structure-reactivity correlation section, the buffer-catalyzed hydrolysis of **1-5** represent a continuum of mechanism from concerted to stepwise.

It is possibly quite significant that the rate ratio for the buffer-catalyzed hydrolysis of the two epimers varies from 1 to 10.9 at 70 °C (Table V). At lower tempertures, the k_b/k_a ratio is even larger (up to 37.5 for hydroxide-catalyzed hydrolysis of **4** at 0 °C). This fairly large sensitivity of the rate ratio to temperature is attributable to the favorable enthalpy of activation for **4b** (2.9 kcal/mol lower) and an *unfavorable* entropy of activation for **4b** (3.5 eu more negative than **4a**) (Table I).

The k_b/k_a buffer rate ratio in Table X varies between 1 and 3.5 for reaction of **4b**/**4a** with buffers having pK's less than 4.05 (excepting fluoride) and varies between 5.5 and 10.3 (excepting hexafluoroisopropoxide with **3**) for reaction of more basic buffers (pK > 5) with epimers of **2** and **3**. We have already suggested that the reaction of strong nucleophiles (or general bases) with phosphates having poor leaving groups such as **2** or **3** should follow a path along the edges of Figure 10. This stepwise path accounts for the net retention of configuration in these reactions *and* the higher k_b/k_a ratios. Thus, the transition states for the **b** and **a** epimers have nearly equal energies so that as explained earlier the faster rate for the **b** epimer is entirely explained by ground-state destabilization. This is shown in Figure 13 for a mechanism with a diequatorial transition state, **7**, which presumably would yield inversion of configuration products. This figure should also be modified to provide for a stepwise mechanism for **1-3** with separate transition states for attack and leaving (the bond length of the two apical groups will be unequal in the two different transition states). The retention pathway (path a in Figure 11) with transition states having the six-membered ring spanning apical and equatorial sites should also be of similar energy for the two epimers.

The concerted pathway through the center of Figure 10c has been suggested for phosphate reactions with weakly basic buffers and good leaving groups (**4** with buffers having pK's $\lesssim$ 4). The low k_b/k_a ratios for these reactions can be explained by transition states that largely *retain* the twist-boat destabilization energy for the **b** epimers.

In a concerted process the transition-state lifetime precludes changes in the conformation of the phosphorinane ring to accommodate the best stereoelectronic interactions for *both* the attacking and leaving groups. The transition-state energy differences between epimers will be about the same as the ground-state energy differences (due to the transition state, twist boat structures) and hence the activation energies for reaction of **4a** and **4b** are comparable, leading to small k_b/k_a ratios.

Conclusions

Together, the stereochemical data, multiple-structure-reactivity relationships, and epimer rate ratios provide the first evidence for a continuum of mechanism for reactions of phosphate triesters. Proof of the existence of this continuum of mechanism from stepwise to concerted will hopefully be provided by future stereochemical studies in progress.

Acknowledgment. Support of this research by NSF and NIH is gratefully acknowledged. We also wish to acknowledge the helpful comments of Bob Young. Purchase of the WP-80 NMR spectrometer was assisted by an NSF department grant and high-field NMR was done at the NIH-supported (Grant RRO1077) NMR regional facility at Purdue.

Supplementary Material Available: Tables IVb, Vb, VII, and VIIIb, rate constants for reactions of epimers **2b**, **3b**, **4b**, and **5b**, respectively, Figure 2, pH-rate profiles for **4a**, **3b**, and **2b**, Figure 4, dependence of the observed pseudo-first-order rate constants for the hydrolysis of **3b** on the concentration of trifluoroethoxide, Figure 8, linear free-energy relationships between rate constants for the attack by anions on the isomers **1b-4b** and the pK_a's of the conjugate acids, and Figure 12b, Brønsted β_{nuc} vs. pK_{lg} and β_{lg} vs. pK_{nuc} for the equatorial isomers (7 pages). Ordering information is given on any current masthead page.

