THE CIRCULAR DICHROISM SPECTRUM OF PEPTIDES IN THE POLY(PRO)II CONFORMATION

Robert W. Woody

Contents:

Derivation of Eqns. 6, 14, and 19-21 in Text

The contributions to the electric and magnetic dipole transition moments that are of interest here result from: (1) mixing of the ground configuration with doubly excited configurations in which one residue is in a discrete excited state (*a*, *b*, *c*,...) and another residue is in a high-energy excited state (α, β, γ,...); (2) mixing of singly excited configurations, one with a residue in a discrete excited state and the other with a different residue in a high-energy excited state. Eq. IIIB-18 of Tinoco[1] gives the electric dipole transition moment for exciton state K, $\boldsymbol{\mu}_{0K}$. Stripped of terms that are not relevant in the present context, this becomes:

$$\boldsymbol{\mu}_{0K} = \sum_{i,a} C_{iaK} \{ \boldsymbol{\mu}_{i0a} - (2/h) \sum_{l \neq i} \sum_{\beta} \frac{\nu_\beta V_{i0a;l0\beta} \boldsymbol{\mu}_{l0\beta}}{(\nu_\beta^2 - \nu_a^2)} \} \qquad \text{S1}$$

where C_{iaK} is defined in Eq. 4 of the text; $\boldsymbol{\mu}_{i0a}$ is the electric dipole transition moment for transition $0 \rightarrow a$ in group *i*; ν_a and ν_β are the frequencies of transitions $0 \rightarrow a$ and $0 \rightarrow \beta$, respectively; and $V_{i0a;l0\beta}$ is defined in Eq. 8 of the text.

Similarly, the magnetic dipole transition moment, $\mathbf{m}_{K0}$, in Tinoco's Eq. IIIB-20 becomes:

$$\mathbf{m}_{K0} = (i\pi/c) \sum_{j,b} C_{jbK} \{ \mathbf{R}_j \times \boldsymbol{\mu}_{j0b} \nu_b - (2/h) \sum_{l \neq j} \sum_{\beta} \frac{\nu_b \nu_\beta V_{j0b;l0\beta} \mathbf{R}_l \times \boldsymbol{\mu}_{l0\beta}}{(\nu_\beta^2 - \nu_a^2)} \}$$

$$+ \sum_{j,b} C_{jbK} \mathbf{m}_{jb0} \qquad \text{S2}$$

where $\mathbf{R}_j$ and $\mathbf{R}_l$ are, respectively, the positions of groups *j* and *l*; and $\mathbf{m}_{jb0}$ is the magnetic dipole transition moment of the transition $0 \rightarrow b$ in group *j*. (A contribution to the intrinsic magnetic dipole transition moment analogous to the second term in brackets has been omitted because it involves $\mathbf{m}_{l\beta 0}$, the magnetic dipole transition moment of a high-energy transition, about which no information is available.)

The exciton rotational strength is the imaginary part of the scalar product of these transition dipole moments:

$$R_{0K} = \mathrm{Im}\,(\boldsymbol{\mu}_{0K}\bullet\mathbf{m}_{0K}) = (\pi/c)\sum_{i,a}\sum_{j,b} C_{iaK}C_{jbK}\{\nu_a\boldsymbol{\mu}_{i0a}\bullet\mathbf{R}_j\times\boldsymbol{\mu}_{j0b}$$

$$-(2/h)\sum_{l\neq j}\sum_{\beta}\frac{\nu_b\nu_\beta V_{j0b;l0\beta}\boldsymbol{\mu}_{i0a}\bullet\mathbf{R}_l\times\boldsymbol{\mu}_{l0\beta}}{(\nu_\beta^2-\nu_b^2)}$$

$$-(2/h)\sum_{l\neq j}\sum_{\beta}\frac{\nu_a\nu_\beta V_{i0a;l0\beta}\boldsymbol{\mu}_{l0\beta}\bullet\mathbf{R}_j\times\boldsymbol{\mu}_{j0b}}{(\nu_\beta^2-\nu_a^2)}\}$$

$$+\mathrm{Im}\sum_{i,a}\sum_{j,b}C_{iaK}C_{jbK}[\boldsymbol{\mu}_{i0a}\bullet\mathbf{m}_{jb0}-(2/h)\sum_{l\neq i}\sum_{\beta}\frac{\nu_\beta V_{i0a;l0\beta}\boldsymbol{\mu}_{l0\beta}\bullet\mathbf{m}_{jb0}}{(\nu_\beta^2-\nu_a^2)}] \qquad \text{S3}$$

The first term and the first term in the last line of Eq. S3 are the zeroth-order exciton contributions, which are included in the matrix method, so we shall drop them. The second and third lines are the first-order correction to the exciton rotational strength for electrically allowed transitions and give rise to Eq. 6 in the paper. Because *i0a* and *j0b* are equivalent, we can interchange these indices in line 2 and, using the properties of the scalar triple product, combine lines 2 and 3 to give:

$$(R_\mu)_{KK} = -(2\pi/c)\sum_{i,a}\sum_{j,b}\sum_{l\neq j}\sum_{\beta} C_{iaK}C_{jbK}\frac{\nu_a\nu_\beta V_{j0b;l0\beta}\mathbf{R}_{il}\bullet\boldsymbol{\mu}_{l0\beta}\times\boldsymbol{\mu}_{i0a}}{h(\nu_\beta^2-\nu_a^2)} \qquad \text{S4}$$

where $\mathbf{R}_{il} = \mathbf{R}_l - \mathbf{R}_i$. Substituting $\nu_a \approx \nu_K$, we obtain:

$$(R_\mu)_{KK} = -(2\pi/\lambda_K)\sum_{i,a}\sum_{j,b}\sum_{l\neq j}\sum_{\beta} C_{iaK}C_{jbK}\frac{\nu_\beta V_{j0b;l0\beta}\mathbf{R}_{il}\bullet\boldsymbol{\mu}_{l0\beta}\times\boldsymbol{\mu}_{i0a}}{h(\nu_\beta^2-\nu_K^2)} \qquad \text{S5}$$

This is Eq. 6 in the text of the paper.

