

Crystal State Conformation of Three Model Monomer Units for The β -Bend Ribbon Structure

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SYNOPSIS

The molecular and crystal structures of three compounds, representing the repeating units of the β -bend ribbon (an approximate 3_{10} -helix, with an intramolecular hydrogen-bonding donor every two residues), have been determined by x-ray diffraction. They are Boc-Aib-Hib-NHBzl, Z-Aib-Hib-NHBzl, and Z-L-Hyp-Aib-NHMe (Aib, α -aminoisobutyric acid; Bzl, benzyl; Boc, *t*-butyloxycarbonyl; Hyp, hydroxyproline Hib, α -hydroxyisobutyric acid; Z, benzyloxycarbonyl). The two former compounds are folded in a β -bend conformation: type III (III') for Boc-Aib-Hib-NHBzl, while type II (II') for the Z analogue. Conversely, the structure of Z-L-Hyp-Aib-NHMe, although not far from a type II β -bend, is partially open.

INTRODUCTION

The incorporation of α -aminoisobutyric acid (Aib) residues into peptides stabilizes β -turn conformations.¹⁻⁵ A crystal structure determination of a 16-residue peptide has provided a clear characterization of a " β -bend ribbon," which is a 3_{10} -helical conformation interrupted by Pro residues at alternate positions.⁶ Such structures have been earlier suggested for (Aib-Pro)_n sequences on the basis of nmr data⁷ and conformational energy calculations.⁸ We have undertaken further analysis of sequences of the type (Aib-X)_n, using specifically chosen X residues for interrupting the backbone hydrogen-bonding pat-

tern. The N-alkylated amino acids Pro, Hyp, and MeAib, and the hydroxyacid α -hydroxyisobutyric acid (Hib; forms an ester bond instead of an amide bond) are being investigated. We describe in this report crystal structures of three model compounds—Boc-Aib-Hib-NHBzl (**1**; Bzl, benzyl), Z-Aib-Hib-NHBzl (**2**; Z, benzyloxycarbonyl), and Z-L-Hyp-Aib-NHMe (**3**)—which contain the repeating unit of potential β -bend ribbon structures.

EXPERIMENTAL

The synthesis and characterization of Boc-Aib-Hib-NHBzl (**1**) and Z-Aib-Hib-NHBzl (**2**) have been described.⁹ Z-Hyp-Aib-NHMe (**3**) was prepared by saturating a methanolic solution of Z-L-Hyp-Aib-OMe with gaseous CH₃NH₂. The dipeptide ester was

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Table I Crystal Data for Boc-Aib-Hib-NHBzl (1), Z-Aib-Hib-NHBzl (2), and Z-L-Hyp-Aib-NHMe (3)

	1	2	3
Molecular formula	C ₂₀ H ₃₀ N ₂ O ₅	C ₂₃ H ₂₇ N ₂ O ₅	C ₁₈ H ₂₅ N ₃ O ₅
MW (amu)	378.5	411.5	363.4
Crystal dimensions (mm)	0.2 × 0.3 × 0.4	0.6 × 0.5 × 0.5	0.2 × 0.2 × 0.4
Density (calcd) g/cm ³	1.193	1.214	1.265
Density (exptl.) g/cm ³	1.19	1.21	1.26
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C _c	C _c	P2 ₁
Z	4	4	2
a (Å)	19.560 (2)	17.411 (2)	9.666 (3)
b (Å)	6.262 (1)	13.004 (2)	12.017 (3)
c (Å)	17.485 (2)	10.519 (1)	8.924 (3)
V (Å ³)	2107.8	2251.9	954.4
β (°)	100.2 (2)	109.0 (2)	112.9 (1)
Independent reflections	2631	2859	1770
Reflections [I ≥ 3σ(I)]	1284	2305	1468
R value	0.052	0.081	0.039
R _w value	0.052	0.081	0.040
Crystallization solvent	Acetone–water	Acetone–water	Dimethyl sulfoxide
Radiation	MoK _α , λ = 0.7107 Å	MoK _α , λ = 0.7107 Å	MoK _α , λ = 0.7107 Å
(Δ/σ) _{max}	1.1	1.2	0.09
Maximum and minimum heights in final ΔF (e. Å ⁻³)	±0.2	±0.2	±0.2

