C(5)—C(6)—C(7)—C(8)] of bufothionin is almost planar within the maximum deviations of 0·04 Å [C(5)].

Fig. 2 depicts the crystal structure projected along the *b* axis. The shortest distance between the positive charge center $N(2)^+$ and the negative charge center SO_3^- is 3·64 Å [N(2)···O(3)($1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$)]; two methyl groups, C(11) and C(12), block intermolecular interaction between the positive and negative charge centers. A short intermolecular distance of 2·905 (1) Å between the N(1) and O(3) atoms is observed around the center of inversion, which suggests that the two centrosymmetrically related molecules form a dimer linked by hydrogen bonds. Slight enlargement of the double-bond length to 1·452 (2) Å for S(1)—O(3), compared with those for S(1)—O(2) [1·432 (2) Å] and S(1)—O(4) [1·427 (2) Å] is in good agreement with the formation of the hydrogen bond.

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Proline Conformations in Linear Peptides. Structure Determination of the Methyl Ester of *N*-Benzyloxycarbonyl-L-prolyl-D-alanine (*N*-Z-L-Pro-D-Ala-OMe)

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Abstract. *N*-Z-L-Pro-D-Ala-OMe, $C_{17}H_{22}N_2O_5$, M_r = 334·38, crystallizes in the orthorhombic space group $P2_12_12_1$, with the cell dimensions a = 5·005 (5), b = 17·690 (9) and c = 18·70 (1) Å^3, V = 1656·3 Å^3, Z = 4, D_x = 1·341 g cm^{-3}, Cu $K\alpha$, λ = 1·54184 Å, μ = 7·830 cm^{-1}, $F(000)$ = 712, T = 198 K, final R (on F) = 0·036 for 1575 observed reflections with $I \geq 3\sigma(I)$. The pyrrolidine ring takes on the C_2-C$^\gamma$-*endo* conformation. The urethane bond is in the *cis* conformation [ω_0 = 6·0 (3)°] while the peptide bond is in the *trans* conformation [ω_1 = 170·8 (2)°]; φ_1/ψ_1 values are −88·0 (3)° and 151·3 (2)°. Intermolecular hydrogen bonding occurs between the C-terminus and the symmetry-related amide. Systematic examination of the pyrrolidine ring in linear peptides reveals no correlation exists between the *cis–trans* orientation of the proline and the conformation of the pyrrolidine ring.

Introduction. Proline is an important constituent of many proteins. Its presence in proteins imposes certain conformational restrictions, particularly as a helix breaker. Peptides containing proline residues have been extensively studied because of the possibility of *cis–trans* isomerization about the *X*-Pro bond (Carver & Blout, 1976; Grathwohl & Wuthrich, 1976; Nair & Vijayan, 1981) and the different modes of puckering that the pyrrolidine ring can undergo (Balasubramanian, Lakshminarayanan, Sabesan, Tegoni, Venkatesan & Ramachandran, 1971; Ashida & Kakudo, 1974).

Recently it was proposed (Trikha, Patel & Singh, 1990) that for proline in the *cis* conformation the pyrrolidine ring adopts only the C_2-C$^\gamma$-*endo* conformation. The structure of *N*-Z-L-Pro-D-Ala-OMe displays an *X*-Pro bond which is *cis* and in which the pyrrolidine ring geometry is C_2-C$^\gamma$-*endo*. Observation of this ring conformation in conjuction with a *cis* proline appears to further confirm the previously drawn correlations. However, closer examination of a larger database of linear proline-containing peptides reveals the previous assertion to be erroneous.

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Experimental. For X-ray examination and data collection, a suitable crystal obtained from ethanol–hexane (approximate dimensions 0·28 × 0·10 × 0·13 mm) was mounted on the tip of a glass fiber. Intensity data were collected at 198 K on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters were obtained by least-squares refinement of the angular settings from 25 reflections lying in a 2θ range of 50–70°. Intensity data (1746 reflections) were collected using variable speed ω–2θ scans with $2 \le 2\theta \le 135°$ as follows: $0 \le h \le 6$; $0 \le k \le 21$; $0 \le l \le 22$. Three standard reflections ($0\bar{6}9$; $\bar{2}90$; 275) monitored every 3 h of X-ray exposure time showed negligible nonsystematic intensity changes of +0·4%; no correction for deterioration was made. The data were corrected for absorption effects (correction: min. 0·826, max. 1·244%) based on the *DIFABS* algorithm of Walker & Stuart (1983). The data were also corrected for Lorentz and polarization effects.