Crystal Structures of Repeating Peptides of Elastin. 1. *N*-(*tert*-Butoxycarbonyl)-L-valyl-L-prolyglycyl-L-valylglycine

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Abstract: The crystal structure of the pentapeptide Boc-Val[1]-Pro[2]-Gly[3]-Val[4]-Gly[5]-OH, one of the repeating sequences of tropoelastin, has been determined by the X-ray diffraction method. It crystallizes as a monohydrate in space group $P2_12_12_1$ with a = 15.480 (3), b = 21.052 (4), c = 9.387 (2) Å and Z = 4. The molecular structure does not have a β turn as proposed for Boc-Val-Pro-Gly-Val-Gly-OMe in solution but takes a rather extended form at the central part from C′ of Pro[2] to N-H of Gly[5]. The peptide molecules arranged along a 2-fold screw axis are linked by the hydrogen bonds to make an infinite antiparallel β sheet.

Introduction

In this decade, the studies of structure-function correlations of elastin have been developed. In 1973, Gray et al. have determined the amino acid sequences in tropoelastin isolated from aortas of copper-deficient pigs to reveal two basic types of regions: a cross-link region and an extensible region.[1-4] The latter contains repeating sequences such as Val-Pro-Gly-Gly, Val-Pro-Gly-Val-Gly, and Val-Ala-Pro-Gly-Val-Gly. The conformations of these peptides, as well as those of high polymers, in solution have been studied by Urry and his co-workers with NMR.[5-9] They

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Table I. Crystal Data

chemical formula	$C_{24}H_{41}N_5O_8 \cdot H_2O$
space group	$P2_12_12_1$
a	15.480 (3) Å
b	21.052 (4) Å
c	9.387 (2) Å
Z	4
ρ(calcd)	1.184 g cm^{-3}
ρ(obsd)	1.18 g cm^{-3}
μ(Cu Kα)	7.65 cm^{-1}

have proposed that all these peptides possess a β-turn structure with proline and glycine residues at the corners of the turn. In addition, the crystal structure of *cyclo*(Val-Pro-Gly-Val-Gly)$_3$ has recently been determined,[10] in which the molecule also contains three β turns encompassing each Pro-Gly.

A current investigation in our laboratory is aimed at determining the tertiary structure of these linear peptides, by the X-ray method. The present paper is concerned with the crystal structure of the pentapeptide Boc-Val-Pro-Gly-Val-Gly·H_2O. This sequence occurred at least four times in a tryptic peptide of tropoelastine.[1] A detailed description of the molecular structure is given, in comparison with the structure proposed for Boc-Val-Pro-Gly-Val-Gly-OMe in solution.[6]