The contribution of the high-energy transitions to the rotational strength of exciton level K through the magnetically allowed transitions is obtained from the last term of Eq. S3.

$$(R_m)_{KK} = -2\sum_{i,a}\sum_{j,b}\sum_{l\neq \mathbf{l}}\sum_{\beta} C_{iaK}C_{jbK}\frac{\nu_\beta V_{i0a;l0\beta}\,\mathrm{Im}[\boldsymbol{\mu}_{l0\beta}\bullet \mathbf{m}_{jb0}]}{h(\nu_\beta^2-\nu_a^2)} \qquad \text{S6}$$

With the substitution of ν_K for ν_a, this becomes

$$(R_m)_{KK} = -2\sum_{i,a}\sum_{j,b}\sum_{l\neq \mathbf{l}}\sum_{\beta} C_{iaK}C_{jbK}\frac{\nu_\beta V_{i0a;l0\beta}\,\mathrm{Im}[\boldsymbol{\mu}_{l0\beta}\bullet \mathbf{m}_{jb0}]}{h(\nu_\beta^2-\nu_K^2)} \qquad \text{S7}$$

which is equivalent to Eq. 14 in the text of the paper.

The standard exciton model only considers the mixing of a number of low-energy singly excited configurations. Doubly excited configurations are neglected. These doubly excited configurations can mix with the ground configuration and with the singly excited configurations. However, only mixing with the ground state contributes to the electric and magnetic dipole transition moments. Therefore, we will neglect the perturbation terms in the excited-state wave function and keep only the zeroth-order term.

$$\Psi_0 = \psi_0 - 2^{-1}\sum_{i,a}\sum_{k,c}\frac{V_{i0a;k0c}}{h(\nu_a+\nu_c)}\psi_{ia,kc} \qquad \text{S8}$$

$$\Psi_K = \sum_{i,a} C_{iaK}\psi_{ia} \qquad \text{S9}$$

where $\psi_{ia,kc}$ is the wave function for the doubly excited configuration in which group *i* is in excited state *a* and group *k* is in excited state *c*, all other groups being in their ground states.

To calculate the contributions to the CD of this mixing with doubly excited configurations, we use the dipole velocity formalism of Moffitt[2] because this yields rotational strengths that are origin-independent.

$$R_{0K} = \frac{e^2\hbar^3}{2m^2cE_K}(\Psi_0|\nabla|\Psi_K)\bullet(\Psi_0|\mathbf{r}\times\nabla|\Psi_K) \qquad \text{S10}$$

where $\nabla = \mathbf{i}\,\partial/\partial x + \mathbf{j}\,\partial/\partial y + \mathbf{k}\,\partial/\partial z$ is the gradient operator and E_K is the transition energy for exciton level *K*. The gradient operator has matrix elements that are proportional to those of the dipole moment operator [3]:

$$\nabla_{i0a} = \frac{2\pi m\nu_a}{e\hbar}\boldsymbol{\mu}_{0a} \qquad \text{S11}$$

Similarly, the matrix elements of the $\mathbf{r}\times\nabla$ operator are proportional to those of the **m** operator:

$$\mathbf{r}\times\nabla = -\frac{2imc}{e\hbar^2}\mathbf{m}_{i0a} \qquad \text{S12}$$

To first order in V,

$$(\Psi_0|\nabla|\Psi_K) = (\psi_0 - 2^{-1}\sum_{k,c}\sum_{l.d}\frac{V_{k0c;l0d}}{h(\nu_c+\nu_d)}\psi_{kc,ld}|\nabla|\sum_{i,a}C_{iaK}\psi_{ia}) \qquad \text{S13}$$

$$= \sum_{i,a}C_{iaK}\{(\psi_0|\nabla|\psi_{ia}) - 2^{-1}\sum_{k,c}\sum_{l,d}\frac{V_{k0c;l0d}}{h(\nu_c+\nu_d)}(\psi_{kc,ld}|\nabla|\psi_{ia})\} \qquad \text{S14}$$

The second term in this equation will vanish unless *ia=ld* or *ia=me*. Thus, for a given *ia*, we have two equivalent non-zero terms, permitting us to simplify Eq. S14 to:

$$(\Psi_0|\nabla|\Psi_K) = \sum_{i,a}C_{iaK}\{(\psi_0|\nabla|\psi_{ia}) + \sum_{k,c}\frac{V_{i0a;k0c}}{h(\nu_a+\nu_c)}(\psi_0|\nabla|\psi_{kc})\} \qquad \text{S15}$$

where we have reversed the sign of the summation by interchanging the order of the wave functions in the matrix element. Similarly, the angular momentum matrix element can be written:

$$(\Psi_0|\mathbf{r}\times\nabla|\Psi_K) = \sum_{j,b}C_{jbK}\{(\psi_0|\mathbf{r}\times\nabla|\psi_{jb}) + \sum_{l,d}\frac{V_{j0b;l0d}}{h(\nu_b+\nu_d)}(\psi_0|\mathbf{r}\times\nabla|\psi_{ld})\} \qquad \text{S16}$$