prepared by coupling Z-L-Hyp-OH to H-Aib-OMe, using N,N'-dicyclohexylcarbodiimide in CH₂Cl₂, followed by the standard workup as described for related peptides.¹⁰ The compounds were characterized by ¹H-nmr. Crystallization solvents and all relevant crystal parameters are summarized in Table I. The x-ray diffraction data were collected on a Phillips PW 1100 four-circle diffractometer, θ-2θ scan mode to 2θ = 50°. Structures of compounds **1** and **2** were solved by direct methods using the SHELX S-86 program¹¹ and refined by block-matrix least-squares procedures (*w* = 1), using anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were in part stereochemically fixed and the remaining found in the difference Fourier map and not refined. The SHELX-76 program¹² was used for all calculations. The structure of **3** was solved using the direct methods program MULTAN-80.¹³ Hydrogen atoms were located in the difference Fourier map, but they were introduced in calculated positions and refined in the last cycle. The quantity minimized was $w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F) + 0.00037|F^2|]^{-1}$. Fractional coordinates for the nonhydrogen atoms and equivalent isotropic thermal factors in compounds 1–3 are listed in Tables

II–IV. Structure factors and hydrogen atom coordinates have been deposited and are available from the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The molecular structures of compounds 1–3 are illustrated in Figures 1–3. The relevant backbone and pyrrolidine ring torsion angles¹⁴ are listed in Table V. For the two achiral compounds **1** and **2** the signs of the torsion angles listed correspond to those for the “D-D” isomer. The geometry of the intra- and intermolecular hydrogen bonds are reported in Table VI.

Bond lengths and angles are in general agreement with previously described results for the geometry of the *tert*-butyloxycarbonyl,¹⁵ benzyloxycarbonyl,¹⁶ amide,¹⁷ and ester¹⁸ groups; Aib,^{19,20} Hib,²¹ and Hyp²² residues; and the peptide unit.²³ The bond angles at the C^α atom of the Aib and Hib residues deviate significantly from the ideal tetrahedral value; in particular, the τ (N-C^α-C' or O-C^α-C') bond angle has values in the range of 111.2°–112.7°, for residues

Table II Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for Boc-Aib-Hib-NHBzl (1) [Estimated Standard Deviations (ESDs) Are Given in Parentheses]

Atom	x	y	z	$U_{\text{eq}}^{* a}$
O _u	10000	6382 (8)	0000	49 (2)
O ₀	9798 (2)	3639 (8)	788 (3)	49 (2)
O ₁	8127 (3)	1601 (9)	1005 (3)	62 (2)
"O ₂ "	8472 (2)	5015 (8)	1081 (3)	41 (2)
O ₂	8595 (3)	3427 (9)	3095 (3)	58 (2)
N ₁	8993 (3)	4760 (1)	-238 (3)	45 (2)
N ₃	9377 (3)	3180 (1)	2279 (3)	48 (2)
C (1)	10887 (4)	8860 (1)	0000 (5)	68 (3)
C (2)	10525 (4)	7860 (1)	1266 (5)	65 (3)
C (3)	11194 (4)	5220 (1)	578 (5)	64 (3)
C (4)	10668 (4)	7030 (1)	499 (4)	51 (3)
C' ₀	9618 (4)	4790 (1)	234 (4)	42 (2)
C' ₁ ^α	8459 (4)	3210 (1)	-122 (4)	47 (2)
C ₁ ^{β1}	8639 (5)	960 (2)	-389 (5)	73 (4)
C ₁ ^{β2}	7768 (4)	3980 (1)	-602 (4)	61 (3)
C' _{1α}	8351 (3)	3130 (1)	715 (4)	41 (2)
C' ₂ ^α	8316 (3)	5250 (1)	1868 (4)	47 (3)
C ₂ ^{β1}	8534 (5)	7520 (1)	2093 (5)	63 (3)
C ₂ ^{β2}	7544 (4)	4930 (2)	1868 (5)	66 (4)
C' ₂	8768 (4)	3780 (1)	2465 (5)	44 (3)
C (5)	9925 (5)	2220 (1)	2841 (5)	53 (3)
C (6)	10552 (4)	3680 (1)	2983 (5)	47 (3)
C (7)	11169 (5)	3150 (2)	2755 (6)	59 (4)
C (8)	11736 (5)	4500 (2)	2862 (6)	73 (4)
C (9)	11692 (6)	6400 (2)	3245 (6)	74 (4)
C (10)	11077 (7)	7000 (2)	3476 (6)	74 (5)
C (11)	10514 (7)	5660 (2)	3358 (6)	65 (5)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