Experimental Section

The peptide was prepared by the DCC (*N,N'*-dicyclohexylcarbodiimide) coupling method. A powder of Boc-Val-Pro-Gly-OH was dissolved in a dichloromethane solution of equimolar amounts of H-Val-Gly-OBzl·CF_3COOH neutralized with triethylamine, and to the resulting solution was added dropwise DCC in dichloromethane at 0 °C. The mixture was left to stand for 20 h at room temperature. After the mixture was washed with 10% citric acid solution, 5% sodium bicarbonate solution, and water, the solvent was evaporated. The resulting oily product of Boc-Val-Pro-Gly-Val-Gly-OBzl was solidified by cooling with dry ice/methanol. From it was obtained Boc-Val-Pro-Gly-Val-Gly-OH by catalytic reduction with H_2/Pd in methanol. A crystal large enough for X-ray analysis was obtained from an acetone/water solution; it was a colorless plate elongated along the *c* axis. Elemental analysis indicated that the crystals contained one water molecule per peptide. The crystal used for data collection had the dimensions 0.3 × 0.15 × 0.08 mm. The cell constants were determined from 2θ measurements made on a Rigaku four-circle diffractometer. The crystal data are listed in Table I. The intensity data with $2\theta \leq 132°$ were collected on the diffractometer with Ni-filtered Cu Kα radiation using the θ–2θ scan technique. The scan range $\Delta\theta$ was 0.8 + 0.142 tan θ°. The scan speed and the background counting time were 10°/min and 1 s at each terminus of the scans for $0 < 2\theta \leq 80°$, 5°/min and 2 s for $80° < 2\theta \leq 100°$, 3°/min and 4 s for $100° < 2\theta \leq 110°$, and 1°/min and 10 s for $110° < 2\theta \leq 132°$. A total of 3008 unique reflections were measured, of which 2851 were above the background level. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by the multiple-solution tangent formula program MULTAN 78.[11] The 248 normalized structure factors with $|E| < 1.61$ were included in the phase determination. The set of phases with the highest combined figure of merit gave a reasonable structure containing all the nonhydrogen atoms, except for three atoms: a C$^\gamma$ atom of Val^1, a C$^\beta$ of Pro^2, and a water oxygen. Successive Fourier calculations revealed these three atom positions. Hydrogen atoms were located by a difference Fourier map. The parameters were refined by the block-diagonal least-squares program HBLS V.[12] The final refinement in which anisotropic temperature factors were assigned to the nonhydrogen atoms and isotropic ones to the hydrogen atoms gave $R = 0.074$ for all reflections and $R = 0.066$ for nonzero reflections. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + a|F_o| + b|F_o|^2]^{-1}$ for $|F_o| > 0$, where $\sigma(F_o)$ is the standard deviations based on counting statistics and $w = c$ for $F_o = 0$. The final values of *a*, *b*, and *c* were −0.0937, 0.0037 and

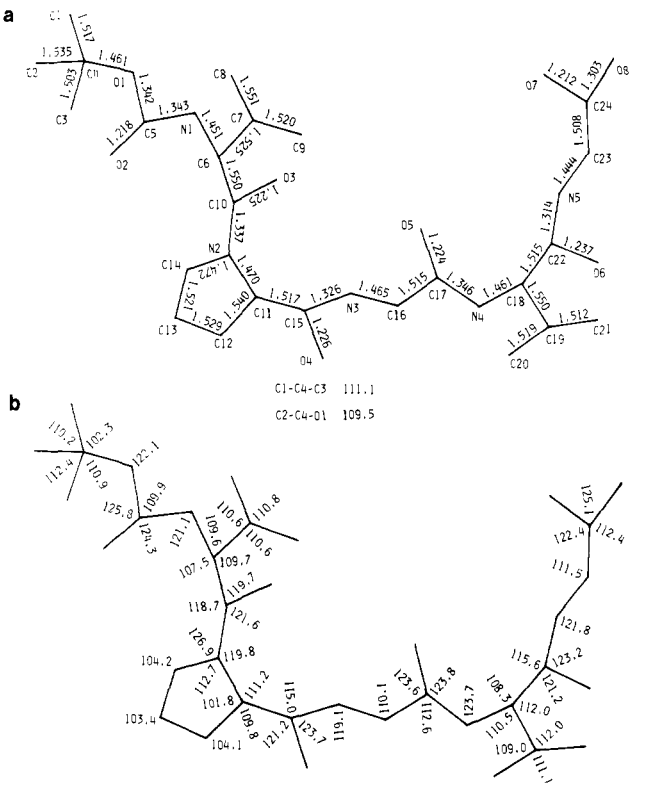

Figure 1. (a) Bond lengths in angstroms. Estimated standard deviations are 0.005–0.011 Å. (b) Bond angles in degrees. Estimated standard deviations are 0.4–0.5°.

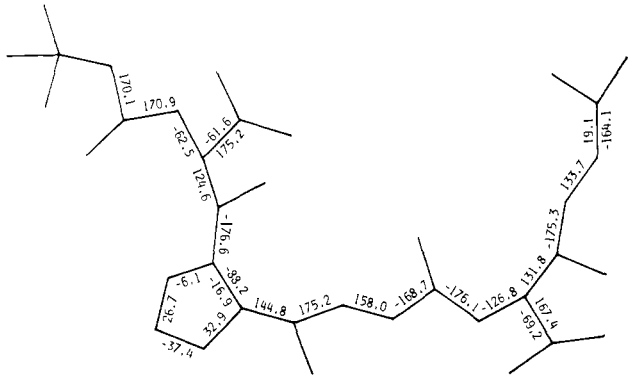

Figure 2. Conformation angles in degrees. Estimated standard deviations are 0.4–0.8°.