We therefore have the rotational strength in the dipole velocity form:

$$R_{0AK} = \frac{\gamma_P}{E_K}(\Psi_0|\nabla|\Psi_{AK}) \bullet (\Psi_0|\mathbf{r}\times\nabla|\Psi_{AK}) = \frac{\gamma_P}{E_K}\sum_{i,a}\sum_{j,b} C_{iaK}C_{jbK}\{\nabla_{i0a} \bullet (\mathbf{r}\times\nabla)_{j0b}$$

$$+\sum_{k,c}\frac{V_{i0a;k0c}}{h(\nu_a+\nu_c)}\nabla_{i0a} \bullet (\mathbf{r}\times\nabla)_{l0c} + \sum_{l,d}\frac{V_{j0b;l0d}}{h(\nu_b+\nu_d)}\nabla_{i0a} \bullet (\mathbf{r}\times\nabla)_{l0d}\} \qquad \text{S17}$$

where $\gamma_P = e^2\hbar^3/2m^2c$. We have omitted the second-order term arising from the product of the two summations. Eq. S17 contains the zeroth- and first-order exciton contributions:

$$R_{0K} = R_{0K}^{(0)} + R_{0K}^{(1)} \qquad \text{S18}$$

The zeroth-order term, the first term in Eq. S17, has been included via the matrix method. We are interested here in the first-order correction:

$$R_{0K}^{(1)} = \frac{\gamma_p}{E_K}\sum_{i,a}\sum_{j,b} C_{iaK}C_{jbK}\{\sum_{k,c}\frac{V_{i0a;k0c}}{h(\nu_a+\nu_c)}\nabla_{k0c} \bullet (\mathbf{r}\times\nabla)_{j0b}$$

$$+\sum_{l,d}\frac{V_{j0b;l0d}}{h(\nu_b+\nu_d)}\nabla_{i0a} \bullet (\mathbf{r}\times\nabla)_{l0d}\} \qquad \text{S19}$$

which is Eq. 19 in the text.

According to perturbation theory[4], the energy shift for exciton state K due to mixing with high-energy transitions is:

$$\Delta E_K = \sum_{l,\beta}\frac{H_{Kl\beta}H_{l\beta K}}{h(\nu_K-\nu_\beta)} \qquad \text{S20}$$

where ν_K is the unperturbed frequency of exciton state *K*; ν_β is the unperturbed frequency of the transition $0 \rightarrow \beta$ in group *l*; and

$$\boldsymbol{H}_{\boldsymbol{Kl\beta}} = (\Psi_{\boldsymbol{K}} \left| \sum_{\boldsymbol{i}} \sum_{\boldsymbol{l>i}} \boldsymbol{V}_{\boldsymbol{ij}} \right| \psi_{\boldsymbol{l\beta}}) = (\sum_{\boldsymbol{i,a}} \boldsymbol{C}_{\boldsymbol{iaK}} \psi_{\boldsymbol{ia}} \left| \sum_{\boldsymbol{i}} \sum_{\boldsymbol{l>i}} \boldsymbol{V}_{\boldsymbol{il}} \right| \psi_{\boldsymbol{l\beta}}) = \sum_{\boldsymbol{i,a}} \sum_{\boldsymbol{l,\beta}} \boldsymbol{C}_{\boldsymbol{iaK}} \boldsymbol{V}_{\boldsymbol{i0a;l0\beta}} \qquad \text{S21}$$

Using the monopole approximation for the charge density of the discrete transition $0 \rightarrow a$ (Eq. 8 in the text), we obtain:

$$H_{Kl\beta} = -\sum_{i,a} \sum_{s} \sum_{l,\beta} C_{iaK} \frac{q_{is0a} \mathbf{R}_{is,l\beta} \bullet \boldsymbol{\mu}_{l0\beta}}{R^3_{is,l\beta}} \qquad \text{S22}$$

Correspondingly,

$$H_{l\beta K} = -\sum_{j,b} \sum_{t} \sum_{l,\beta} C_{jbK} \frac{q_{jt0b} \boldsymbol{\mu}_{l0\beta} \bullet \mathbf{R}_{is,l\beta}}{R^3_{is,l\beta}} \qquad \text{S23}$$

Thus,

$$\Delta E_K = -\sum_{i,a} \sum_{j,b} \sum_{l,\beta} C_{iaK} C_{jbK} \frac{\mathbf{R}_{is,l\beta} \bullet \boldsymbol{\mu}_{l0\beta} \boldsymbol{\mu}_{l0\beta} \bullet \mathbf{R}_{jt,l\beta}}{h(\nu^0_\beta - \nu^0_K) R^3_{is,l\beta} R^3_{jt,l\beta}} \qquad \text{S24}$$

We can approximate[1] the summation over the high-energy states β in group *l* by introducing the polarizability of group *l*, $\boldsymbol{\alpha}_l$:

$$\sum_{\beta} \frac{\boldsymbol{\mu}_{l0\beta} \boldsymbol{\mu}_{l0\beta}}{\nu_\beta - \nu_K} \cong \frac{h \nu_0 \boldsymbol{\alpha}_l}{2(\nu_0 - \nu_K)} \qquad \text{S25}$$

where ν_0 is an average frequency for the high-energy transitions, assumed in this work to be (in wavenumbers) 10^5 cm^{-1}. With this substitution, we have:

$$\Delta E_K = -\frac{\nu_0}{2(\nu_0 - \nu_K)} \sum_{i,a} \sum_{j,b} \sum_{l,\beta} C_{iaK} C_{jbK} \frac{\mathbf{R}_{is,l\beta} \bullet \boldsymbol{\alpha}_l \bullet \mathbf{R}_{jt,l\beta}}{h(\nu_\beta - \nu_K) R^3_{is,l\beta} R^3_{jt,l\beta}} \qquad \text{S26}$$

Eq. 20 in the text is now obtained by recognizing that the multiple summations in Eq. S26 are equivalent to the matrix product:

$$\Delta E_K = -\frac{\nu_0}{2(\nu_0 - \nu_K)} \sum_l \mathbf{C}^+ \mathbf{G}\, \boldsymbol{\alpha}_l \mathbf{G}^+ \mathbf{C} \qquad \text{S27}$$

where the matrices **C** and $\mathbf{C}^+$ are the eigenvector matrix and its transpose, respectively, from the diagonalization of the Hamiltonian matrix in the matrix method; the matrix **G** is defined in Eq. 12 in the text and $\mathbf{G}^+$ is its transpose; and the polarizability matrix $\boldsymbol{\alpha}_l$ is constructed from the matrices representing the group polarizability tensors as described in the text.