with helical conformations, while a value of 105° is observed for the *semi* extended Aib residue of Z-Aib-Hib-NHBzl (*vide infra*), thus confirming the interdependence between geometry at the tetrahedral C^α atom and backbone conformation.^{19,20}

The conformation of the urethane moiety, as defined by the torsion angles ω_0 and θ^1 , in the three compounds is type *b* or *trans-trans*.¹⁵ The θ^2 torsion angle, which gives the orientation of the phenyl group with respect to the rest of the molecule,¹⁶ is also *trans* in the two Z-protected compounds. The distribution of the θ^3 and $\theta^{3'}$ values, which give the extent of rotation of the phenyl ring about the ben-

zylic bond, is broad, as commonly found in Z-containing compounds.¹⁶ The amide,¹⁷ ester,¹⁸ and peptide²³ groups in the three compounds are all in the common *trans* disposition, the only significant deviation from planarity being given by the amide group of Boc-Aib-Hib-NHBzl ($\omega_2 = 166.1^\circ$). The θ^1 angle of the benzyl-amido moiety is -115.0° for **1** [angle C'₂-N₃-C(5)-C(16)] and -102.8° for **2** [angle C'₂-N₃-C(8)-C(9)].

The pyrrolidine ring of the L-Hyp residue of **3** exhibits an approximate C_s (envelope) symmetry, the mirror plane passing through the C' atom. This

Table III Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for Z-Aib-Hib-NHBzl (2) (ESDs Are Given in Parentheses)

Atom	x	y	z	$U_{\text{eq}}^{* a}$
O _u	10000	2511 (4)	10000	56 (8)
O ₀	9050 (3)	1544 (4)	8524 (5)	56 (8)
O ₁	9211 (3)	2565 (4)	5872 (6)	61 (8)
"O ₂ "	8783 (3)	935 (4)	5431 (6)	60 (8)
O ₂	6863 (3)	2244 (4)	4126 (6)	68 (8)
N ₁	10284 (3)	1771 (4)	8309 (6)	48 (9)
N ₃	7573 (3)	1767 (5)	6246 (6)	53 (8)
C (1)	9807 (4)	3504 (6)	11757 (7)	54 (9)
C (2)	10139 (5)	3185 (6)	13097 (8)	68 (9)
C (3)	10520 (6)	3892 (7)	14113 (8)	82 (9)
C (4)	10547 (5)	4911 (7)	13787 (8)	75 (9)
C (5)	10216 (5)	5249 (6)	12496 (8)	78 (9)
C (6)	9850 (5)	4560 (6)	11447 (8)	74 (8)
C (7)	9413 (4)	2745 (6)	10648 (7)	60 (9)
C' ₀	9732 (4)	1908 (5)	8913 (7)	48 (9)
C' ₁ ^α	10110 (4)	1187 (5)	7045 (7)	49 (9)
C ₁ ^{β1}	10772 (4)	1373 (6)	6444 (7)	62 (9)
C ₁ ^{β2}	10010 (5)	32 (7)	7321 (8)	76 (8)
C' ₁	9314 (4)	1677 (5)	6070 (7)	52 (9)
C' ₂ ^α	8018 (4)	1219 (6)	4383 (8)	66 (9)
C ₂ ^{β1}	7647 (5)	179 (7)	3902 (9)	93 (9)
C ₂ ^{β2}	8201 (5)	1829 (7)	3196 (8)	79 (9)
C' ₂	7456 (4)	1815 (5)	4948 (7)	52 (9)
C (8)	7038 (4)	2222 (6)	6889 (7)	57 (9)
C (9)	7348 (4)	3224 (5)	7632 (7)	51 (9)
C (10)	7074 (5)	3502 (7)	8682 (8)	70 (9)
C (11)	7324 (5)	4426 (7)	9374 (8)	80 (9)
C (12)	7834 (5)	5072 (7)	8968 (9)	81 (9)
C (13)	8129 (5)	4798 (7)	7962 (8)	76 (9)
C (14)	7889 (5)	3860 (6)	7297 (7)	63 (9)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

