 1.41 \times 10^5$ deg cm^2 dmol^{-1}) and a negative counterpart at 210 nm ($[\theta] = -8.7 \times 10^4$). The CD pattern of the weakly allowed transition (ca. 280 nm) also looks almost the same. The similarity in CD spectra may suggest the resemblance in the helical conformations of the two polymers. However, a more detailed discussion will require the theoretical CD calculations for the two polymers, although that for poly(L-tryptophan) may encounter some difficulties due to the complexity of the electronic structure of the excited states of the indole group.

Fluorescence Spectra. Figure 4 shows the fluorescence spectra of poly(L-1-NapAla), poly(DL-1-NapAla), and the model compound in trimethyl phosphate. The polymer spectra were also measured in dimethylformamide, dimethyl sulfoxide, trifluoroethanol, and 95% tetrahydrofuran/5% trimethyl phosphate, but they were almost identical with those in Figure 4. The polymer spectra consist mostly of monomer emission of the naphthyl group with a little contribution from the excimer emission. Little excimer emission implies that the naphthyl groups are fixed along the chain with their interchromophore distance longer than 4 Å, and their movement is practically prohibited. This situation contrasts with the case of such polymers as poly(1- and 2-vinylnaphthalene)s,[6-9] poly(1-naphthylmethyl L-glutamate),[25] and poly(1-naphthylmethyl L-aspartate),[29] in which excimer emissions dominate their fluorescence spectra. In poly(vinylnaphthalene)s, a pair of nearest naphthyl groups is separated by three carbon atoms and, as the "$n = 3$" rule[49] states, this situation is the most favorable for the excimer formation. The marked excimer fluorescence observed in naphthylmethyl esters of poly(L-glutamate) and poly(L-aspartate) violates the $n = 3$ rule. This is a consequence of the flexible spacers between the aromatic groups and the polypeptide main chain, which has been suggested from the weak aromatic CD peaks of these poly(α-amino acid)s.

Little excimer emission in poly(L-1-NapAla) is not necessarily characteristic of a regular array of naphthyl groups along the helix,

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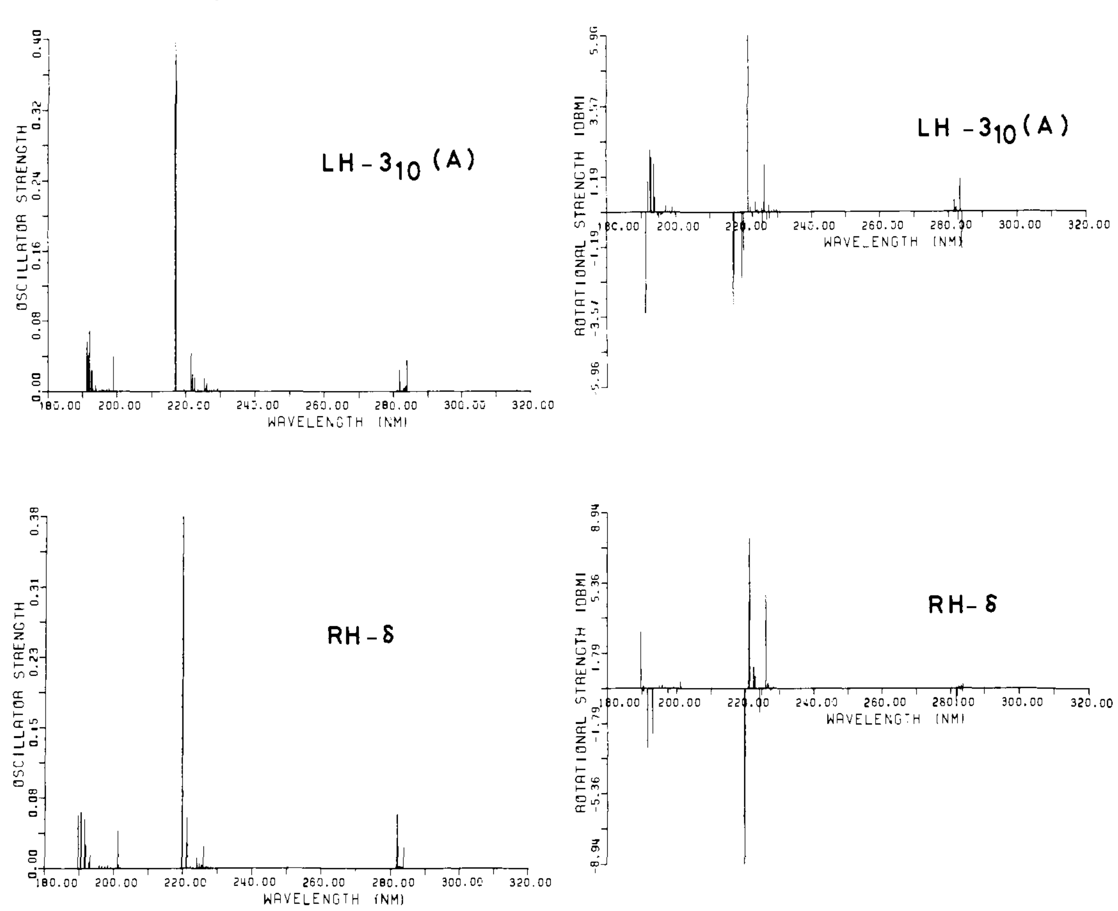