To calculate the change in dipole strength of exciton level *K* due to mixing with high-energy transitions, we start with Eq. S1. We wish to calculate:

$$D_K = \boldsymbol{\mu}_{0K}\, \boldsymbol{\mu}_{K0} = \sum_{i,a} C_{iaK} \{ \boldsymbol{\mu}_{i0a} - 2 \sum_{l \neq i} \sum_{\alpha} \frac{V_{i0a;l0\alpha}\, \boldsymbol{\mu}_{l0\alpha} \nu_\alpha}{h(\nu_\alpha^2 - \nu_a^2)} \} \bullet \sum_{j,b} C_{jbK} \{ \boldsymbol{\mu}_{j0b} - 2 \sum_{m \neq j} \sum_{\beta} \frac{V_{j0b;m0\beta}\, \boldsymbol{\mu}_{m0\beta} \nu_\beta}{h(\nu_\beta^2 - \nu_b^2)} \} \qquad \text{S28}$$

The leading (zeroth-order) term in this scalar product is the usual exciton dipole strength that is calculated in the matrix method. We are interested in the two first-order terms, which are equivalent and can be combined to give:

$$\Delta D_K = -4 \sum_{i,a} \sum_{j,b} C_{iaK} C_{jbK}\, \boldsymbol{\mu}_{i0a} \bullet \sum_{m \neq j} \sum_{\beta} \frac{V_{j0b;m0\beta}\, \boldsymbol{\mu}_{j0b} \nu_\beta}{h(\nu_\beta^2 - \nu_b^2)} \qquad \text{S29}$$

Using the monopole approximation for $\boldsymbol{\mu}_{j0b}$ (Eq. 8 in text), we have:

$$\Delta D_K = \frac{4}{h} \sum_{i,a} \sum_{j,b} \sum_{t} C_{iaK} C_{jbK} \sum_{m \neq j} \sum_{\beta} \frac{q_{j0bt}\, \boldsymbol{\mu}_{i0a} \bullet \boldsymbol{\mu}_{m0\beta}\, \boldsymbol{\mu}_{m0\beta} \bullet \mathbf{R}_{jbt,m\beta}}{R^3_{jbt,m\beta}(\nu_\beta^2 - \nu_b^2)} \qquad \text{S30}$$

Replacing ν_β by ν_0, ν_b by ν_K, and $\sum_\beta \boldsymbol{\mu}_{m0\beta}\, \boldsymbol{\mu}_{m0\beta}$ by $h\nu_0 \boldsymbol{\alpha}_m/2$, we obtain:

$$\Delta D_K = \frac{2\nu_0^2}{\nu_0^2 - \nu_K^2} \sum_{i,a} \sum_{j,b} \sum_{t} \sum_{m \neq j} C_{iaK} C_{jbK} \frac{q_{j0bt} \boldsymbol{\mu}_{10a} \bullet \boldsymbol{\alpha}_m \bullet \mathbf{R}_{jbt,m\beta}}{R^3_{jbt,m\beta}} \qquad \text{S31}$$

$$= \frac{2\nu_0^2}{\nu_0^2 - \nu_K^2} \sum_{m} \mathbf{C}^+ \boldsymbol{\mu}_{m} \boldsymbol{\alpha}_m \mathbf{G}^+ \mathbf{C} \qquad \text{S32}$$

This is Eq. 21 in the text. The *Kth* diagonal element of the matrix product on the right-hand side of Eq. S32 is the correction to the dipole strength of exciton level *K*.

Table S1. Coordinates[a] of N-Methylacetamide Used in

Polarizability Tensor Calculations

	ATOMIC POSITIONS		
Atom	X	Y	Z
C' (carbonyl C)	1.530000	.000000	.000000
O (carbonyl O)	2.154272	1.059804	.000000
C_1 (C-methyl C)	0.000000	0.000000	.000000
H_1 (C-methyl H)	–0.363333	1.027662	.000000
H_2 (C-methyl H)	–0.363333	–0.513831	– .889981
H_3 (C-methyl H)	–0.363333	–0.513831	.889981
N (amide N)	2.089969	–1.200858	.000000
C_2 (N-methyl C)	3.535009	–1.352738	.000000
H_4 (N-methyl H)	3.788932	–2.412749	.000000
H_5 (N-methyl H)	3.950062	–0.879701	– .889981
H_6 (N-methyl H)	3.950062	–0.879701	.889981
H_N (amide H)	1.574931	–2.058025	.000000

[a] The coordinate system is the standard coordinate system of Ooi et al.[5], with the x-axis along the C_α–C' bond, the carbonyl O having a positive y-coordinate, and the origin at C_α. Coordinates are in Å.

Table S2. Positions of Bond and Lone-Pair Tensors in N-Methylacetamide

TENSOR POSITIONS[a]				
Tensor	x	y	z	Comment
CO1	3.685810	1.333735	–.471490	CARBONYL BANANA BOND
CO2	3.685810	1.333735	.471490	CARBONYL BANANA BOND
O-LP1	3.707191	2.464276	.000000	CARBONYL OXYGEN LONE PAIR
O-LP2	4.664518	1.913979	.000000	CARBONYL OXYGEN LONE PAIR
CC_1	1.426908	–.028686	.000000	C METHYL CC BOND
C_1-H_1	–.466819	1.297037	.000000	C METHYL CH BOND
C_1-H_2	– .446901	–.670431	–1.133331	C METHYL CH BOND
C_1-H_3	– .446901	–.670431	1.133331	C-METHYL CH BOND
CN1	3.646710	–1.665251	–.512077	AMIDE CN BANANA BOND
CN2	3.646710	–1.665251	.512077	AMIDE CN BANANA BOND
NH	3.351576	–3.229547	.000000	AMIDE NH BOND
NC_2	5.103751	–2.392518	.000000	N METHYL NC BOND
C_2-H_4	6.987396	–3.933881	.000000	N METHYL CH BOND
C_2-H_5	7.215265	–1.959871	–1.142717	N METHYL CH BOND
C_2-H_6	7.215265	–1.959871	1.142717	N METHYL CH BOND