Table IV Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for Z-L-Hyp-Aib-NHMe (3) (ESDs Are Given in Parentheses)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
O _u	4861 (2)	-344 (2)	-2783 (3)	65 (1)
O _o	2482 (2)	53 (3)	-3019 (3)	78 (1)
O ^δ	4554 (2)	-3138 (2)	359 (4)	77 (1)
O ₁	3314 (2)	1004 (2)	638 (3)	65 (1)
O ₂	351 (3)	3080 (2)	110 (4)	83 (1)
N ₁	4132 (3)	-834 (2)	-802 (3)	52 (1)
N ₂	1109 (2)	162 (2)	220 (3)	47 (1)
N ₃	304 (4)	1938 (2)	-1907 (4)	76 (1)
C (1)	5993 (4)	266 (0)	-4587 (4)	63 (1)
C (2)	6140 (4)	1055 (4)	-5652 (4)	78 (2)
C (3)	7398 (5)	1048 (4)	-6042 (5)	91 (2)
C (4)	8532 (5)	294 (5)	-5333 (5)	92 (2)
C (5)	8411 (4)	-473 (4)	-4278 (5)	88 (2)
C (6)	7143 (4)	-488 (3)	-3894 (5)	76 (2)
C (7)	4581 (4)	263 (4)	-4248 (4)	75 (2)
C' ₀	3718 (4)	-351 (3)	-2261 (4)	59 (1)
C ₁ ^α	3091 (3)	-958 (3)	-15 (4)	50 (1)
C ₁ ^β	4039 (4)	-1534 (3)	1581 (4)	61 (1)
C ₁ ^γ	5231 (3)	-2156 (3)	1204 (4)	57 (1)
C ₁ ^δ	5598 (3)	-1347 (3)	110 (4)	57 (1)
C' ₁	2514 (3)	168 (3)	296 (4)	49 (1)
C ₂ ^α	413 (3)	1128 (2)	648 (4)	48 (1)
C ₂ ^{β1}	-1234 (3)	821 (3)	279 (5)	65 (1)
C ₂ ^{β2}	1218 (4)	1426 (3)	2427 (4)	66 (1)
C' ₂	386 (3)	2137 (3)	-421 (4)	51 (1)
C (8)	214 (5)	2833 (4)	-3051 (5)	100 (2)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

conformation may be designated as C₈-C^γ *exo* or conformation A.^{24,25} The puckering coordinates for the five-membered ring²⁶ are: $q_2 = 0.379(3) \text{ \AA}$, $\phi_2 = -101.3(5)^\circ$.

The backbone conformations of all three compounds are folded. Compounds **1** and **2** take up a β -bend conformation, but interestingly they differ in the type of β -bend that is formed.^{27,28} A type III' (III) β -bend is adopted by Boc-Aib-Hib-NHBzl **1** ($\phi_1 = 48.7^\circ$, $\psi_1 = 30.9^\circ$; $\phi_2 = 63.9^\circ$, $\psi_2 = 24.1^\circ$), while a type II' (II) β -bend is observed for Z-Aib-Hib-NHBzl **2** ($\phi_1 = 51.9^\circ$, $\psi_1 = -134.2^\circ$; $\phi_2 = -66.3^\circ$, $\psi_2 = -18.9^\circ$). In both cases, the intramolecular hydrogen bond involves the amide NH and urethane CO groups. The N₃ ··· O₀ separation is 2.88(1) and 2.90(1) \AA ^{29,30} for **1** and **2**, respectively. The type

