C7	0.40283 (32)	0.8081 (5)	0.5148 (4)	5.62
C8	0.48586 (29)	0.6440 (4)	0.4730 (4)	5.16
C9	0.44540 (25)	0.6933 (4)	0.4134 (4)	4.67
C10	0.50690 (28)	0.8997 (4)	0.3862 (4)	5.25
C11	0.47195 (29)	0.9402 (4)	0.3309 (4)	5.67
C12	0.37303 (30)	0.7784 (5)	0.3015 (4)	5.88
C13	0.30981 (27)	0.5739 (4)	0.3281 (4)	5.78
C14	0.34644 (27)	0.5317 (4)	0.3833 (4)	5.22
H1*A**	0.3182	1.0829	0.6000	5.48
H2*A**	0.3752	1.0391	0.6950	5.48
H3*A**	0.5326	0.7053	0.7267	5.48
H4*A**	0.6313	0.4151	0.6632	5.48
H5*A**	0.5759	0.4567	0.5686	5.48
H8*A**	0.6042	0.6600	0.4778	5.48
H8B*	0.4572	0.4772	0.4815	5.48
H10*A**	0.5750	1.0147	0.4061	5.48
H11*A**	0.5151	1.0829	0.3126	5.48
H12*A**	0.3484	0.8085	0.2630	5.48
H13*A**	0.2416	0.4608	0.3077	5.48
H14*A**	0.3021	0.3885	0.4012	5.48

*Refined isotropically.

Table 2. *Bond lengths* (Å) *and angles* (°)

O1—C7	1.2204 (30)	C8—C7	1.5017 (32)
C1—C2	1.374 (4)	C8—C9	1.493 (4)
C1—C6	1.3984 (34)	C9—C10	1.3927 (32)
C3—C2	1.3808 (35)	C9—C14	1.3913 (32)
C3—C4	1.386 (4)	C11—C10	1.376 (4)
C5—C4	1.371 (4)	C11—C12	1.382 (4)
C5—C6	1.3929 (32)	C13—C12	1.384 (4)
C6—C7	1.486 (4)	C13—C14	1.377 (4)
C2—C1—C6	120.37 (22)	O1—C7—C8	120.76 (23)
C1—C2—C3	120.51 (23)	C7—C8—C9	115.97 (18)
C2—C3—C4	119.46 (25)	C8—C9—C10	121.30 (20)
C3—C4—C5	120.46 (22)	C8—C9—C14	120.68 (21)
C4—C5—C6	120.57 (22)	C10—C9—C14	118.02 (22)
C1—C6—C5	118.63 (23)	C9—C10—C11	120.78 (22)
C5—C6—C7	122.39 (21)	C10—C11—C12	120.59 (22)
C1—C6—C7	118.97 (21)	C11—C12—C13	119.26 (25)
C6—C7—C8	118.90 (20)	C12—C13—C14	120.15 (22)
O1—C7—C6	120.34 (23)	C9—C14—C13	121.19 (21)

Systematic absences allowed for the space groups *Pca*2_1 and *Pcam* but *Pcam* was ruled out as it would require $Z = 8$ (leading to an unrealistic density) or disorder of the molecules. The successful refinement of the structure confirmed our choice.

The lattice parameters and atomic coordinates of the non-H atoms were determined by direct methods and refined using *SHELXTL-Plus* (Sheldrick, 1987). The H-atom positions were calculated using a fixed C—H bond length of 0.96 Å and a fixed isotropic thermal parameter, taking into account the geometry of the site. The data were then re-refined using *GSAS* (Larson & Von Dreele, 1990). The origin along *z* was fixed at the centre of mass of the molecule and all atom positions refined relative to that origin.

The authors wish to thank Robert Von Dreele (LANSCE) for helpful discussions regarding *GSAS* and Vi Alured (Department of Chemistry, University of Colorado) for her assistance with the data files. This work was supported by LANSCE, NSF DMR 8901657, and the Office of Naval Research.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55519 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1010]

References

Adams, J. M. & Morsi, S. E. (1976). *Acta Cryst.* **B32**, 1345–1347.
Demus, D., Demus, H. & Zashke, H. (1974). *Flüssige Kristallen in Tabellen.* Leipzig: VEB Deutscher Verlag für Grundstoffindustrie.
Haisa, M., Kashino, S. & Morimoto, M. (1980). *Acta Cryst.* **B36**, 2832–2834.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.
Larson, A. C. & Von Dreele, R. B. (1990). *GSAS*. Report LA-UR 86-748. Los Alamos National Laboratory, New Mexico, USA.
Sheldrick, G. M. (1987). *SHELXTL-Plus*. Version 2.1. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1993). C**49**, 408–410