[a] The coordinate system is the standard coordinate system of Ooi et al.[5], with the x-axis along the C_α–C' bond, the carbonyl O having a positive y-coordinate, and the origin at the C_α. Coordinate values are in atomic units, a_0. Based upon bond and lone-pair polarizability tensors calculated for *trans*-N-methylacetamide by Walter Stevens using the method of Garmer and Stevens.[6]

Table S3. Polarizability Tensor Components for N-Methylacetamide[a]

Tensor[b]	xx	Yy	zz	xy	xz	yz	yx	zx	zy
CO1	2.3415	4.0788	2.1384	.7521	.1762	.5742	1.5538	–.5978	– .2989
CO2	2.3420	4.0787	2.1383	.7519	–.1759	–.5738	1.5542	.5978	.2990
O-LP1	1.3778	2.4885	1.3635	.2190	.0002	.0001	–.2610	.0000	.0001
O-LP2	2.3898	1.6498	.4983	.3743	– .0004	– .0004	.5707	.0000	.0000
CC_1	5.6466	2.1853	1.6693	–.5428	–.0001	–.0001	–.4168	.0000	.000 1
C_1-H_1	3.5448	4.4530	2.3873	–1.2985	.0000	.0000	–.9856	.0000	.0002
C_1-H_2	3.9332	2.8193	4.1044	.5402	1.2184	.8375	.2821	.7221	.8784
C_1-H_3	3.9333	2.8193	4.1042	.5402	–1.2183	–.8375	.2822	–.7219	– .8782
CN1	3.4114	4.2605	3.2452	–1.5968	.4432	–.7879	–1.6077	–2.8432	6. 3464
CN2	3.4115	4.2599	3.2483	–1.5971	–.4431	.7880	–1.6075	2.8431	–6.3460
NH	2.3879	2.9124	– .2239	.3929	.0000	.0000	.6230	– .0002	– .0002
NC_2	4.5585	1.7751	–.0224	–.5299	.0000	.0000	–1.1250	.0000	– .0003
C_2-H_4	3.0773	4.8056	2.3651	–1.2281	.0000	.0000	–.9114	.0001	– .0002
C_2-H_5	3.5593	2.6216	3.9689	.2678	–1.1500	–.4886	–.3180	–.6668	– .7248
C_2-H_6	3.5593	2.6215	3.9686	.2678	1.1500	.4886	–.3180	.6665	.7247

[a] The coordinate system is the standard coordinate system of Ooi et al.[5], with the x-axis along the C_α–C' bond, the carbonyl O having a positive y-coordinate, and the origin at the C_α. Polarizabilities are in atomic units, a_0^3 = 0.148 Å^3. Based upon bond and lone-pair polarizability tensors calculated for *trans*-N-methylacetamide by Walter Stevens using the method of Garmer and Stevens.[6]

[b] For more complete identification of the tensors, see Table S2.

Table S4. Positions and Symmetry Axes of Polarizability Ellipsoids

Group	Position[a]			Symmetry axis[b]		
	x	y	z	e_x	e_y	e_z
C′ = O	–0.003273	0.0	0.821519	0.0	0.0	1.0
O lone pair 1	–0.301802	0.0	1.340094	–0.515207	0.0	0.857066
O lone pair 2	0.282415	0.0	1.351514	0.544937	0.0	0.838477
C_α – C′	–0.656331	0.0	–0.412251	0.857066	0.0	0.515207
C′ – N	0.796624	0.0	–0.549301	0.930247	0.0	–0.365437
N – H[c]	1.089253	0.0	–1.339235	0.0	–1.0	0.0
N – C_α	1.65573	0.0	–0.481903	0.927517	0.0	0.373779
$\pi\pi^*$ trans	0.0	0.0	0.0	–0.881463	0.0	0.472254
C_α – H	0.74	0.0	0.0	1.0	0.0	0.0
C_α – C_β	0.765	0.0	0.0	1.0	0.0	0.0
C_β methyl	1.711667	0.0	0.0	1.0	0.0	0.0

[a] The coordinate system used for amide polarizability ellipsoids has the z-axis along the C=O bond, with the x-axis in the plane and directed such that the amide N has a positive x-coordinate. The y-axis is perpendicular to the amide plane. The origin is at the carbonyl C. For the side-chain and the C_α – H groups, the x-axis is along the bond direction, with the origin at the C_α and directed toward C_β or H_α. Coordinates are in Å. Based upon bond and lone-pair polarizability tensors calculated for *trans*-N-methylacetamide by Walter Stevens using the method of Garmer and Stevens.[6]

[b] The directions of the symmetry axes are specified by their components along the axes of the coordinate system described in footnote *a*.

[c] All of the polarizability ellipsoids are prolate, except that for the NH bond, which is oblate. The out-of-plane polarizability is much smaller than the two in-plane components, so the symmetry axis is perpendicular to the amide plane.

Table S5. Monopoles for ππ* Transitions and the Ground State in Amides[a]

	x [b]	y[b]	z [b]	NV_1 (–55°)[c]	NV_1 (–40°)[d]	NV_2[c]	G. S.[e]
C1	0.0	1.0806	0.0	1.1211	0.4914	1.4469	1.0496
	0.0	–1.0806	0.0	1.1211	0.4914	1.4469	1.0496
O2	0.0	0.7737	0.0	0.0130	0.3986	–0.7586	–1.1181
	0.0	–0.7737	0.0	0.0130	0.3986	–0.7586	–1.1181
N3	0.0	0.9813	0.0	–1.1341	–0.8900	–0.6883	0.0705
	0.0	–0.9813	0.0	–1.1341	–0.8900	–0.6883	0.0705
	0.0	0.0	0.0				–1.3
H4	0.0	0.0	0.0				1.3

[a] The origin is at the carbonyl carbon. The z axis is along the carbonyl bond with O in the positive direction. The x-axis is in-plane and directed such that the N has a positive x coordinate.

[b] Monopole positions relative to atomic centers [7]. Coordinates are in Å.

