$S = 4.39$
763 reflections
103 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max} = 0.114$

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV, Table
2.3.1)

Table 1. Bond-length and angle comparison between p- and o-nitrobenzaldehydes

	N—O	N—C	C_{co}—C_{aryl}	C—O	C_{aryl}–C_{co}–O_{co}	O–N–O
ortho*	1.226 (10)	1.468 (8)	1.490 (9)	1.200 (9)	122.2 (6)	125.0 (6)
	1.234 (6)					
para	1.236 (7)	1.446 (8)	1.521 (6)	1.197 (6)	116.3 (8)	120.0 (6)
	1.248 (6)					

* Coppens & Schmidt (1964).

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)

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

	x	y	z	U_{eq}
C(1)	−0.1557 (7)	0.0000	−0.8147 (4)	0.020 (1)
C(2)	−0.0333 (6)	−0.1163 (15)	−0.7133 (4)	0.018 (1)
C(3)	−0.1249 (7)	−0.3210 (16)	−0.6474 (4)	0.021 (1)
C(4)	−0.3361 (7)	−0.3982 (9)	−0.6818 (4)	0.017 (1)
C(5)	−0.4572 (6)	−0.2809 (17)	−0.7881 (4)	0.023 (1)
C(6)	−0.3653 (7)	−0.0821 (15)	−0.8557 (4)	0.020 (1)
N(1)	−0.0595 (6)	0.2095 (15)	−0.8852 (4)	0.027 (1)
O(2)	0.1283 (6)	0.2823 (18)	−0.8485 (4)	0.054 (1)
O(3)	−0.1645 (5)	0.3286 (15)	−0.9738 (3)	0.032 (1)
C(7)	−0.4374 (7)	−0.6224 (15)	−0.6101 (4)	0.016 (1)
O(1)	−0.3346 (5)	−0.7241 (16)	−0.5207 (3)	0.015 (1)
O(1B)	−0.6294 (19)	−0.681 (4)	−0.6482 (11)	0.010 (0)

Table 3. Geometric parameters ($\mathring{A}$, °)

C(1)—C(2)	1.375 (6)	C(4)—C(7)	1.521 (8)
C(1)—C(6)	1.395 (6)	C(5)—C(6)	1.377 (9)
C(1)—N(1)	1.446 (7)	N(1)—O(2)	1.248 (6)
C(2)—C(3)	1.389 (9)	N(1)—O(3)	1.236 (7)
C(3)—C(4)	1.382 (6)	C(7)—O(1)	1.197 (6)
C(4)—C(5)	1.412 (6)	C(7)—O(1B)	1.256 (13)
C(2)—C(1)—C(6)	123.0 (4)	C(4)—C(5)—C(6)	119.4 (4)
C(2)—C(1)—N(1)	118.5 (4)	C(1)—C(6)—C(5)	118.4 (4)
C(6)—C(1)—N(1)	118.4 (4)	C(1)—N(1)—O(2)	118.3 (5)
C(1)—C(2)—C(3)	118.3 (4)	C(1)—N(1)—O(3)	121.4 (4)
C(2)—C(3)—C(4)	120.0 (4)	O(2)—N(1)—O(3)	120.0 (7)
C(3)—C(4)—C(5)	120.7 (5)	C(4)—C(7)—O(1)	119.1 (4)
C(3)—C(4)—C(7)	120.3 (4)	C(4)—C(7)—O(1B)	116.3 (8)
C(5)—C(4)—C(7)	118.8 (4)	O(1)—C(7)—O(1B)	124.6 (9)

Data collection: Siemens *R3m/V* software. Cell refinement: *SHELXTL-Plus* (Sheldrick, 1990). Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: manual.

References

Bryant, G. L. Jr & King, J. A. Jr (1995). *Acta Cryst.* C51, 1141–1143.
Coppens, P. (1964). *Acta Cryst.* 17, 573–578.
Coppens, P. & Schmidt, G. M. J. (1964). *Acta Cryst.* 17, 222–228.