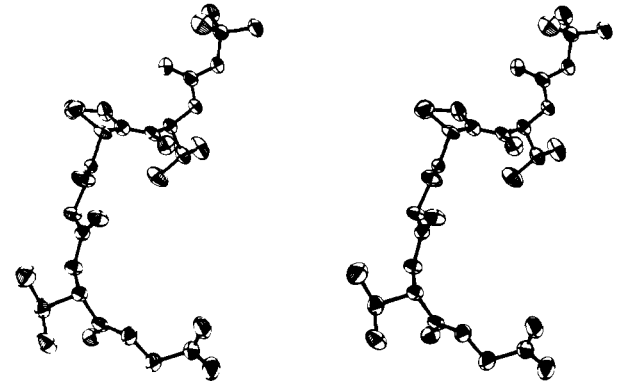

Figure 3. ORTEP II[15] drawing of the peptide molecule. Thermal ellipsoids are drawn at the 50% probability level.

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Table II. Positional (×10⁴) and Thermal (×10) Parameters of Nonhydrogen Atoms

atom	x	y	z	B_{eq},[a] Å²
C(1)	3 678 (4)	6 299 (3)	−3514 (7)	56 (3)
C(2)	3 222 (5)	7 407 (3)	−2900 (7)	61 (3)
C(3)	2 481 (4)	6 463 (3)	−1780 (7)	52 (3)
C(4)	3 316 (3)	6 723 (2)	−2352 (5)	39 (2)
C(5)	3 921 (3)	7 002 (2)	−19 (5)	37 (2)
C(6)	4 707 (3)	7 144 (2)	2202 (5)	33 (2)
C(7)	5 452 (4)	6 826 (2)	2992 (5)	43 (2)
C(8)	5 231 (6)	6 124 (3)	3335 (7)	62 (3)
C(9)	5 668 (6)	7 190 (3)	4345 (7)	65 (4)
C(10)	4 946 (3)	7 842 (2)	1859 (5)	34 (2)
C(11)	4 660 (3)	8 973 (2)	2081 (5)	35 (2)
C(12)	3 784 (4)	9 291 (3)	2384 (8)	52 (3)
C(13)	3 417 (4)	8 914 (3)	3637 (7)	51 (3)
C(14)	3 694 (4)	8 235 (3)	3318 (6)	45 (2)
C(15)	5 347 (3)	9 252 (2)	3049 (4)	26 (2)
C(16)	6 517 (3)	9 997 (2)	3300 (5)	34 (2)
C(17)	7 251 (3)	10 231 (2)	2372 (5)	27 (2)
C(18)	8 701 (3)	10 724 (2)	2508 (5)	27 (2)
C(19)	8 744 (3)	11 442 (2)	2862 (5)	35 (2)
C(20)	8 028 (4)	11 784 (3)	2063 (8)	54 (3)
C(21)	9 618 (4)	11 724 (2)	2516 (6)	43 (2)
C(22)	9 485 (3)	10 368 (2)	3055 (5)	30 (2)
C(23)	10 791 (4)	9 811 (3)	2429 (6)	50 (3)
C(24)	10 905 (3)	9 272 (3)	1389 (6)	43 (2)
N(1)	4 560 (3)	6 821 (2)	858 (4)	38 (2)
N(2)	4 480 (3)	8 307 (2)	2451 (4)	34 (2)
N(3)	5 875 (2)	9 663 (2)	2430 (4)	27 (1)
N(4)	7 930 (2)	10 438 (2)	3137 (4)	30 (2)
N(5)	10 046 (3)	10 194 (2)	2081 (4)	37 (2)
O(1)	3 994 (2)	6 699 (2)	−1271 (4)	46 (2)
O(2)	3 380 (3)	7 401 (2)	276 (4)	49 (2)
O(3)	5 559 (2)	7 956 (2)	1075 (4)	45 (2)
O(4)	5 370 (3)	9 123 (2)	4322 (3)	43 (2)
O(5)	7 219 (2)	10 247 (2)	1069 (3)	38 (1)
O(6)	9 573 (2)	10 250 (2)	4338 (3)	38 (1)
O(7)	10 571 (3)	9 272 (2)	221 (4)	53 (2)
O(8)	11 429 (3)	8 837 (2)	1865 (5)	64 (2)
OW	6 707 (3)	7 088 (2)	−138 (5)	56 (2)