[c]Monopole charges in 10^{-10} esu. Transition moment for secondary amide group in N-acetylglycine [8]. This was the transition moment direction used by Woody and Sreerama.[9] The signs of the charges are reversed relative to those used by Woody and Sreerama, as indicated by the red font.

[d]Monopole charges in 10^{-10} esu. These monopole charges yield a transition moment close to that reported for myristamide.[10] This is the transition moment direction that gives the best results for the P_{II} conformation, as found in the present work..

[e] These are the ground-state permanent monopoles for secondary amide groups.[11] Monopole charges in 10^{-10} esu. For tertiary (Pro) amides, the π monopoles are the same, but the two in-plane σ monopoles are set to zero.

Table S6. Transition Parameters for ππ* Transitions in the Amide Group[a]

Transition	E (eV)	∇_x (A^{-1})[b]	∇_z (A^{-1})[b]	$(r \times \nabla)_y$ (BM)	Bandwidth (nm)
NV_1 (–55°)[c]	6.5255[d]	0.4416	–0.3092	0	11.3
NV_1 (–40°)[c]	6.5255[d]	0.3465	–0.4130	0	11.3
NV_2[e]	8.9275	0.3663	0.2031	0	7.2

[a] Because of the plane of symmetry, the y-component of the **∇** matrix element and the x, z components of the **(r x ∇)** matrix element are zero.

[b] The origin is at the carbonyl carbon. The z axis is along the carbonyl bond with O in the positive direction. The x-axis is in-plane and directed such that the N has a positive x coordinate.

[c] Two NV_1 transition moment directions are used in this work, corresponding to the angles of –55° and –40° relative to the carbonyl bond direction.[8, 10].

[d] For the tertiary amide of an X-Pro bond, the NV_1 transition energy is 6.1993 eV.

[e] The gradient matrix element for the NV_2 transition is reversed in direction relative to that used by Woody and Sreerama. [9] This is indicated by the red font.

Table S7. Monopoles for *nπ** Transitions in Amides[a]

Atom	x[b]	y[b]	z[b]	nπ*[c,d]	nπ*-NV$_1$[c]	nπ*-NV$_2$[c,e]
O2	0.6064	0.6064	0.0	0.4761	0.4171	–0.3720
	0.6064	–0.6064	0.0	–0.4761	–0.4171	0.3720
	–0.6064	–0.6064	0.0	0.4761	0.4171	–0.3720
	–0.6064	0.6064	0.0	–0.4761	–0.4171	0.3720
C1	0.8470	0.8470	0.0	0.1318	0.0	0.0521
	0.8470	–0.8470	0.0	–0.1318	0.0	–0.0521
	–0.8470	–0.8470	0.0	0.1318	0.0	0.0521
	–0.8470	0.8470	0.0	–0.1318	0.0	–0.0521
N3	0.7716	0.7716	0.0	0.0	–0.0681	0.0
	0.7716	–0.7716	0.0	0.0	0.0681	0.0
	–0.7716	–0.7716	0.0	0.0	–0.0681	0.0
	–0.7716	0.7716	0.0	0.0	0.0681	0.0

[a] The z axis is along the carbonyl bond with O positive. The x-axis is in-plane and directed such that the N has a positive x coordinate. The origin is at the carbonyl carbon.

[b] Monopole positions relative to the atomic centers.[7]. Coordinates are in Å.

[c] Monopole charges in 10^{-10} esu. Calculated from INDO/S[12] wave functions for N-methylacetamide.

[d] The signs of the nπ* monopole charges are reversed relative to those used by Woody and Sreerama,[9] as indicated by the red font.

[e] For transitions connecting the nπ* state with the ground-, NV$_1$ and NV$_2$ states, the transition charge density has quadrupolar charge arrays at O, C, and N. Our program limits the number of monopoles to eight, so the charges at one of the three centers were neglected. Naturally, those with the smallest magnitudes were eliminated. In the case of the nπ*-NV$_2$ transition, the magnitudes of the monopoles at the C and N were similar (0.0521 vs. 0.0421), both significantly smaller than those at the carbonyl O (0.3720). Woody and Sreerama[9] inadvertently used the somewhat smaller N monopoles rather than the C monopoles. This is reflected by the red font in the altered nπ*-NV$_2$ monopoles.

Table S8. Transition Parameters for the nπ* Transition in the Amide Group[a]

Transition	E (eV)[b]	∇_y (A^{-1})	$(r \times \nabla)_x$ (BM)[c]	$(r \times \nabla)_z$ (BM)[c]	Bandwidth (nm)
nπ*	5.6357	0.0	0.0904	–0.9094	10.5

[a] Because of the plane of symmetry, the x and z components of the ∇ matrix element and the y component of the (r x ∇) matrix element are zero.

[b] Corresponds to the standard wavelength for the nπ* transition in polypeptides, 220 nm. Note that INDO/S[12] significantly underestimates the nπ* transition energy, placing the transition at about 300 nm.

[c] Calculated from INDO/S[12] wave functions for N-methylacetamide.