The structure was solved by a combination of direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and the difference Fourier technique and refined by full-matrix least squares (on F). Non-H atoms were refined with isotropic displacement factors, then with anisotropic displacement factors. H-atom positions were located directly from the difference Fourier maps and refined. H-atom isotropic displacement factors were assigned as 1·3 × B_{eq} of the adjacent atom; they were not refined. The refinement converged [$(\Delta/\sigma)_{max} = 0·04$] to values of the standard crystallographic agreement factors of $R = 0·036$, $wR = 0·045$ and $S = 1·690$ for 1575 observations with $I \ge 3\sigma(I)$ and 284 parameters. Weights were assigned to the data as $4F^2/\sigma(F^2)$ where $\sigma(F^2) = [\sigma(I)^2 + (0·02F^2)^2]^{1/2}$. An extinction coefficient of the form proposed by Zachariasen (1963) was applied and refined: $g = 1·19 \times 10^{-6}$. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV) except for the H atoms (Stewart, Davidson & Simpson, 1965). The effects of anomalous dispersion for non-H atoms were included. A final difference map showed maximum excursions of $(\Delta\rho)_{max} = 0·177$, $(\Delta\rho)_{min} = -0·174$ e Å^{-3}. Final atom positions and equivalent isotropic temperature factors for the non-H atoms are given in Table 1.* All programs used were from the locally modified Enraf–Nonius (1979) *SDP*.

* Lists of anisotropic temperature factors, least-squares planes, torsion angles, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53881 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and e.s.d.'s for N-Z-Pro-Ala-OMe*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å^2)
O8	−0·1493 (4)	0·1419 (1)	0·14108 (9)	2·98 (3)
O9	0·1602 (4)	0·2331 (1)	0·11838 (9)	3·15 (4)
O15	0·2444 (4)	−0·0105 (1)	0·0434 (1)	3·35 (4)
O18	0·0856 (5)	−0·1938 (1)	0·1560 (1)	5·94 (6)
O19	−0·2465 (4)	−0·1129 (1)	0·17691 (9)	3·79 (4)
N10	0·0638 (4)	0·1417 (1)	0·0374 (1)	2·60 (4)
N16	−0·1834 (4)	−0·0511 (1)	0·0446 (1)	2·43 (4)
C1	−0·4195 (5)	0·1319 (1)	0·2461 (1)	2·84 (5)
C2	−0·4855 (6)	0·1513 (2)	0·3159 (2)	3·74 (6)
C3	−0·6840 (7)	0·1123 (2)	0·3521 (2)	4·17 (6)
C4	−0·8189 (6)	0·0537 (2)	0·3191 (2)	4·10 (6)
C5	−0·7533 (7)	0·0339 (2)	0·2497 (2)	4·25 (7)
C6	−0·5526 (6)	0·0726 (2)	0·2135 (2)	3·61 (6)
C7	−0·2093 (6)	0·1777 (2)	0·2087 (1)	3·16 (5)
C9	0·0358 (5)	0·1770 (1)	0·1006 (1)	2·53 (5)
C11	0·2360 (5)	0·1732 (1)	−0·0187 (1)	2·81 (5)
C12	0·2033 (5)	0·1173 (2)	−0·0801 (1)	2·92 (5)
C13	−0·0798 (5)	0·0864 (1)	−0·0696 (1)	2·71 (5)
C14	−0·1020 (5)	0·0789 (1)	0·0126 (1)	2·30 (4)
C15	0·0050 (5)	0·0025 (1)	0·0363 (1)	2·34 (4)
C17	−0·1141 (5)	−0·1297 (1)	0·0567 (1)	2·55 (5)
C18	−0·0752 (6)	−0·1483 (1)	0·1351 (2)	3·08 (5)
C20	−0·2481 (8)	−0·1350 (2)	0·2520 (2)	5·35 (8)
C21	−0·3303 (6)	−0·1810 (2)	0·0270 (2)	3·52 (6)

Discussion. The molecular structure of *N*-Z-L-Pro-D-Ala-OMe is shown in Fig. 1. The stereo unit-cell diagram is shown in Fig. 2. Principal bond distances and angles are given in Table 2. Selected torsion angles are given in Table 3.