III' β -bend of **1** is additionally stabilized by a weak N₃ ··· "O₂" intramolecular interaction [2.74(1) \AA].³¹ These findings should be compared with the crystal structures of Ac-(Aib)₂-Aib-OMe and Ac-(Aib)₂-R-Iva-OMe, the former assuming a type III (III') β -bend conformation while the latter adopts a type II β -bend.³² Z-L-Hyp-Aib-NHMe (**3**) adopts a conformation not far from a regular type II β -bend ($\phi_1 = -60.5^\circ$, $\psi_1 = 147.5^\circ$; $\phi_2 = 59.3^\circ$, $\psi_2 = 29.7^\circ$). The N₃ ··· O₀ distance is 3.49(1) \AA , which is too long for an acceptable N-H ··· O=C hydrogen bond. Interestingly, the closely related peptide Piv-L-Pro-Aib-NHMe (Piv, pivaloyl) folds into a type-II β -turn in the solid state.¹⁰

The crystal packing modes for compounds **1** and **2** are characterized by the same type of intermolecular hydrogen bonds, involving the urethane NH and amide CO groups of symmetry-related molecules (figure not shown). The N₁ ··· O₂ distance is 3.10(1) \AA in **1** and 2.90(1) \AA in **2**. In Z-L-Hyp-Aib-NHMe, the molecules are held together in the crystal by two types of intermolecular hydrogen bonds, of the (peptide) N-H ··· O=C (amide) and (Hyp side chain) O-H ··· O=C (peptide) types (figure not shown). The N₂ ··· O₂ separation is 2.83 \AA , while the O^δ ··· O₁ separation is 2.74(1) \AA .^{33,34}

The structures of compounds **1**–**3** demonstrate that modification of the central peptide unit by replacement of the amide with an ester bond (**1**, **2**) or by N-alkylation (**3**) leaves the β -bend conformation favored in Aib-containing sequences largely unaffected. The differences between the energies of the type III' (III) and type II' (II) conformations for the Aib-Hib sequences appear small, and changes in the nature of the N-terminal blocking group lead to an alteration in the β -turn type. The observation of a *semiextended* conformation at Aib ($\phi \sim \pm 60^\circ$, $\psi \sim \mp 120^\circ$) is rather unusual, but there are a growing number of examples of this conformation,^{32,35} with Aib at the *i* + 1 position of a type II' (II) β -turn. The distorted type II β -turn conformation, observed for Z-L-Hyp-Aib-NHMe, may be contrasted to the type III β -turn established for the -L-Hyp-Aib- segment in Boc-L-Hyp-Aib-Aib-L-Phol.²² Clearly, in sequences of the type Pro/Hyp-Aib the energy differences between type II and type III β -turn structures is marginal,¹⁰ and equilibration in solution is a possibility.³⁶ In repetitive sequences of the kind observed at the C-terminal end of anti-amoebins³⁷ or zervamicins,³⁸ β -bend ribbons may be favored, as observed for a 16-residue synthetic analogue of zervamicin.⁶