Structure of *Z*-L-(αMe)Phe-(L-Ala)$_2$-OMe Monohydrate

GIOVANNI VALLE, FERNANDO FORMAGGIO,
MARCO CRISMA AND CLAUDIO TONIOLO

Biopolymer Research Centre, CNR, Department of Organic Chemistry, University of Padova,
35131 *Padova, Italy*

JOHAN KAMPHUIS

DSM Research, Bio-organic Chemistry Section,
6160 *MD Geleen, The Netherlands*

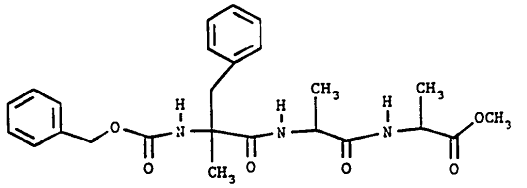
(*Received* 22 *April* 1992; *accepted* 24 *September* 1992)

Abstract

This folded N- and C-protected tripeptide is stabilized by a (peptide) N—H···O═C (urethane) intramolecular hydrogen bond which closes a ten-membered ring. This results in a β-turn structure that can be classified as type I on the basis of the φ, ψ conformational angles for the L-(αMe)Phe^1 and L-Ala^2 residues. The χ^1 side-chain conformational angle for the L-(αMe)Phe residue is *gauche*$^+$.

Comment

As a part of our ongoing conformational analysis of C^α-methylphenylalanine [(αMe)Phe] containing peptides, the X-ray diffraction structural determination of the title compound (I) (N^α-benzyloxycarbonyl-C^α-methyl-L-phenylalanyl-L-alanyl-L-alanine methyl ester) was undertaken to establish the influence of an optically active protein amino acid (L-Ala) on the screw sense of the helical conformation adopted by a preceding L-(αMe)Phe residue. The synthesis and characterization of the N- and C-protected tripeptide have been reported elsewhere (Toniolo, Formaggio, Crisma, Bonora, Pegoraro, Polinelli, Boesten, Schoemaker, Broxterman & Kamphuis, 1992).



(I)

The molecule is folded in an intramolecularly hydrogen bonded type I β-turn conformation (Venkatachalam, 1968). The backbone torsion angles φ_1, ψ_1, φ_2, and ψ_2 (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) are −60.1 (8), −27.8 (8), −94.5 (7) and −2.5 (9)°, respectively. The intramolecular N3···O2 separation is 2.931 (8) Å. The L-Ala^3 residue is semi-extended, with the φ_3, ψ_T torsion angles −95.1 (8) and −160.9 (6)°, respectively. The (*Z*)-urethane and peptide —CONH— bonds are all *trans* [$\omega_0 = -160.5$ (6), $\omega_1 = -174.0$ (6) and $\omega_2 = -175.6$ (6)°], but the urethane is markedly nonplanar. The ester bond is also *trans* [$\omega_T = -179.8$ (8)°]. The χ_1^1 side-chain torsion angle for the L-(αMe)Phe residue is *gauche*$^+$ [69.4 (7)°], while the $\chi_1^{2,1}$ and $\chi_1^{2,2}$ torsion angles are −76.8 (9) and 103.3 (8)°, respectively. The co-crystallized water molecule plays the role of a double hydrogen-bonding donor, to the O3 carbonyl O atom of a symmetry related ($x-1$, y, $z-1$) peptide molecule and to the N2 amide N atom of a symmetry related ($x-1$, y, z) peptide molecule. The corresponding O···O and O···N distances are 2.859 (8) and 3.045 (7) Å, respectively.

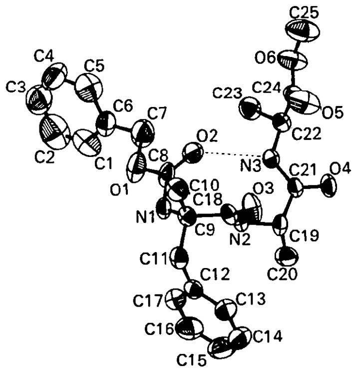


Fig. 1. View of the *Z*-L-(αMe)Phe-(L-Ala)$_2$-OMe molecule showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels.