Figure 8. Oscillator strengths (left) and rotational strengths (right) for the left-handed 3_{10}-helix A form (upper) and for the right-handed δ helix (lower).

since an excimer emission increased only a little in the racemic polymer. The increase may result from the interaction between chromophores far separated along the polymer chain, which becomes possible due to a random conformation of the racemic polymer. A molecular model (see Figue 9) suggests that a pair of the closest naphthyl groups in poly(L-1-NapAla) consists not of the neighboring naphthyl groups along the polymer chain but of the two naphthyl groups attached to the nearest turn in the helix. The center-to-center interchromophore distance of the latter pair is about 6 Å according to the model.

Absence of excimer emission in poly(L-1-NapAla) suggests that the polymeric chromophore may be suitable as a molecular device for the through-chain long-distance energy or electron transfer, because of the absence of low-energy traps as well as its rodlike shape which can be retained even in solution.

Empirical Conformation Energy Calculation for Poly(L-1-NapAla). The empirical potential energies are calculated for the side-chain conformations of poly(L-1-NapAla), the main-chain conformation being fixed to right- and left-handed α-helices (ϕ,ψ) = ($\mp50°$, $\mp56°$), δ-helices ($\mp75°$, $\mp4°$),[50] and 3_{10}-helices ($\mp60°$, $\mp30°$).[51] The β structures, which are the intermolecularly hydrogen-bonded aggregates, were not considered, since it is very unlikely that the polymer can aggregate without forming excimer in the excited state. Unfortunately, strong amide absorption of polysarcosine unit prevented IR measurement of the amide region of poly(L-1-NapAla) in solution. However, the IR spectrum of the homopolymer of poly(L-1-NapAla) in the solid state (amide I, 1650 cm^{-1}; amide II, 1542 cm^{-1}) showed no indication of the presence of the β structure (ca. 1630 cm^{-1} for amide I).[52]

Side-chain energy contour maps for right- and left-handed α, δ, and 3_{10}-helices are shown in Figure 5. Since the left-handed δ helix (ϕ,ψ) = (75°, 4°), γ helix (82°, 93°),[53] and π helix (−57°, −69°)[54,55] were found to have no stable side-chain conformations, their contour maps are not presented. The allowed area in the contour map for right-handed α helix is much more restricted than that for poly(L-phenylalanine).[56] Evidently, the large naphthyl group restricted the side-chain orientation to a very limited region. Local minima in each contour map are labeled as A, B, C., ... in the decreasing order of the energy. Table IV lists the positions, the helix parameters, and the empirical energies of the local minima.

Table V tabulates the conformations obtained in the total energy minimization in the four-dimensional conformational space of ϕ, ψ, χ_1, χ_2. The starting conformations are those listed in Table IV. Some of the starting conformations converged to the same energy minimum conformation as shown in the first column of Table V, and in some cases, the energy minimum conformation differs significantly from the starting conformation. Therefore, in the theoretical CD calculation the two sets of conformations listed in Tables IV and V are considered.

Theoretical CD Spectra. Figure 6 displays theoretical CD spectra for the standard right- and left-handed α helices, 3_{10}-helices, and the right-handed δ helix, the side-chain conformations being fixed at the positions shown in Table IV. All α-helical conformations gave frequently oscillating CD curves which resulted from strong electronic interactions among compactly stacked naphthyl groups. However, these are not consistent with the experimental spectrum shown in Figure 3. Only two conformations, i.e., the left-handed 3_{10}-helix (A form) and the right-handed δ helix, gave compatible CD curves. The former conformation