Forbes, W. F. (1962). *Can. J. Chem.* 40, 1891–1898.
Gordon, A. J. & Ford, R. A. (1972). *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, pp. 124–127. New York: John Wiley & Sons.
King, J. A. Jr & Bryant, G. L. Jr (1990). *Acta Cryst.* C46, 1330–1334.
Margerum, J. D. & Miller, L. J. (1971). *Photochromism*, edited by G. H. Brown, p. 580. New York: Wiley.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

The Linear Tripeptide L-Alanylglycyl-L-alanine

G. Sreekanta Padiyar and T. Parthasarathy Seshadri

Department of Physics, Indian Institute of Science, Bangalore 560 012, India. E-mail: gspadiya@physics.iisc.ernet.in

Abstract

L-Alanylglycyl-L-alanine, $C_8H_{15}N_3O_4$, exists as zwitterion in the crystal with the N terminus protonated and the C terminus in an ionized form. Both the peptide units are in *trans* configurations and deviate significantly from planarity. Backbone torsion angles are $\psi_1 = 172.7\,(2)$, $\omega_1 = -178.2\,(2)$, $\varphi_2 = 91.7\,(2)$, $\psi_2 = -151.9\,(2)$, $\omega_2 = -176.9\,(2)$, $\varphi_3 = -71.3\,(2)$, $\psi_{31} = -7.0\,(3)$ and $\psi_{32} = 172.4\,(2)°$. The protonated NH_3^+ group forms three hydrogen bonds with atoms of symmetry-related molecules.

Comment

Accurate geometric parameters of simple peptides are extensively utilized in theoretical conformational studies of polypeptides and proteins. In addition, knowledge of the hydrogen-bonding scheme and van der Waals contacts in simple peptides will aid understanding of the secondary structures of polypeptides and proteins. We report here the crystal structure of L-alanylglycyl-L-alanine, AGA.
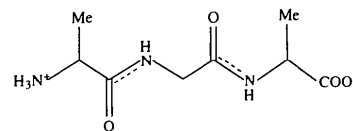
AGA

The atomic numbering and molecular conformation of the AGA molecule are shown in Fig. 1. AGA exists as a zwitterion with terminal NH_3^+ and COO^- groups. Both peptide units (C1A, C1', N2, C2A and O1; C2A,

C2', N3, C3A and O2') show deviations of 0.04 Å from their respective least-squares planes. The peptide backbone assumes a folded conformation with torsion angles ψ_1 = 172.7 (2), φ_2 = 91.7 (2), ψ_2 = −151.9 (2), φ_3 = −71.3 (2), ω_1 = −178.2 (2), ω_2 = −176.9 (2), ψ_{31} = −7.0 (3) and ψ_{32} = 172.4 (2)°. The dihedral angle between the two peptide planes is 76.7 (1)° and the carboxyl group makes a dihedral angle of 73.6 (2)° with the adjacent peptide unit.
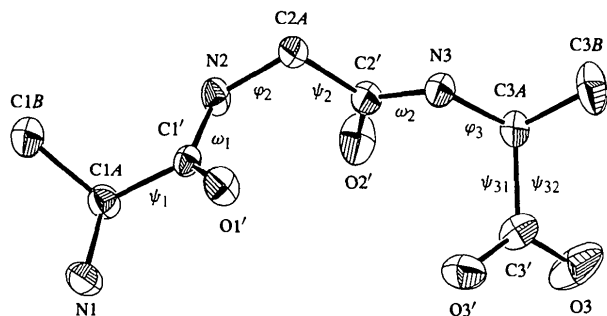

Fig. 1. Atomic numbering and molecular conformation of AGA. Displacement ellipsoids are drawn at the 50% probability level.

The crystal packing of AGA is shown in Fig. 2. The NH_3^+ group forms three hydrogen bonds with the O1' and carboxyl O3' atoms of symmetry-related molecules. The packing is further stabilized by intermolecular hydrogen bonds between N2 and O3, and N3 and O3' atoms. The hydrogen-bonding geometry is given in Table 3. The conformation of AGA is different from those of AAA (Fawcett, Camerman & Camerman, 1975), which has conformational angles for an antiparallel pleated-sheet arrangement, and AGG (Subramanian & Lalitha, 1983), which has a poly(glycine)-II type conformation.
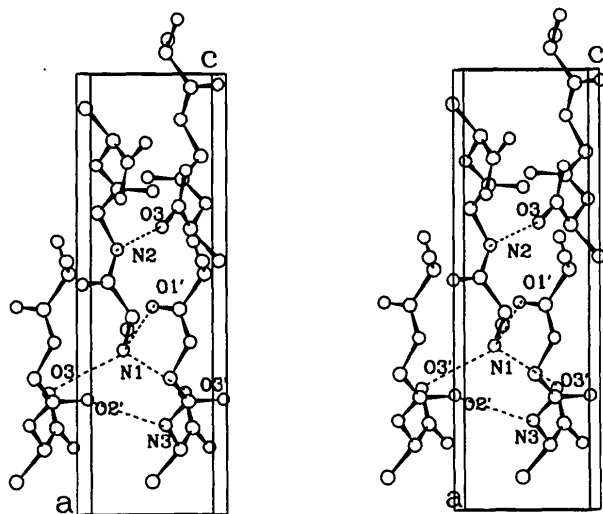

Fig. 2. Stereoview of the crystal packing of AGA viewed down the b axis. Hydrogen bonds are shown by broken lines.