The benzyloxycarbonyl-blocked N-terminus (Benedetti, Pedone, Toniolo, Dudek, Nemethy & Scheraga, 1983) and methyl ester-blocked C-terminus (Schweizer & Dunitz, 1982) display bond distances and bond angles consistent with other peptides containing these groups. As is consistent with other proline-containing peptides, the phenyl and proline rings tend to stack in the crystals as is illustrated in Fig. 2.

The urethane bond in *N*-Z-Pro-Ala-OMe is in the *cis* conformation [$\omega_0 = 6·0$ (3)°] while the peptide bond is in the *trans* conformation [$\omega_1 = 170·8$ (2)°]. The observed values for ω are comparable to the normal values of 0 and 180° for peptide bonds with *cis* and *trans* conformations, respectively (Benedetti, 1982). The urethane group is nearly planar, as seen by comparing the two torsion angles θ^1 = C7—O8—C9—N10 = −176·2 (2) and $\theta^{1'}$ = C7—O8—C9—O9 = 3·5 (4)°. As is generally found in esters, the C9=O9 bond is synperiplanar to the C7—O8 bond, the $\theta^{1'}$ torsion angle being nearly 0° (Benedetti, Pedone, Toniolo, Dudek, Nemethy & Scheraga, 1983). The principal torsion angles φ_1 and ψ_1 are −88·0 (3) and 151·3 (2)°, respectively, and are consistent with other *cis* proline residues.

There is no evidence of disorder in the C$^\gamma$ atom for *N*-Z-Pro-Ala-OMe although such disorder is frequently observed in proline-containing peptides

(Ashida & Kakudo, 1974). The bond angles of the pyrrolidine ring, particularly about the N atom, are strongly dependent on the *cis–trans* conformation. The *cis* geometry is characterized by a larger C′—N—C^{α} angle and a smaller C′—N—C^{δ} angle as compared to the *trans* conformation (Benedetti, 1982). The differences in angles can be readily observed if *cis-N*-Z-Pro-Ala-OMe [125·0 (2) and 120·9 (2)°, respectively] is compared to *trans-tert*-Boc-Pro-Leu-Gly.H_2O (120 and 124°, respectively) (Ashida, Tanaka, Shimonishi & Kakudo, 1977) or *trans-N*-Z-Ala-Pro [120·1 (6) and 127·3 (5)°, respectively] (Krause & Eggleston, 1990; Panneerselvam, Chacko & Veena, 1990).

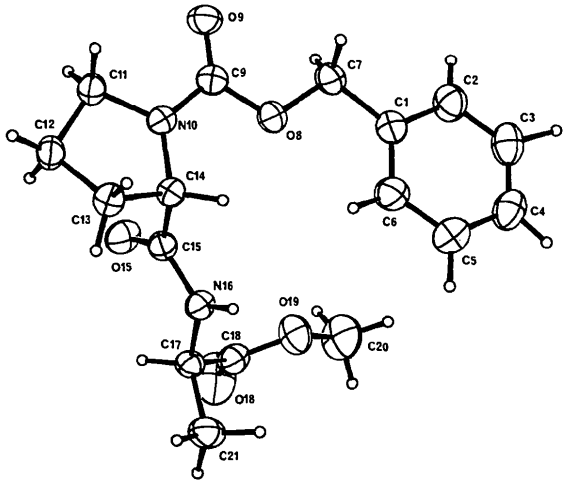

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of *N*-Z-Pro-Ala-OMe showing 50% thermal-ellipsoid probability for the non-H atoms, H atoms as small spheres of arbitrary size and the atomic labelling scheme.