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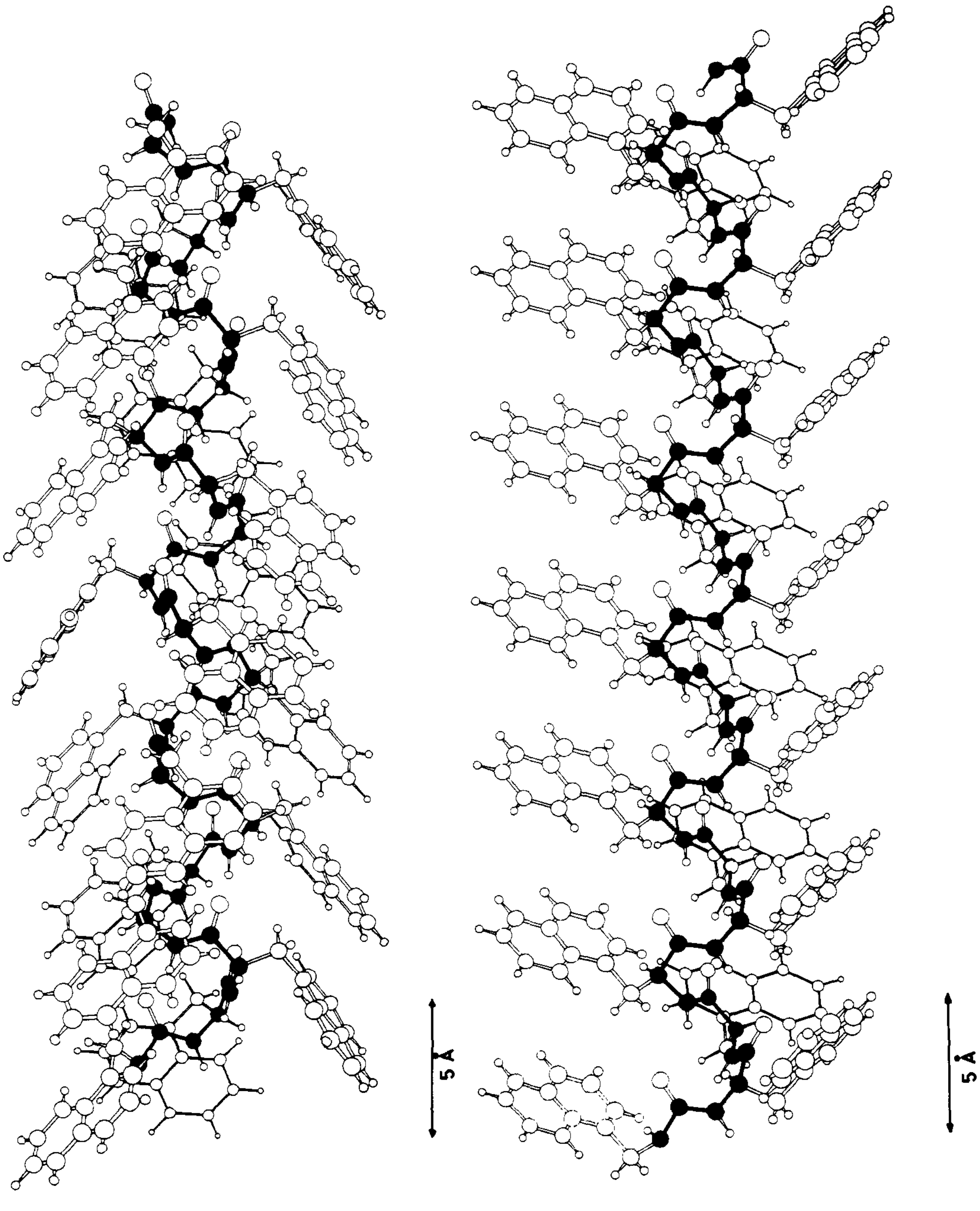

Figure 9. Molecular display of poly(L-1-NapAla) in the left-handed 3_{10}-helix A form (left) and in the right-handed δ helix (right). Solid circles represent atoms involved in the peptide main chain.

is more energetically stable (Table IV), but the CD curve of the latter conformation fits better to the experimental CD. No other conformations listed in Table IV afforded a reasonable CD curve.

Figure 7 shows the theoretical CD curves for some low-energy conformations obtained in the total energy minimization (Table V). The disagreement with the experimental curve indicates that the energy minimum conformations are unacceptable. Other energy minimum conformations listed in Table V also did not give acceptable CD curves.

Figure 8 shows the oscillator and the rotational strengths for the left-handed 3_{10}-helix A form and the right-handed δ helix. It is apparent that the calculated CD curve is a result of the compensation of strongly positive and negative rotational strengths positioned at close wavelengths. In this sense, it will be interesting to study the circularly polarized fluorescence (CPF)[57,58] of the aromatic poly(α-amino acid). Since fluorescence transition occurs only from the lowest singlet excited state, the CPF will provide information on the rotational strength for the fluorescence transition from the bottom of the ^1L_b vibrational manifold, without the ambiguity from the compensation.

It is concluded that likely conformations of poly(L-1-NapAla) in solution are the left-handed 3_{10}-helix A form and the right-handed δ helix. The former is more energetically stable, but the latter gave a more reasonable CD curve. Figure 9 illustrates the atomic model of the two conformations which were drawn with the NAMOD molecular display program.[59] The center-to-center

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(57) Steinberg, I. Z.; Schlessinger, J.; Gafni, A. In "Peptides, Polypeptides, and Proteins"; Blout, E. R., Bovey, F. A., Goodman, M., Lotan, N., Eds.; Wiley: New York, 1974; pp 351–369.