[a] Calculated from anisotropic thermal parameters (supplementary material).

0.1950 Å, respectively. The atomic scattering factors were taken from "International Tables for X-ray Crystallography".[13] Tables II and III contain the final positional and thermal parameters of all the atoms.

Results and Discussion

Bond lengths and angles are shown in Figure 1, together with the numbering of the atoms. They can be compared to the values in peptides given by Marsh and Donohue.[14] The conformation angles are shown in Figure 2. As seen in the stereodrawing of the peptide molecule in Figure 3, it does not have the β turn as suggested for Boc-Val-Pro-Gly-Val-Gly-OMe in solution[6] but takes a rather extended form at the central part from C′ of Pro² to N–H of Gly⁵; there are no intramolecular hydrogen bonds. The Gly³ residue takes a nearly trans-zigzag conformation. The Val⁴ residue has the usual ϕ and ψ values [−126.8 (4) and 131.8 (4)°] for the β sheet: −119 and 113° for the parallel β sheet[16] and −139 and 135° for the antiparallel β sheet.[17] The value of −88.2 (5)° for ϕ (Pro²) deviates from the corresponding values (−72° to ca. −51°) of many other proline-containing peptides.[18] The angles ω are within ±5° of the trans conformation. The side-chain conformations of the two valine residues are both trans, as is compatible with *cyclo*(Val-Pro-Gly-Val-Gly)₃.[10] On the contrary, in several crystals of valine-containing peptides which have two crystallographically independent molecules in the asymmetric unit, such as Boc-Pro-Val-Gly-OH,[19] the side-chain conformations of the two valine residues are usually different, although their main chain conformations are similar to each other. The pyrrolidine ring of

Table III. Hydrogen Positional Parameters (×10³)[a]