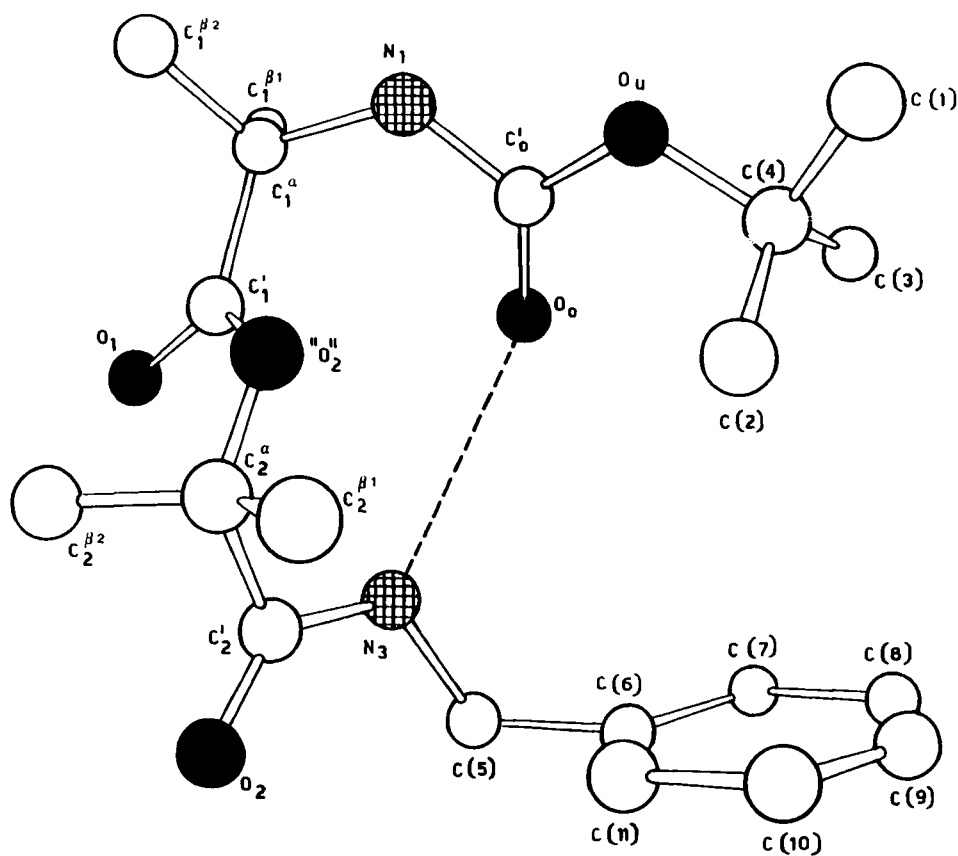


Figure 1. Molecular structure of Boc-Aib-Hib-NHBzl (**1**) with numbering of the atoms. The intramolecular hydrogen bond is shown as a dashed line.

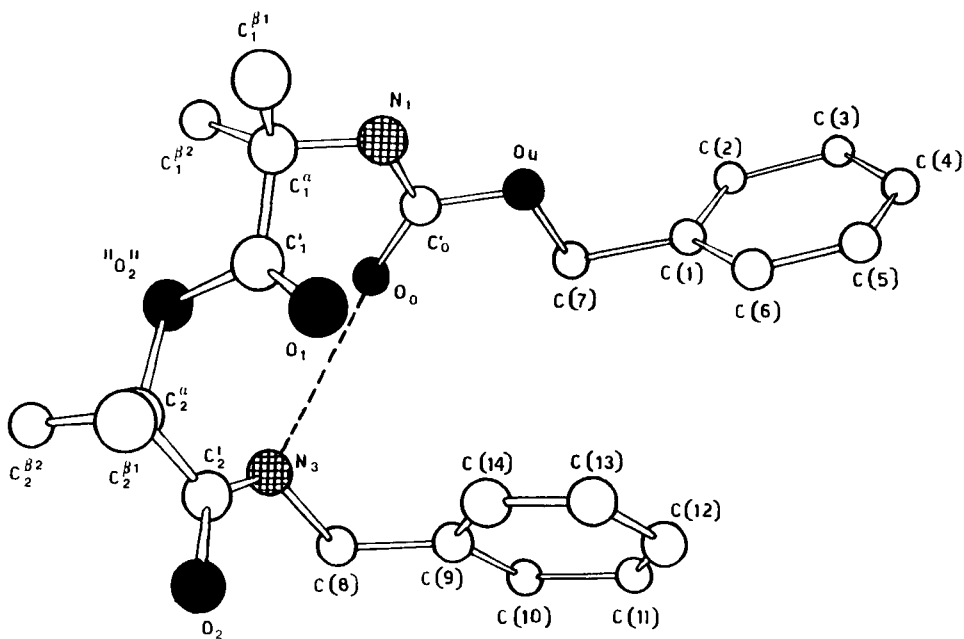


Figure 2. Molecular structure of Z-Aib-Hib-NHBzl (**2**) with numbering of the atoms. The intramolecular hydrogen bond is shown as a dashed line.