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distance between the nearest naphthyl groups which are attached to the neighboring turns is 5.5 Å for the 3_{10}-helix and 5.8 Å for the δ helix. These interchromophore distances are too far to form an excimer. The face-to-face longitudinal distance between the same pair of naphthyl groups is about 3 Å for the 3_{10}-helix and 4 Å for the δ helix, but the overlapping area of the two aromatic rings is very small.

Note Added in Proof: Ueno et al. informed us that they claimed a right-handed helix for a random copolymer of L-1-NapAla and γ-benzyl L-glutamate (67/33).[30a]

Registry No. Poly(L-1-NapAla) tetrablock copolymer, 84117-45-3; Poly(DL-1-NapAla) diblock copolymer, 84109-04-6; *N*-acetyl-L-1-naphthyl ethyl ester, 84109-03-5.

Communications to the Editor

Structures and Energies of $C_6H_6^{2+}$ Isomers. Fragmentation into $C_5H_3^+$ and CH_3^+[1]

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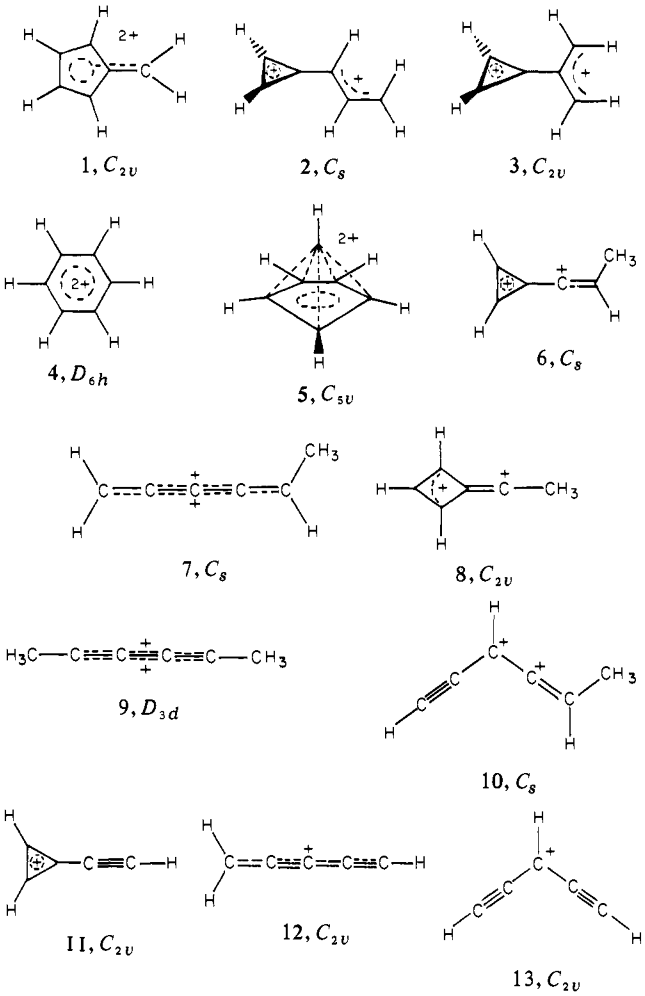
$C_6H_6^{2+}$, produced in high intensity by various ionization and mass spectrometric methods from numerous aromatic and aliphatic compounds, is a commonly observed gas-phase carbodication.[2-4] Structural reorganization may lead to the same $C_6H_6^{2+}$ species from various precursors. Although two $C_3H_3^+$ cyclopropenium ions would be the thermodynamically most stable cleavage products, the predominant fragmentation takes a curious course to give $C_5H_3^+$ (also of unknown structure) and CH_3^+.[2-4] This releases considerable kinetic energy (2.6 eV); the peak shape indicates a rather specific process involved.[2,3] A simple model has been used to interpret this result. If most of the energy release is attributed to Coulombic repulsion of the separating ions, the e^2/r relationship provides an estimate of r (5.5 Å), taken to be the initial intercharge distance (assuming idealized point charges). Since the diameter of the benzene ring (2.9 Å) is much smaller, acyclic $C_6H_6^{2+}$ structures, $CH_3C_4CH_3^{2+}$ in particular, have been postulated.[2,3] However, such idealized point-charge models are quite unrealistic for $C_6H_6^{2+}$ structural candidates; charge would be delocalized not only in the carbon π framework but to the hydrogens as well.[5,6] Charge delocalization also is expected in the fragmentation transition state.

Chart I



We present here the results of the first ab initio calculations on a set of $C_6H_6^{2+}$ isomers that should include the global energy

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