Experimental

Crystals were grown by direct evaporation from an aqueous solution of the title compound (Sigma Chemical Company, USA).

Crystal data

$C_8H_{15}N_3O_4$	Cu $K\alpha$ radiation
M_r = 217.23	λ = 1.5418 Å
Orthorhombic	Cell parameters from 24
$P2_12_12_1$	reflections
a = 4.747 (7) Å	θ = 12–8°
b = 14.399 (2) Å	μ = 0.949 mm^{-1}
c = 15.191 (2) Å	T = 293 (2) K
V = 1038.5 (15) Å^3	Parallelopiped
Z = 4	0.8 × 0.12 × 0.08 mm
D_x = 1.389 Mg m^{-3}	Colourless

Data collection

Enraf–Nonius CAD-4	R_{int} = 0.0129
diffractometer	θ_{max} = 71.91°
ω–2θ scans	h = −5 → 4
Absorption correction:	k = −9 → 17
none	l = −9 → 18
1226 measured reflections	2 standard reflections
1220 independent reflections	frequency: 33 min
1141 observed reflections	intensity variation: 4%
[$I > 2\sigma(I)$]	

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.149 e Å^{-3}
$R(F)$ = 0.0279	$\Delta\rho_{min}$ = −0.134 e Å^{-3}
$wR(F^2)$ = 0.0780	Extinction correction:
S = 1.057	SHELXL93 (Sheldrick,
1220 reflections	1993)
152 parameters	Extinction coefficient:
All H-atom coordinates (but	0.0045 (10)
not occupancies or U's)	Atomic scattering factors
riding on the coordinates	from International Tables
of the parent atom	for Crystallography (1992,
$w = 1/[\sigma^2(F_o^2) + (0.0510P)^2$	Vol. C, Tables 4.2.6.8 and
$+ 0.1903P]$	6.1.1.4)
where $P = (F_o^2 + 2F_c^2)/3$	Absolute configuration:
$(\Delta/\sigma)_{max}$ = 0.009	Flack (1983) parameter
	−0.11 (31)

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

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

	x	y	z	U_{eq}
N1	1.2272 (4)	0.83935 (11)	0.62268 (10)	0.0315 (4)
C1A	1.1514 (4)	0.90207 (12)	0.54878 (11)	0.0265 (4)
C1B	1.1777 (8)	1.00243 (14)	0.5771 (2)	0.0551 (8)
C1'	1.3323 (4)	0.87763 (11)	0.46942 (10)	0.0216 (3)
O1'	1.5264 (3)	0.82158 (9)	0.47548 (8)	0.0321 (3)
N2	1.2623 (3)	0.92150 (10)	0.39590 (9)	0.0267 (3)
C2A	1.4061 (4)	0.90477 (11)	0.31382 (11)	0.0257 (4)
C2'	1.2632 (4)	0.82911 (12)	0.26043 (11)	0.0241 (4)
O2'	1.0067 (3)	0.81594 (11)	0.26477 (11)	0.0411 (4)
N3	1.4297 (3)	0.78090 (10)	0.20660 (9)	0.0239 (3)
C3A	1.3118 (4)	0.70997 (12)	0.14924 (11)	0.0240 (4)
C3B	1.5176 (5)	0.6855 (2)	0.07654 (14)	0.0434 (6)

C3'	1.2142 (4)	0.62256 (12)	0.19913 (13)	0.0310 (4)
O3'	1.2674 (3)	0.61527 (10)	0.28009 (9)	0.0395 (4)
O3	1.0856 (5)	0.56555 (11)	0.15411 (13)	0.0641 (6)