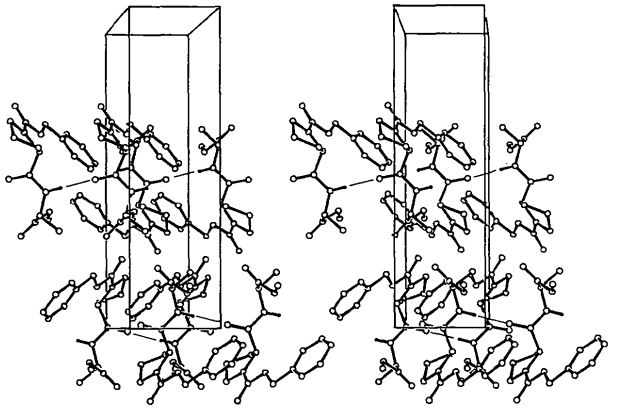

Fig. 2. Stereo unit-cell drawing of *N*-Z-Pro-Ala-OMe indicating the intermolecular hydrogen bonding. Hydrogen-bonding interactions are indicated by single lines. The *a* axis is along the horizontal while the *b* axis runs vertically.

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *for N*-Z-Pro-Ala-OMe *with e.s.d.'s in parentheses*

O8—C7	1·446 (2)	C1—C6	1·385 (3)
O8—C9	1·348 (3)	C1—C7	1·501 (3)
O9—C9	1·218 (2)	C2—C3	1·385 (4)
O15—C15	1·228 (3)	C3—C4	1·382 (4)
O18—C18	1·203 (3)	C4—C5	1·383 (4)
O19—C18	1·318 (3)	C5—C6	1·392 (4)
O19—C20	1·458 (3)	C11—C12	1·524 (3)
N10—C9	1·345 (3)	C12—C13	1·531 (3)
N10—C11	1·469 (3)	C13—C14	1·547 (3)
N10—C14	1·463 (3)	C14—C15	1·520 (3)
N16—C15	1·347 (3)	C17—C18	1·516 (3)
N16—C17	1·450 (3)	C17—C21	1·518 (3)
C1—C2	1·390 (3)		

C7—O8—C9	115·6 (2)	O9—C9—N10	124·5 (2)
C18—O19—C20	116·6 (2)	N10—C11—C12	103·2 (2)
C9—N10—C11	120·9 (2)	C11—C12—C13	103·5 (2)
C9—N10—C14	125·0 (2)	C12—C13—C14	103·0 (2)
C11—N10—C14	113·2 (2)	N10—C14—C13	102·1 (2)
C15—N16—C17	121·7 (2)	N10—C14—C15	112·5 (2)
C2—C1—C6	119·1 (2)	C13—C14—C15	110·0 (2)
C2—C1—C7	118·1 (2)	O15—C15—N16	122·6 (2)
C6—C1—C7	122·7 (2)	O15—C15—C14	122·9 (2)
C1—C2—C3	120·4 (3)	N16—C15—C14	114·4 (2)
C2—C3—C4	120·4 (2)	N16—C17—C18	113·0 (2)
C3—C4—C5	119·5 (3)	N16—C17—C21	110·2 (2)
C4—C5—C6	120·2 (3)	C18—C17—C21	108·4 (2)
C1—C6—C5	120·3 (3)	O18—C18—O19	124·1 (2)
O8—C7—C1	108·5 (2)	O18—C18—C17	123·1 (2)
O8—C9—O9	125·0 (2)	O19—C18—C17	112·7 (2)
O8—C9—N10	110·6 (2)		

Table 3. *Selected torsion angles* (°) *and e.s.d.'s for N*-Z-Pro-Ala-OMe

O8—C9—N10—C14	6·0 (3)	ω_0	C14—C13—C12—C11	−39·0 (2)	χ^2
C14—C15—N16—C17	170·8 (2)	ω_1	C13—C12—C11—N10	29·5 (2)	χ^3
C9—N10—C14—C15	−88·0 (3)	φ_1	C12—C11—N10—C14	−9·0 (3)	χ^4
C15—N16—C17—C18	87·7 (3)	φ_2	C11—N10—C14—C13	−15·0 (3)	$\chi = \theta$
C15—N16—C17—C21	−150·8 (2)	χ_2	C15—C14—C13—C12	−86·9 (2)	θ^{i}
N10—C14—C15—N16	151·3 (2)	ψ_1	C15—C14—N10—C11	102·9 (2)	θ^{ii}
N16—C17—C18—O18	−145·8 (3)	ψ_2	C9—N10—C11—C12	−178·6 (2)	θ^{iii}
N16—C17—C18—O19	38·0 (3)	ψ_3	C9—N10—C14—C13	154·1 (2)	θ^{iv}
N10—C14—C13—C12	32·7 (2)	χ^1			

