

90 to 97.5°). However, for crystals where the solid-state reaction begins on a single (100) face, only one *new* *c** axis is observed, i.e., *twinning about [001]_{reactant} does not occur* to a detectable extent. Thus, the first product which appears on a crystal face appears to determine, in a crystallographically specific manner, unit cell orientation in the product. Further, the established topotaxy demonstrates unequivocally that the phase of the solution-grown polymer crystals is identical with that formed by the solid-state reaction. We note that this strictly linear polymerization process appears to be different from other carefully studied examples,³ (including the polymerization of NiCl₂CEP₂),⁸ in which the polymer appears first in a solid solution with monomer, and crystallization/orientation of product may be effected via annealing.

The relationship between pairs of reactant and product molecules, chosen so as to be representative of the overall polymerization reaction, is presented in Figure 1, which demonstrates the spatial similarities between reactant and product. The reaction mechanism qualitatively involves polymerization in crystal *ac* planes, followed by repacking of the polymer along the *b* direction; further, it may be shown that motion of the centroids of the individual complexes during reaction defines the product *a* axis (and β angle of 97.5°). The direction of slowest front motion (i.e., along the *a* direction) is consistent with the observation that only the *a* axis of the reactant crystal must reorient to form the product pseudomorph.

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Supplementary Material Available: Atomic coordinates for NiBr₂[P(CH₂CH₂CN)₃]₂ monomer and polymer (2 pages). Ordering information is given on any current masthead page.

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Vibrational Circular Dichroism in Amino Acids and Peptides. 1. Alanine

Sir:

We report the first observation of vibrational circular dichroism (VCD) of an amino acid, alanine, which is both the simplest optically active amino acid and the smallest molecule

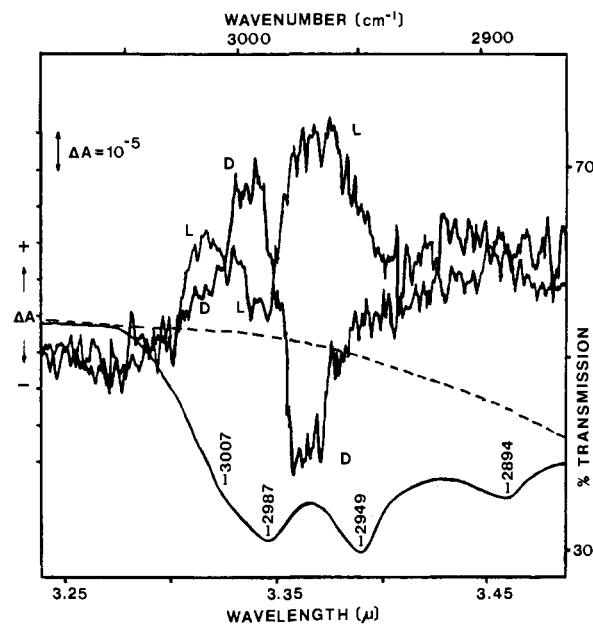


Figure 1. VCD and transmission spectra of saturated solutions of (R)-(-)-alanine-*d*₃ (D) and (S)-(+)-alanine-*d*₃ (L) in D₂O at 0.500-mm path length. The dashed line represents the D₂O background transmission spectrum; spectral band pass is ~ 17 cm⁻¹ at 2950 cm⁻¹. The individual VCD scans required a time of 4 h.

for which vibrational optical activity has been reported. Previous VCD observations¹⁻⁴ have also reported signals in this region; however, for molecules containing more than one type of C-H bond, only tentative vibrational assignments have been made.³ In alanine, the vibrational stretching modes of all four hydrogen atoms attached to carbon can be assigned without ambiguity from previous theoretical and experimental work⁵⁻⁷ (see Table I). With the aid of these assignments, an interpretation of the VCD of alanine, based on a chiral perturbation of the degenerate asymmetric methyl stretching vibrations, is proposed. Degenerate methyl stretching modes in VCD may eventually prove to be sensitive probes of molecular configuration. Analogous behavior for the degenerate asymmetric methyl deformation modes as configurational probes in Raman optical activity have been reported by Hug et al.⁸ and Barron.⁹⁻¹¹

The instrument used in the VCD measurements reported here is similar to a unit described earlier.³ The optical train consists of a 1000-W tungsten-halogen lamp (Sylvania 1000 Q/CL), a mechanical light chopper, a monochromator (Spex 1702), a LiIO₃ polarizer (Interactive Radiation, Inc.), a ZnSe photoelastic modulator,¹² a variable-path-length sample cell equipped with CaF₂ windows, and an InSb detector (Spectronix, Inc.). The electronic system for signal processing uses a variable-gain amplifier circuit and the three lock-in amplifier technique described earlier.³ The VCD spectrum of camphor dissolved in CCl₄ has been obtained with comparable quality and signal magnitude using similar instrumental settings to previously published results.³ In the present study, however, low transmission of the D₂O solutions necessitated long time constants to reduce the noise level. A high level of instrument stability allows spectra to be scanned reliably in times as long as 10 h.