atom	bonded to	x	y	z
H(1)	C(1)	321 (5)	624 (4)	−431 (8)
H(2)	C(1)	426 (5)	649 (3)	−398 (8)
H(3)	C(1)	378 (6)	586 (4)	−314 (8)
H(4)	C(2)	279 (5)	740 (4)	−375 (9)
H(5)	C(2)	306 (5)	769 (3)	−206 (9)
H(6)	C(2)	389 (6)	756 (4)	−342 (10)
H(7)	C(3)	203 (5)	652 (3)	−257 (8)
H(8)	C(3)	257 (5)	599 (3)	−129 (8)
H(9)	C(3)	225 (5)	673 (3)	−93 (7)
H(10)	N(1)	491 (4)	644 (3)	48 (7)
H(11)	C(6)	418 (4)	712 (3)	284 (6)
H(12)	C(7)	598 (4)	678 (3)	230 (7)
H(13)	C(8)	568 (5)	591 (4)	402 (9)
H(14)	C(8)	466 (5)	612 (4)	415 (9)
H(15)	C(8)	513 (5)	586 (3)	238 (8)
H(16)	C(9)	616 (5)	693 (4)	494 (8)
H(17)	C(9)	582 (5)	766 (4)	429 (9)
H(18)	C(9)	513 (5)	721 (3)	508 (8)
H(19)	C(11)	486 (4)	901 (3)	101 (7)
H(20)	C(12)	387 (4)	975 (3)	261 (7)
H(21)	C(12)	343 (5)	923 (3)	140 (7)
H(22)	C(13)	366 (5)	906 (3)	460 (8)
H(23)	C(13)	279 (5)	896 (3)	372 (8)
H(24)	C(14)	384 (4)	799 (3)	433 (7)
H(25)	C(14)	323 (4)	799 (3)	286 (7)
H(26)	N(3)	583 (4)	977 (3)	133 (6)
H(27)	C(16)	625 (4)	1041 (3)	382 (6)
H(28)	C(16)	677 (4)	970 (3)	406 (6)
H(29)	N(4)	791 (4)	1037 (3)	417 (6)
H(30)	C(18)	866 (4)	1069 (3)	138 (6)
H(31)	C(19)	862 (4)	1150 (3)	393 (7)
H(32)	C(20)	801 (4)	1226 (3)	229 (8)
H(33)	C(20)	809 (4)	1172 (3)	98 (8)
H(34)	C(20)	749 (5)	1157 (3)	239 (8)
H(35)	C(21)	966 (4)	1218 (3)	266 (8)
H(36)	C(21)	1010 (4)	1152 (3)	328 (7)
H(37)	C(21)	977 (4)	1164 (3)	139 (7)
H(38)	N(5)	991 (4)	1031 (3)	99 (6)
H(39)	C(23)	1137 (4)	1010 (3)	247 (7)
H(40)	C(23)	1066 (5)	961 (3)	357 (8)
H(41)	O(8)	1154 (5)	848 (3)	105 (8)
H(42)	OW	626 (5)	740 (4)	27 (8)
H(43)	OW	725 (5)	729 (3)	−21 (8)

[a] Isotropic thermal parameters are equal to those of the carrier atoms.

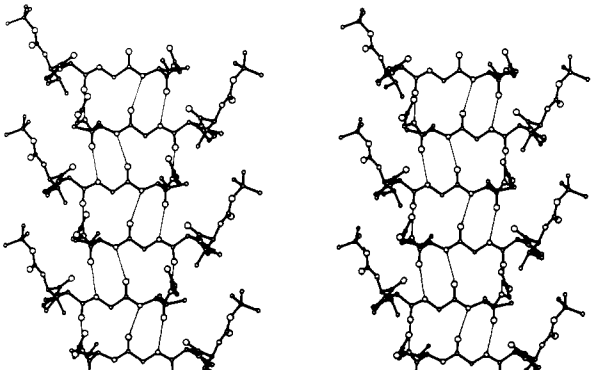

Figure 4. Stereodrawing of the sheet structure. Hydrogen bonds are represented by thin lines. The *c* axis points upward.

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Table IV. Hydrogen Bonds

donor (D)	hydrogen (H)	acceptor (A)	symmetry equiv of acceptor	distance, Å D···A	distance, Å H···A	angle: D-H···A, deg
N(1)	H(10)	O(7)	$-1/2+x, 3/2-y, -z$	2.96	1.94	180
N(3)[a]	H(26)	O(6)	$3/2-x, 2-y, -1/2+z$	2.99	1.97	161
N(4)[a]	H(29)	O(5)	$3/2-x, 2-y, 1/2+z$	3.12	2.21	153
N(5)[a]	H(38)	O(4)	$3/2-x, 2-y, -1/2+z$	3.03	2.02	156
O(8)	H(41)	OW	$1/2+x, 3/2-y, -z$	2.57	1.49	171
OW	H(42)	O(3)	x, y, z	2.79	1.77	175
OW	H(43)	O(2)	$1/2+x, 3/2-y, -z$	2.81	1.87	173

[a] Hydrogen donor of the β sheet.