The pyrrolidine ring in *N*-Z-Pro-Ala-OMe is puckered and adopts the C_2-C^{γ}-*endo* conformation which may be defined as a half-chair with C^{β} and C^{γ} residing on opposite sides of the plane defined by N—C^{α}—C^{δ} and C^{γ} on the same side of this plane as C′ of Pro (Ashida & Kakudo, 1974). It has been proposed, based apparently on the analysis of 13 structures, that a correlation exists between the *cis* orientation of the proline and the conformation of the pyrrolidine ring (Trikha, Patel & Singh, 1990). The structure revealed for Z-L-Pro-D-Ala-OMe thus appears to further substantiate this conclusion. The torsion angle values for a number of proline-containing peptides are compiled in Table 4. Systematic examination of the various ω torsion angles, urethane and peptide angles, associated with the proline reveals that no correlation exists between either a *cis* or *trans* orientation of the proline and the conformation of the pyrrolidine ring. For example, in the structure of Boc-Pro-Val-Gly-NH_2 (Tanaka &

Table 4. *Torsion angles* (°) *and pyrrolidine ring conformations of selected linear proline residues*

For those structures with two independent molecules, values in parentheses are for molecule *B*.

Compound	ω_0*	ω_{x-1}*	ω_x*	Conformation†	Ref.
Z-Pro-Ala-OMe	6·0 (3)		170·8 (2)	C_2-C$^\gamma$-*endo*	1
Boc-Pro-Met-Gly-OBzl	−179		−20	C_2-C$^\gamma$-*endo*	2
	(176)		(−13)	(C_2-C$^\gamma$-*endo*)	
Boc-Pro-Sar-OBzl	−13		−7	C_2-C$^\gamma$-*endo*	3
Z-Gly-Pro-Leu		−4	−177	C_2-C$^\gamma$-*endo*	4
S-Bz-Cys-Pro-Leu-Gly-NHMe		4	4	C_2-C$^\gamma$-*endo*	5
		(3)	(1)	(C_s-C$^\gamma$-*endo*)	
Se-Bz-Cys-Pro-Leu-Gly-NHMe		0	−1	C_s-C$^\beta$-*exo*	5
		(6)	(8)	(C_s-C$^\gamma$-*endo*)	
Boc-Pro	−6			C_2-C$^\gamma$-*endo*	6
Z-Pro-Ala-Thr('Bu)$_2$	3		178	C_2-C$^\gamma$-*endo*	7
Z-Pro-Leu-OEt	−11		171	C_2-C$^\gamma$-*endo*	8
Boc-Pro-Leu-OBzl	−13		157	C_2-C$^\gamma$-*endo*	8
Boc-Pro-Pro	−7		−176	C_s-C$^\gamma$-*endo* (Pro 1)	9
		−176		C_s-C$^\gamma$-*endo* (Pro 2)	
Boc-Pro-Val-OMe:	3		168	C_s-C$^\gamma$-*endo*	
Boc-Pro-C$^\beta$-Me-Val-OMe (1:1)	−1		167	C_s-C$^\gamma$-*endo*	10