Samples of D-alanine (Aldrich Chemical Co.), $[\alpha]_D^{25} -14^\circ$ (*c* 10, 6 N HCl), and L-alanine (Calbiochem), $[\alpha]_D^{21} +14.5^\circ$ (*c* 5.8, 1 N HCl), were dissolved in D₂O and boiled to dryness in vacuo to deuterate the amine function. The NH₃⁺ vibrations, which otherwise may interfere with the C-H stretching modes, are shifted to ~ 2200 cm⁻¹; furthermore the amount of H₂O and HDO produced by the proton exchange was re-

Table I. Frequencies, Intensities, and Assignment of the Vibrational Bands

Alanine						
Obsd frequency, ^b cm ⁻¹	Absorbance ^b	$\Delta A \times 10^5$ for L-alanine ^b	Calcd frequency, ^c cm ⁻¹	Raman frequency, ^d cm ⁻¹	CH ₃ CHFCl, ^a obsd frequency, cm ⁻¹	Assignment
3007	0.18	+0.8 ± 0.5 ^e	3062	3002	3012	$\nu_{\text{C-H}}$
2987	0.24	-1.5 ± 0.5	3011	2988	2985	$\nu_{\text{asym,CH}_3}$
		+4.5 ± 0.7	3010	2964	2974	$\nu_{\text{asym,CH}_3}$
2949	0.20	+1.5 ± 0.5	2921	2932	2945	$\nu_{\text{sym,CH}_3}$
2894	0.07			2891	2894	CH ₃ deformation overtones, combination bands

^a Reference 6. ^b This work. ^c Reference 7. ^d Reference 5. ^e Although some of the reported ΔA values exhibits a very low signal-to-noise ratio, the observed VCD is reliable within the error limits indicated, since the same spectral features have been reproduced on numerous occasions.

duced significantly, resulting in an improved infrared transmission between 3.2 and 3.5 μ .

The VCD spectra in Figure 1 are direct strip chart reproductions without further data treatment. The ΔA values listed in Table I were measured at the VCD peaks, which are near but do not correspond to the absorption peaks. Owing to low solubility, DL-alanine baseline spectra could not be run; however, "absorption baselines"⁴ showed a small baseline dependence on the overall transmission, and followed the average of the D and L spectral curves in Figure 1.

Vibrational frequencies and intensities of alanine and frequencies of 1-chloro-1-fluoroethane are summarized in Table I. To date most infrared studies on alanine were performed in salt pellets, precluding a detailed analysis of the C-H stretching frequencies. As a result, our observed vibrational bands were assigned using alanine single-crystal Raman data by Wang and Storms⁵ and the detailed vibrational analysis of 1-chloro-1-fluoroethane published by Durig et al.⁶ The latter molecule was chosen because the masses of fluorine and chlorine are close to the masses of the amine and acid functions in alanine, respectively.

Barron⁹⁻¹¹ has shown, both experimentally and theoretically, that degenerate asymmetric methyl deformation modes are split by a perturbing chiral environment to yield two components having equal and opposite optical activity. Barron's theoretical arguments are general^{10,11} and apply equally well to Raman optical activity in degenerate asymmetric methyl stretching vibrations. Preliminary theoretical work indicates that similar couplets should appear for degenerate methyl vibrations in VCD.¹³ These preliminary considerations, together with the observation of a couplet in the region of the two asymmetric methyl stretching modes, leads one to the following hypothesis regarding the origin of the VCD spectrum. A conservative bisignate couplet is centered at the peak of the asymmetric methyl stretching absorption band at 2987 cm⁻¹. The high frequency component of this couplet overlaps a VCD band of opposite sign arising from the C α -H stretching mode, reducing the magnitude of these opposing bands. The low frequency component of the couplet overlaps a VCD band of the same sign in the symmetric methyl stretching region, resulting in a low frequency tail.

The observed spectrum is not entirely consistent with this proposed interpretation since the zero crossing of the couplet should be on the high frequency rather than the low frequency side of the absorption maximum. This discrepancy may be due to the mixing of other vibrational modes by the chiral perturbation leading to an inherently asymmetric couplet.^{10,11} In addition, other mechanisms may be responsible for the form of the VCD spectrum; however, they are difficult to estimate and tend to prevent a simple interpretation. These effects include Fermi resonance interactions with combination bands,¹⁴ hydrogen-bonding interactions, and conformational splittings within the absorption envelope. However, the dominant de-

generate methyl couplets observed in Raman optical activity and the large couplet observed in alanine and in certain other methyl-containing compounds reported previously³ suggest that degenerate methyl stretches may play a significant and useful role in the understanding of VCD spectra. A detailed normal coordinate analysis combined with a VCD intensity calculation is in progress to determine the degree of vibrational mixing and to test our interpretation of the VCD spectrum.

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Rearrangement of Cyclobutenylidene

Sir:

There is considerable interest in carbene rearrangements as routes to unique high energy species.¹ Particularly fascinating examples are provided by the vinyl carbenes which