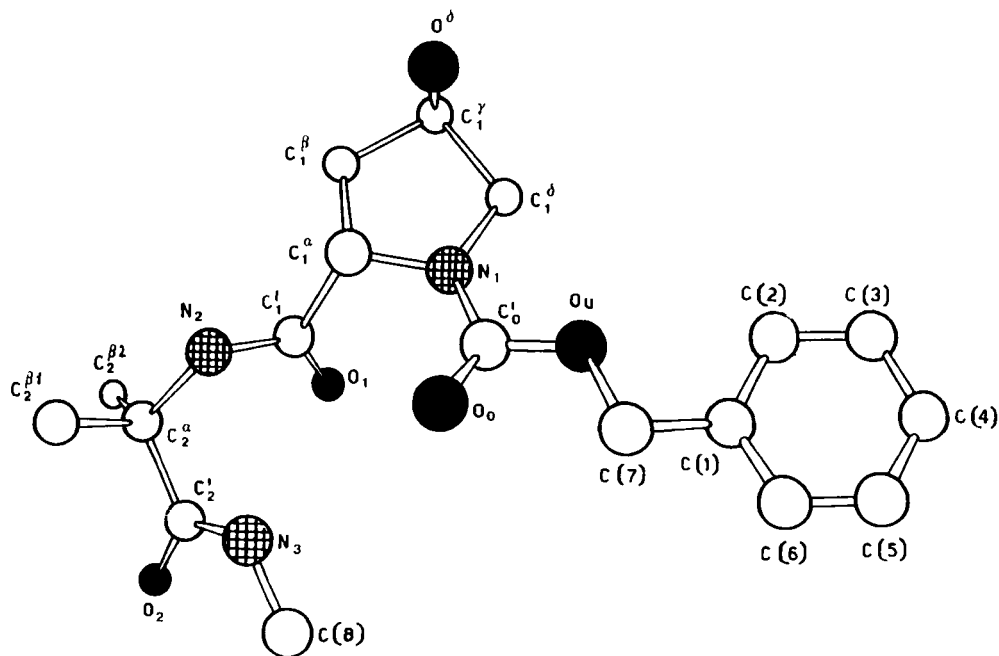


Figure 3. Molecular structure of Z-L-Hyp-Aib-NHMe (3) with numbering of the atoms.

Table V Backbone and Side-Chain Torsion Angles^a (°) in Boc-Aib-Hib-NHBzl (1), Z-Aib-Hib-NHBzl (2), and Z-L-Hyp-Aib-NHMe (3)