Boc-Pro-Ala-Gly-NH$_2$	−13		−171	C_2-C$^\gamma$-*endo*	11
Boc-Pro-Pro-Gly-NH$_2$	−2		−179	C_2-C$^\gamma$-*exo* (Pro 1)	12
		−179	178	C_2-C$^\gamma$-*exo* (Pro 2)	
Boc-Pro$_4$-OBzl.H$_2$O	−1		169	Intermediate (Pro 1)‡	13
		169	176	C_2-C$^\gamma$-*exo* (Pro 2)	
		176	180	C_2-C$^\beta$-*exo* (Pro 3)	
		180		C_s-C$^\beta$-*exo* (Pro 4)	
Boc-Pro-Sar	−7		170	C_2-C$^\gamma$-*endo*	14,15
Boc-Pro-Ile-Gly	11		172	C_2-C$^\gamma$-*endo*	16
Boc-Pro-Leu-Gly-NH$_2$.1/2H$_2$O	−10		180	C_s-C$^\gamma$-*exo*	17
	(−13)		(−171)	(C_2-C$^\gamma$-*endo*)	
Boc-Pro-Leu-Gly-NH$_2$ (γ-lactam)	−4		174	C_2-C$^\gamma$-*endo*	17
Boc-Pro-Leu-Gly-NH$_2$ (δ-lactam)	−10		178	C_2-C$^\gamma$-*exo*	17
Boc-Pro-Val-Gly.1/2H$_2$O	8		163	C_2-C$^\gamma$-*endo*	18
	(2)		(154)	(C_2-C$^\gamma$-*endo*)	
Boc-Pro-Val	−8			C_2-C$^\gamma$-*exo*	19
Boc-Pro-Val-Gly-NH$_2$	0·1		166	C_s-C$^\gamma$-*endo*	20
	(4)		(153)	(C_s-C$^\beta$-*exo*)	
Boc-Pro-HGly-OEt	−11		−178	C_s-C$^\beta$-*exo*	21
Boc-Pro-Ala	8		−171	C_s-C$^\gamma$-*endo*	22
	(4)		(174)	(C_s-C$^\gamma$-*endo*)	
Boc-Pro-Ala-Ala	−177		174	C_2-C$^\gamma$-*endo*	22
Boc-Pro-dehydro-Leu-OMe	−2		169	C_s-C$^\beta$-*exo*	23
	(−3)		(167)	(C_2-C$^\gamma$-*endo*)	
Boc-Pro-dehydro-Leu-NHMe	176		−179	C_2-C$^\gamma$-*exo*	24
Boc-Pro-dehydro-Phe-Gly	179		175	C_2-C$^\gamma$-*exo*	25
Boc-Pro-His-NHMe	−178		177	C_2-C$^\gamma$-*exo*	26
Tos-Pro-hydroxy-Pro.H$_2$O	−78		176	C_s-C$^\gamma$-*endo* (Pro 1)	27,28
		176		C_2-C$^\gamma$-*exo* (Pro 2)	
Poc-Pro-Ala-Gly	−3		−179	C_s-C$^\beta$-*exo*	29
	(3)		(−178)	(C_s-C$^\beta$-*exo*)	
Aoc-Pro-Pro-Pro	−10		172	C_s-C$^\beta$-*exo* (Pro 1)	30
			−179	C_s-C$^\beta$-*exo* (Pro 2)	
				C_2-C$^\gamma$-*endo* (Pro 3)	
Aoc-Pro	−2			C_s-C$^\gamma$-*endo*	31
Z-Ala-Pro		171		C_s-C$^\gamma$-*endo*	32,33
p-Br-Z-Gly-Pro-Leu-Gly		−174	175	C_2-C$^\gamma$-*exo*	34
o-Br-Z-Gly-Pro-Leu-Gly-Pro		−168	−178	C_s-C$^\beta$-*endo* (Pro 1)	35
		178		C_2-C$^\gamma$-*endo* (Pro 2)	
Z-Gly-Pro-Leu-Gly-Pro.2H$_2$O		−177	−179	C_s-C$^\gamma$-*exo* (Pro 1)	36
		181		C_s-C$^\gamma$-*endo* (Pro 2)	
Tyr-Pro-Asp-Gly		176	182	C_2-C$^\gamma$-*endo*	37