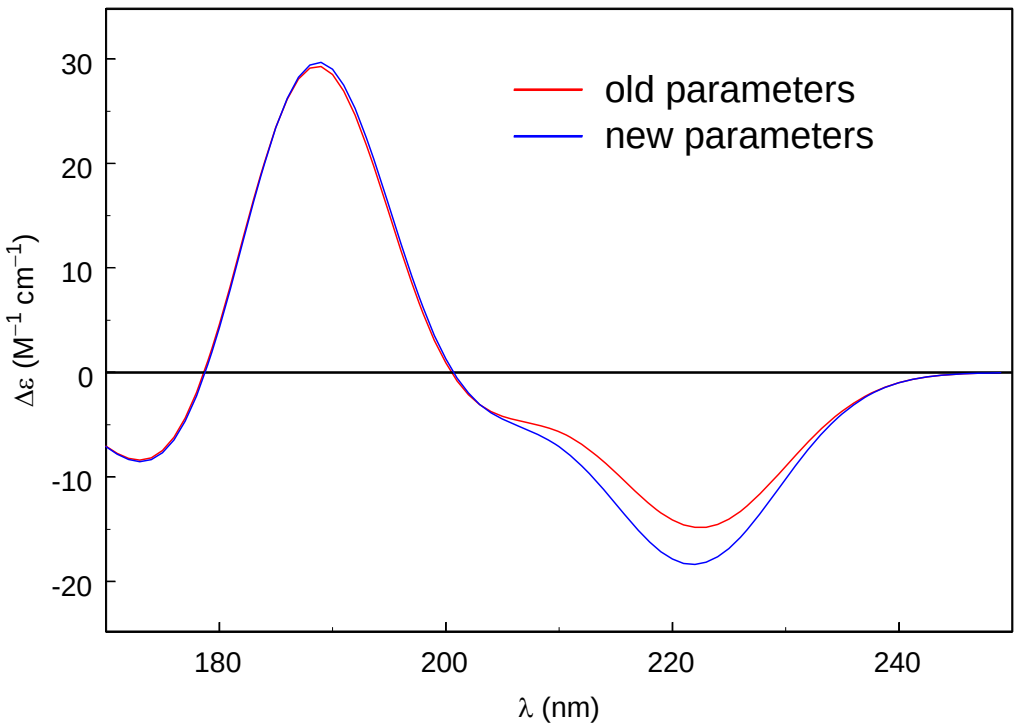

Figure S1. Comparison of the exciton CD spectrum calculated for $(Ala)_{20}$ in a Pauling and Corey[13] α-helix using the amide transition parameters of Woody and Sreerama[9] (red spectrum) and the corrected parameters used in this work (blue spectrum).

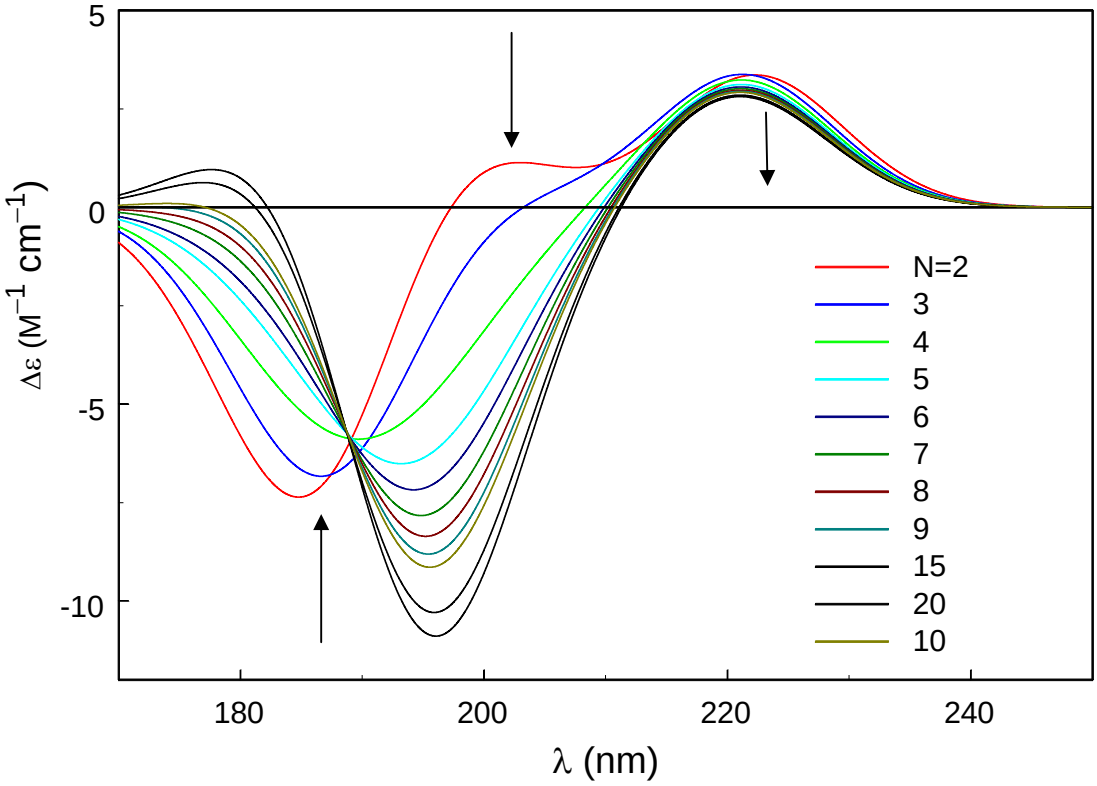

Figure S2. CD spectra of PII helices of $(Ala)_n$ as a function of n. $(\phi,\psi) = (-60°, 160°)$. The arrows indicate the direction of increasing n: 2, 3, ..., 10, 15, 20.