Peptide 1		Peptide 2	
$\omega_0(\text{O}_u - \text{C}'_0 - \text{N}_1 - \text{C}'_1)$	-179.2 (7)	$\omega_0(\text{O}_u - \text{C}'_0 - \text{N}_1 - \text{C}'_1)$	-176.2 (7)
$\phi_1(\text{C}'_0 - \text{N}_1 - \text{C}'_1 - \text{C}'_1)$	48.7 (10)	$\phi_1(\text{C}'_0 - \text{N}_1 - \text{C}'_1 - \text{C}'_1)$	51.9 (10)
$\psi_1(\text{N}_1 - \text{C}'_1 - \text{C}'_1 - \text{"O}_2\text{"})$	30.9 (10)	$\psi_1(\text{N}_1 - \text{C}'_1 - \text{C}'_1 - \text{"O}_2\text{"})$	-134.2 (7)
$\omega_1(\text{C}'_1 - \text{C}'_1 - \text{"O}_2\text{"} - \text{C}'_2)$	173.4 (7)	$\omega_1(\text{C}'_1 - \text{C}'_1 - \text{"O}_2\text{"} - \text{C}'_2)$	-175.1 (7)
$\phi_2(\text{C}'_1 - \text{"O}_2\text{"} - \text{C}'_2 - \text{C}'_2)$	63.9 (10)	$\phi_2(\text{C}'_1 - \text{"O}_2\text{"} - \text{C}'_2 - \text{C}'_2)$	66.3 (10)
$\psi_2(\text{"O}_2\text{"} - \text{C}'_2 - \text{C}'_2 - \text{N}_3)$	24.1 (10)	$\psi_2(\text{"O}_2\text{"} - \text{C}'_2 - \text{C}'_2 - \text{N}_3)$	-18.9 (10)
$\omega_2(\text{C}'_2 - \text{C}'_2 - \text{N}_3 - \text{C}_5)$	166.1 (8)	$\omega_2(\text{C}'_2 - \text{C}'_2 - \text{N}_3 - \text{C}_5)$	-174.2 (8)
Peptide 3			
$\omega_0(\text{O}_u - \text{C}'_0 - \text{N}_1 - \text{C}'_1)$	-178.7 (3)	$\theta(\text{C}'_1 - \text{N}_1 - \text{C}'_1 - \text{C}'_1)$	3.9 (4)
$\phi_1(\text{C}'_0 - \text{N}_1 - \text{C}'_1 - \text{C}'_1)$	-60.5 (5)	$\chi^1(\text{N}_1 - \text{C}'_1 - \text{C}'_1 - \text{C}'_1)$	-26.3 (4)
$\psi_1(\text{N}_1 - \text{C}'_1 - \text{C}'_1 - \text{N}_2)$	147.5 (3)	$\chi^2(\text{C}'_1 - \text{C}'_1 - \text{C}'_1 - \text{C}'_1)$	38.5 (4)
$\omega_1(\text{C}'_1 - \text{C}'_1 - \text{N}_2 - \text{C}'_2)$	173.4 (3)	$\chi^3(\text{C}'_1 - \text{C}'_1 - \text{C}'_1 - \text{N}_1)$	-35.0 (4)
$\phi_2(\text{C}'_1 - \text{N}_2 - \text{C}'_2 - \text{C}'_2)$	59.3 (4)	$\chi^4(\text{C}'_1 - \text{C}'_1 - \text{N}_1 - \text{C}'_1)$	19.8 (4)
$\psi_2(\text{N}_1 - \text{C}'_2 - \text{C}'_2 - \text{N}_3)$	29.7 (5)		
$\omega_2[\text{C}'_2 - \text{C}'_2 - \text{N}_3 - \text{C}(8)]$	177.6 (4)		

^a Torsion angles are defined according to the IUPAC-IUB Commission on Biochemical Nomenclature.¹⁴

Table VI Geometry of the Intra- and Intermolecular Hydrogen Bonds in the Crystals of Boc-Aib-Hib-NHBzl (1), Z-Aib-Hib-NHBzl (2), and Z-L-Hyp-Aib-NHMe (3)

Compound	Donor <i>D</i> — <i>H</i>	Acceptor <i>A</i>	Symmetry Equivalent of <i>A</i>	Distances (Å)		Angle (°) <i>D</i> — <i>H</i> — <i>A</i>
				<i>D</i> — <i>A</i>	<i>H</i> — <i>A</i>	
1	N ₃ —H	O ₀	<i>x</i> , <i>y</i> , <i>z</i>	2.88 (1)	2.10 (1)	134 (1)
	N ₁ —H	O ₂	<i>x</i> , 1— <i>y</i> , <i>z</i> — $\frac{1}{2}$	3.10 (1)	2.10 (1)	156 (1)
2	N ₃ —H	O ₀	<i>x</i> , <i>y</i> , <i>z</i>	2.90 (1)	1.98 (1)	139 (1)
	N ₁ —H	O ₂	$\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$	2.90 (1)	1.82 (1)	167 (1)
3	N ₁ —H	O ₂	— <i>x</i> , <i>y</i> — $\frac{1}{2}$, — <i>z</i>	2.83 (1)	1.95 (1)	170 (1)
	O ^δ —H	O ₁	1— <i>x</i> , <i>y</i> — $\frac{1}{2}$, — <i>z</i>	2.74 (1)	2.01 (1)	153 (1)

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