References: (1) This work; (2) Yamane, Shiraishi & Ashida (1985); (3) Kojima, Kido, Itoh, Yamane & Ashida (1980); (4) Yamane, Ashida, Shimonishi, Kakudo & Sasada (1976); (5) Rudko & Low (1975); (6) Benedetti, Ciajolo & Maisto (1974); (7) Baoguang, Yicheng, Zhengjiong & Youqi (1984); (8) Sugino, Tanaka & Ashida (1978); (9) Kamwaya, Oster & Bradaczek (1981); (10) Trikha, Patel & Singh (1990); (11) Kojima, Tanaka & Ashida (1982); (12) Tanaka, Ashida, Shimonishi & Kakudo (1979); (13) Matsuzaki (1974); (14) Itoh, Yamane & Ashida (1978); (15) Benedetti, Ciajolo, Di Blasio, Pavone, Pedone, Toniolo & Bonora (1979*a*); (16) Yamada, Tanaka & Ashida (1980); (17) Valle, Crisma, Toniolo, Yu & Johnson (1989); (18) Tanaka & Ashida (1980); (19) Bosch, Schmitt, Jung & Winter (1984); (20) Ashida, Kojima, Tanaka & Yamane (1986); (21) Viret, Collet, Pichon-Pesme & Aubry (1988); (22) Ananthanarayanan & Cameron (1988); (23) Narula, Patel & Singh (1988); (24) Singh, Narula, Chauhan, Sharma & Hinrichs (1989); (25) Patel, Singh, Chauhan & Kaur (1990); (26) Aubry, Vlassi & Marraud (1986); (27) Sabesan & Ventatesan (1971); (28) Fridrichsons & Mathieson (1962); (29) Yamada, Tanaka & Ashida (1981); (30) Kartha, Ashida & Kakudo (1974); (31) Benedetti, Ciajolo, Di Blasio, Pavone, Pedone, Toniolo & Bonora (1979*b*); (32) Panneerselvam, Chacko & Veena (1990); (33) Krause & Eggleston (1990); (34) Ueki, Ashida, Kakudo, Sasada & Katsube (1969); (35) Ueki, Bando, Ashida & Kakudo (1971); (36) Bando, Tanaka, Ashida & Kakudo (1978); (37) Precigoux, Geoffre, Hospital & Leroy (1982).

* ω_0 refers to urethane bond, ω_{x-1} refers to peptide bond preceding proline, ω_x refers to peptide bond following proline.

† Conformation is based on the proline torsion angles as defined by Ashida & Kakudo (1974).

‡ Virtually planar ring, conformation may be described as C_s-C$^\gamma$-*exo*.

Ashida, 1980), in which the urethane group is *cis*, the pyrrolidine ring conformation is C_s-C$^\gamma$-*endo*. Likewise, the structure of *S*-Bz-Cys-Pro-Leu-Gly-NHMe (Rudko & Low, 1975), which contains two independent molecules, both with *cis X*-Pro bonds, has the pyrrolidine rings in both the C_2-C$^\gamma$-*endo* and C_s-C$^\gamma$-*endo* conformations. Secondly, the conformation of one pyrrolidine ring does not influence the conformation of an adjacent ring, as revealed in the structures of Boc-Pro$_4$-OBzl (Matsuzaki, 1974) and Aoc-Pro$_3$-OH (Kartha, Ashida & Kakudo, 1974). Considering the rather modest energy requirements for pyrrolidine ring deformation along the pseudorotational pathway and the effects which crystal packing forces could be expected to induce, the lack of such a correlation upon examination of a suitably sized database is not surprising.

The crystal structure of Z-Pro-Ala-OMe displays intermolecular hydrogen bonding between the symmetry-related amide groups [N16···O15 = 2·953 (2), N16—H15 = 0·87 (1), H15···O15 = 2·08 (1) Å and N16—H15···O15 = 179 (1)°] along the *x* axis as indicated in Fig. 2. No intramolecular hydrogen bonding is observed.

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6-Amino-1,3-dimethyl-5-(2-ethylphenylazonio)uracil Bromide Dihydrate

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Abstract. $C_{14}H_{18}N_5O_2^+.Br^-.2H_2O$, $M_r = 404{\cdot}3$, triclinic, $P\bar{1}$, $a = 7{\cdot}1738\ (8)$, $b = 10{\cdot}110\ (2)$, $c = 13{\cdot}394\ (2)$ Å, $\alpha = 70{\cdot}34\ (1)$, $\beta = 75{\cdot}61\ (1)$, $\gamma = 79{\cdot}34\ (1)°$, $V = 880{\cdot}6\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}52$ g cm^{-3}, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 27{\cdot}3$ cm^{-1}, $F(000) = 416$, $T = 298$ K, $R = 0{\cdot}052$ for 2640 observed reflections. The bulky organic cation is essentially coplanar and the protonation takes place at the azo nitrogen N(8). The additional proton participates in

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