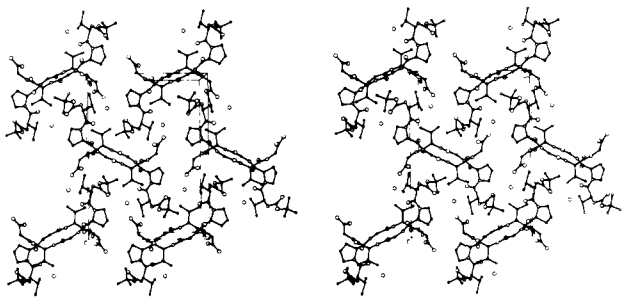

Figure 5. Stereodrawing of the crystal packing viewed down the *c* axis.

Pro[2] has the C_2-C^γ-endo conformation following the classification by Ashida et al.[18]

All seven possible hydrogen donors participate in the hydrogen bonds; details are given in Table IV. Three N–H···C=O bonds are formed between peptide molecules related by the 2-fold screw axis parallel to the *c* axis. Figure 4 shows this hydrogen-bonding scheme. The molecules form an infinite antiparallel β sheet. There are, however, some differences from the antiparallel β-sheet structures proposed by Pauling et al.[20] and observed in other oligopeptides, in which hydrogen bonds are formed between molecules related by a (pseudo) 2-fold rotation axis, the sheet being perpendicular to the 2-fold axis. In oligopeptides, only tri-L-alanine[21] has been reported to make an infinitely extended sheet in such an antiparallel fashion. On the other hand, in the present crystal the rather extended central part of the molecule is located close to, and almost perpendicularly to, the 2-fold screw axis. Another feature of the present sheet structure is that the sheet is not "pleated" because the Gly[3] residue at the central part of the sheet is fully extended.

Figure 5 shows a stereodrawing of the crystal packing viewed down the *c* axis. There exist a polar region with a water molecule in the center and nonpolar region comprising the hydrophobic side groups of the valine and proline residues and the *tert*-butyl group. Excepting the hydrogen-bond interactions, there are no closer intermolecular contacts than those of van der Waals interactions. The water molecule participates in three hydrogen bonds with peptide molecules. Of these, the bond COOH···OW(acceptor) is appreciably shorter than the others. Such a case has been reported elsewhere, e.g., in Boc-Pro-Leu-Gly-OH.[22]

As is described above, the pentapeptide Boc-Val-Pro-Gly-Val-Gly-OH has a rather extended structure in the crystalline state instead of the folded one proposed for Boc-Val-Pro-Gly-Val-Gly-OMe in solution.[6] In general, oligopeptides may be stabilized by intramolecular interactions in a dilute solution and mainly by intermolecular interactions in an aggregated state. Thus, the inconsistency of the conformations formed in the different environments, solution and crystal, seems to be not unreasonable. Of course, the difference in the C-terminal part, esterified or not, may be of importance.

As Chou and Fasman evaluated,[23] the valine residue has the least tendency to occur in any of four positions of the β turn in protein. Valine and isoleucine have C^β-branched bulky side chains, which may impose severe restrictions on the main chain structure. Therefore, the β turn is more difficult to form, especially in the aggregated state, when valine residues need to occupy both the first and fourth positions. In fact, the structure of Boc-Pro-Leu-Gly-OH[22] has a β turn, while those of Boc-Pro-Val-Gly-OH[19] and Boc-Pro-Ile-Gly-OH[24] do not. In a cyclic peptide like *cyclo*(Val-Pro-Gly-Val-Gly)$_3$,[10] turns are easily formed because of its covalently constrained main chain structure.

The present study does not show a model for the elastin structure, but there is no doubt that in the structure and function of elastin, important roles are played by the three repeating sequences mentioned above, especially by the presence of hydrophobic valine residues and the inflexibility imparted to the peptide chain by the proline residues. In order to reveal the role of the valine residues in elastin, it may be of great use to investigate the analogous peptides in which the valine residue is replaced by another amino acid. Further studies of the linear oligopeptides related to elastin are in progress.

Supplementary Material Available: Listing of observed and calculated structure factors and anisotropic thermal parameters of nonhydrogen atoms (15 pages). Ordering information is given on any current masthead page.

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