Table 2. *Selected geometric parameters (Å, °)*

N1—C1A	1.485 (2)	C2'—N3	1.333 (2)
C1A—C1B	1.513 (3)	C2'—O2'	1.234 (3)
C1A—C1'	1.521 (2)	N3—C3A	1.455 (2)
C1'—O1'	1.229 (2)	C3A—C3B	1.516 (3)
C1'—N2	1.325 (2)	C3A—C3'	1.541 (2)
N2—C2A	1.442 (2)	C3'—O3	1.231 (2)
C2A—C2'	1.518 (2)	C3'—O3'	1.260 (2)
N1—C1A—C1B	110.3 (2)	O2'—C2'—C2A	121.5 (2)
N1—C1A—C1'	108.76 (14)	N3—C2'—C2A	115.9 (2)
C1B—C1A—C1'	113.6 (2)	C2'—N3—C3A	120.3 (2)
O1'—C1'—N2	124.3 (2)	N3—C3A—C3B	110.6 (2)
O1'—C1'—C1A	121.07 (15)	N3—C3A—C3'	113.25 (14)
N2—C1'—C1A	114.6 (2)	C3B—C3A—C3'	111.2 (2)
C1'—N2—C2A	122.0 (2)	O3—C3'—O3'	125.9 (2)
N2—C2A—C2'	111.7 (2)	O3—C3'—C3A	114.9 (2)
O2'—C2'—N3	122.6 (2)	O3'—C3'—C3A	119.2 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N1⋯O1''	0.89	2.12	2.916 (2)	150.8
N1—H2N1⋯O3''	0.89	1.89	2.716 (3)	154.3
N3—HN3⋯O2'''	0.86	2.12	2.922 (4)	154.2
N1—H3N1⋯O3'''	0.89	2.17	3.030 (4)	161.3
N2—HN2⋯O3'ᵛ	0.86	1.97	2.758 (3)	151.7

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (ii) $1 + x, y, z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (iv) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Data collection: *SDP* (Enraf–Nonius, 1985). Cell refinement: *SDP*. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *INSIGHTII* (Biosym Technologies, 1995); *Xtal-GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: local program.

References

Biosym Technologies (1995). *INSIGHTII*. Biosym Technologies, 9685 Scranton Road, San Diego, CA 92121-2777, USA.
Enraf–Nonius (1985). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
Fawcett, J. K., Camerman, N. & Camerman, A. (1975). *Acta Cryst.* B31, 658–665.
Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.
Hall, S. R. & du Boulay, D. (1995). *Xtal-GX Package*. University of Western Australia, Australia.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Subramanian, E. & Lalitha, V. (1983). *Biopolymers*, 22, 833–838.

γ-Lactones: Methyl 11-Oxa-10-oxobicyclo-[6.3.0]undec-4-ene-9-carboxylate, Methyl 11-Oxa-10-oxobicyclo[6.3.0]undec-2-ene-9-carboxylate and Methyl 9-Oxa-10-oxobi-cyclo[6.3.0]undecane-11-carboxylate

Gérard Pèpe,[a] Jean-Pierre Astier,[a] Laurent Lamarque,[b] Alain Méou[b] and Pierre Brun[b]

[a]*CRMC2-CNRS, Campus de Luminy, Case 913, F13288, Marseille Cédex 9, France, and* [b]*Laboratoire de Chimie Organique Sélective, Faculté des Sciences de Luminy, F13288, Marseille Cédex 9, France. E-mail: genmol@crmc2. univ-mrs.fr*

Abstract

The structures of three γ-lactone derivatives, methyl 11-oxa-10-oxobicyclo[6.3.0]undec-4-ene-9-carboxylate, $C_{12}H_{16}O_4$, methyl 11-oxa-10-oxobicyclo[6.3.0]undec-2-ene-9-carboxylate, $C_{12}H_{16}O_4$, and methyl 9-oxa-10-oxobicyclo[6.3.0]undecane-11-carboxylate, $C_{12}H_{18}O_4$, have been solved in order to determine the relative configuration of their three asymmetric stereocentres.

Comment

γ-Lactone rings are key structural features of many perfume oils (Mori, 1989). They also exhibit important biological activities such as cytotoxic, antitumoral and bactericidal properties (Hoffmann & Rabe, 1985).

Among butyrolactone derivatives, α-methylene lactones are particularly important and can be prepared by decarboxylation–methylation of α-carbomethoxy- or α-carboxy-substituted lactones (Petragnani, Ferraz & Silva, 1986). Such substrates can be conveniently prepared by Mn^{III}-mediated addition of acetic acid derivatives on saturated systems (de Klein, 1986; Melikyan, 1993).

The potassium salt of monomethylmalonate is of particular interest as it allows the direct synthesis of γ-lactones α-substituted by a carbomethoxy group which are the precursors of α-methylene lactones (Lamarque, Méou & Brun, 1994). When applied to 1,3-cyclooctadiene, such an approach leads to different stereoisomers as three stereocentres are formed during the reaction. While the geometry of two of them can be determined easily by NMR spectroscopy [*cis* or *trans* junction between the γ-lactone ring and the cyclooctene (Lamarque, Méou & Brun, 1994)], it is very difficult to assign the relative configuration of the remaining stereocentre (i.e. the C atom bearing the