Experimental

Crystal data

$C_{25}H_{30}N_3O_6.H_2O$
$M_r = 486.56$
Monoclinic
$P2_1$
$a = 8.518$ (1) Å
$b = 23.151$ (3) Å
$c = 7.112$ (1) Å
$\beta = 111.6$ (2)°
$V = 1304$ (2) Å^3
$Z = 2$
$D_x = 1.239$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 7$–14°
$\mu = 0.085$ mm^{-1}
$T = 293$ K
Prism
0.6 × 0.6 × 0.6 mm
Colourless

Data collection

Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3447 measured reflections
3216 independent reflections
2042 observed reflections [$F \geq 7\sigma(F)$]

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 28°$
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 30$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 180 min
intensity variation: 10%

Refinement

Refinement on F
Final $R = 0.065$
$wR = 0.075$
$S = 1.48$
2042 reflections
316 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F)+0.0027F^2]$

$(\Delta/\sigma)_{\rm max} = 0.36$
$\Delta\rho_{\rm max} = 0.64$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}
Extinction correction: *SHELX*76 (Sheldrick, 1976)
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	−0.2485 (5)	−0.3193 (2)	−0.8088 (8)	0.088 (2)
O2	−0.1157 (4)	−0.3315 (2)	−0.4773 (7)	0.072 (2)
O3	−0.1312 (4)	−0.4559 (3)	−0.1629 (5)	0.071 (2)
O4	0.4183 (4)	−0.4338 (2)	−0.0319 (6)	0.061 (1)
O5	0.2421 (9)	−0.3165 (3)	0.1444 (8)	0.099 (3)
O6	0.3509 (7)	−0.2390 (2)	0.0652 (8)	0.082 (2)
N1	−0.2926 (5)	−0.4010 (2)	−0.6691 (6)	0.047 (1)
N2	−0.0070 (4)	−0.4540 (2)	−0.3917 (5)	0.036 (1)
N3	0.2212 (4)	−0.3701 (2)	−0.2133 (6)	0.046 (1)
C1	−0.208 (1)	−0.2435 (5)	−1.149 (1)	0.100 (4)
C2	−0.270 (2)	−0.2088 (7)	−1.306 (2)	0.128 (6)
C3	−0.334 (2)	−0.1585 (6)	−1.285 (2)	0.125 (5)
C4	−0.339 (1)	−0.1386 (4)	−1.112 (2)	0.110 (4)
C5	−0.278 (1)	−0.1759 (5)	−0.941 (2)	0.109 (4)
C6	−0.2083 (7)	−0.2321 (3)	−0.965 (1)	0.067 (2)
C7	−0.139 (1)	−0.2679 (4)	−0.778 (2)	0.099 (4)
C8	−0.2106 (5)	−0.3495 (3)	−0.6389 (9)	0.061 (2)
C9	−0.3114 (5)	−0.4317 (2)	−0.5007 (7)	0.043 (1)
C10	−0.4198 (7)	−0.3976 (3)	−0.412 (1)	0.068 (2)
C11	−0.4012 (5)	−0.4909 (2)	−0.5807 (8)	0.049 (2)
C12	−0.2998 (6)	−0.5351 (2)	−0.6429 (8)	0.052 (2)
C13	−0.2276 (9)	−0.5816 (3)	−0.516 (1)	0.072 (3)
C14	−0.138 (1)	−0.6225 (3)	−0.564 (2)	0.092 (4)
C15	−0.110 (1)	−0.6192 (4)	−0.742 (2)	0.099 (4)
C16	−0.178 (1)	−0.5734 (4)	−0.873 (1)	0.086 (3)

C17	−0.2739 (8)	−0.5323 (3)	−0.8207 (9)	0.064 (2)
C18	−0.1394 (5)	−0.4467 (2)	−0.3371 (7)	0.045 (2)
C19	0.1564 (5)	−0.4735 (2)	−0.2518 (7)	0.043 (2)
C20	0.2370 (6)	−0.5143 (3)	−0.356 (1)	0.063 (2)
C21	0.2767 (5)	−0.4234 (2)	−0.1542 (6)	0.044 (1)
C22	0.3278 (6)	−0.3189 (2)	−0.1425 (7)	0.048 (2)
C23	0.2979 (8)	−0.2780 (3)	−0.3174 (9)	0.063 (2)
C24	0.2996 (7)	−0.2925 (3)	0.0367 (8)	0.054 (2)
C25	0.333 (2)	−0.2081 (4)	0.231 (1)	0.110 (5)
OW	−0.9285 (6)	−0.4204 (3)	−0.7617 (6)	0.088 (2)

Table 2. *Geometric parameters* (Å, °)