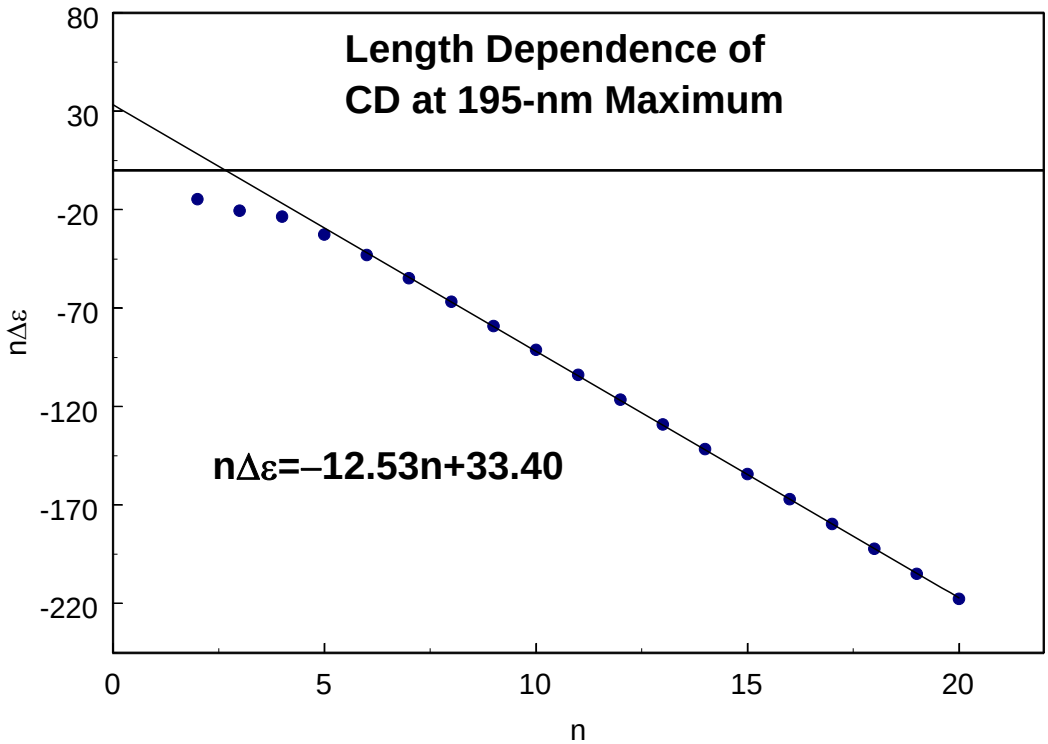

Figure S3. Length dependence of the CD of $(Ala)_n$ in the P_{II} conformation, $(\phi,\psi) = (-60°, 160°)$, at the short-wavelength negative maximum. The length dependence is described by the empirical equation of Chen et al.[14]: $\Delta\varepsilon_\lambda = \Delta\varepsilon_\lambda(\infty)(n-k)/n$, where $\Delta\varepsilon_\lambda(\infty)$ is the per residue CD at wavelength λ for the infinite helix and *k* is an end-effect correction, the "number of missing residues" due to end effects. A plot of $n\Delta\varepsilon_\lambda$ vs. n gives $\Delta\varepsilon_\lambda(\infty)$ as the slope and $-k\,\Delta\varepsilon_\lambda(\infty)$ as the intercept. In the present plot, the data are not for a single wavelength but for the peak of the short-wavelength negative maximum, which shifts from 185 nm to 196 nm as *n* increases. Data for $n < 6$ deviated from linearity, so only points for $n \geq 6$ were used for linear regression, which gave the equation shown on the plot. From this, we obtain $\Delta\varepsilon_\lambda(\infty) = -12.53$ and $k = 2.67$, i.e., each residue in the infinite helix contributes $-12.53\ M^{-1}cm^{-1}$ to the CD near 200 nm and 2.7 residues are effectively missing from the helix due to end effects.

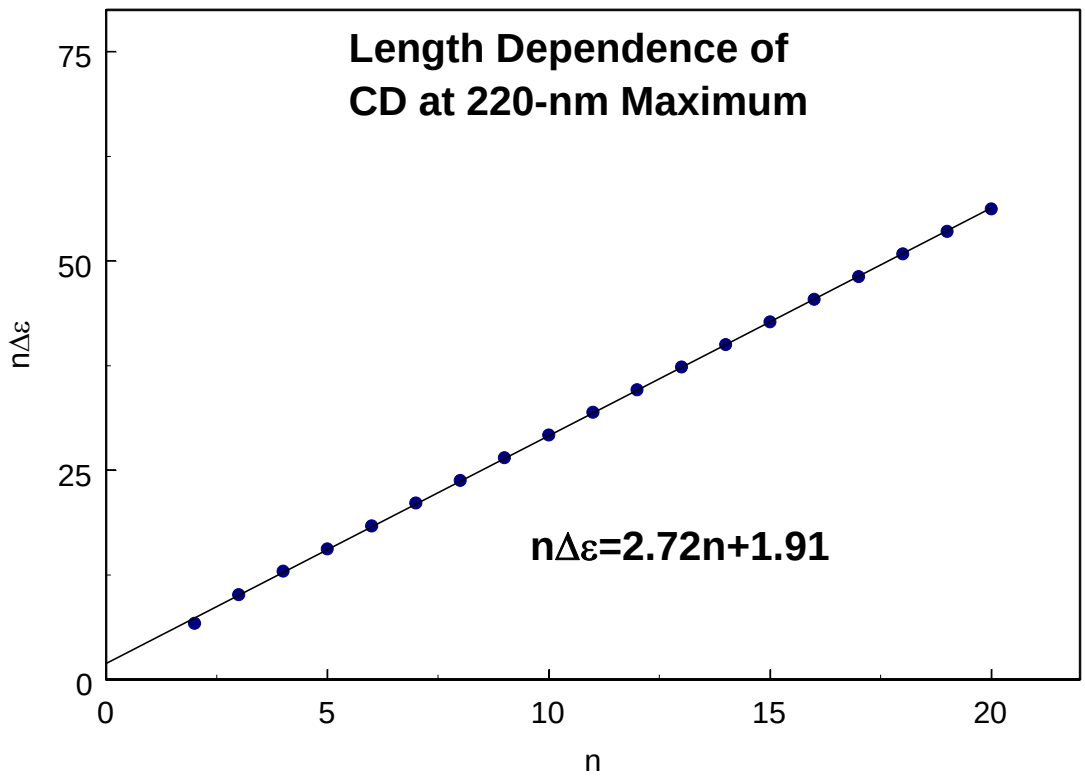

Figure S4. Length dependence of the CD of $(Ala)_n$ in the P_{II} conformation, $(\phi,\psi) = (-60°, 160°)$, at the long-wavelength positive maximum, at 221 nm for all *n*. For details, see the caption to Fig. S3. Linear regression using all of the data points gives the expression shown on the plot. From this, we conclude that each residue contributes 2.72 $M^{-1}cm^{-1}$ to the CD near 220 nm and that the end effects *decrease* the effective helix length by –0.70, i. e., they *increase* the effective helix length.

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