O1—C7	1.478 (10)	N3—C21	1.332 (7)
O1—C8	1.329 (9)	N3—C22	1.466 (7)
O2—C8	1.210 (7)	C6—C7	1.492 (14)
O3—C18	1.234 (6)	C9—C10	1.518 (9)
O4—C21	1.224 (6)	C9—C11	1.571 (7)
O5—C24	1.187 (10)	C9—C18	1.538 (6)
O6—C24	1.304 (8)	C11—C12	1.506 (8)
O6—C25	1.435 (12)	C19—C20	1.512 (9)
N1—C8	1.359 (8)	C19—C21	1.534 (7)
N1—C9	1.452 (7)	C22—C23	1.508 (8)
N2—C18	1.332 (7)	C22—C24	1.510 (9)
N2—C19	1.454 (6)		
C7—O1—C8	111.2 (7)	N2—C18—C9	118.8 (5)
C24—O6—C25	118.1 (7)	O3—C18—C9	119.0 (7)
C8—N1—C9	120.4 (5)	O3—C18—N2	122.0 (6)
C18—N2—C19	122.7 (5)	N2—C19—C21	112.7 (5)
C21—N3—C22	122.5 (6)	N2—C19—C20	110.5 (5)
O1—C7—C6	107.4 (7)	C20—C19—C21	110.3 (6)
O2—C8—N1	125.3 (6)	N3—C21—C19	117.2 (5)
O1—C8—N1	112.3 (6)	O4—C21—C19	119.4 (5)
O1—C8—O2	122.4 (6)	O4—C21—N3	123.4 (6)
N1—C9—C10	110.9 (5)	N3—C22—C24	110.2 (6)
N1—C9—C11	108.4 (5)	N3—C22—C23	109.3 (5)
N1—C9—C18	111.8 (6)	C23—C22—C24	114.3 (5)
C11—C9—C18	106.2 (5)	O6—C24—C22	111.5 (6)
C10—C9—C18	111.1 (5)	O5—C24—C22	126.0 (6)
C10—C9—C11	108.4 (6)	O5—C24—O6	122.5 (7)
C9—C11—C12	116.3 (6)		

Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Structure refined by blocked full-matrix least squares with anisotropic thermal parameters for all non-H atoms. H atoms located on a ΔF map, but not refined. Program used to refine structure: *SHELX*76 (Sheldrick, 1976).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55601 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1012]

References

IUPAC–IUB Commission on Biochemical Nomenclature (1970). *Biochemistry*, **9**, 3471–3479.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Toniolo, C., Formaggio, F., Crisma, M., Bonora, G. M., Pegoraro, S., Polinelli, S., Boesten, W. H. J., Schoemaker, H. E., Broxterman, Q. B. & Kamphuis, J. (1992). *Pept. Res.* **5**, 56–61.

Venkatachalam, C. M. (1968). *Biopolymers*, **6**, 1425–1436.

Acta Cryst. (1993). C**49**, 410–413

Tricyclo[9.3.0.0^{3,7}]tetradec-3-ene-5,10-dione (I), Tetracyclo[9.3.0.0^{1,5}.0^{5,9}]tetradecane-2,7-dione (II) and *cis-cisoid-cis*-2,9-Epoxy-9-methyltricyclo[9.3.0.0^{4,8}]tetradecan-2-ol (III)

TAKASHI KAWATA, MASAMI OKUDA
AND SHIGERU OHBA*

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, *Kohoku-ku, Yokohama* 223, *Japan*

MISAO UMEHARA AND HIROMI HONNAMI

Department of Chemistry, Keio University, Hiyoshi 4-1-1, *Kohoku-ku, Yokohama* 223, *Japan*

SHINZABURO HISHIDA

Naka Works, Hitachi Ltd, Ichige, Katsuta, Ibaraki 312, *Japan*

(*Received* 15 *June* 1992; *accepted* 8 *September* 1992)

Abstract

The crystal structures of the three title compounds, which were obtained during studies of the preparation and reactions of 5–8–5 fused-ring compounds, have been determined by X-ray diffraction.

Comment

The syntheses of compounds (I)–(III) are reported separately (Umehara, Honnami, Hishida, Kawata, Ohba & Zen, 1992). The conformations of the cyclooctane rings in the related 5–8 or 5–8–5 fused-ring compounds have been investigated previously (Okumoto, Ohba, Saito, Ishii, Umehara & Hishida, 1987; Okumoto, Ohba, Saito, Umehara & Hishida, 1988; Umehara, Hishida, Okuda, Ohba, Ito, Saito & Zen, 1990). The eight-membered ring takes a boat–chair form in (I) and a boat–boat form in (III). There is an intermolecular hydrogen bond in (III), O(1)···O(2) $(1-x, -y, -z)$ = 2.838 (2) Å.