International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

KAHN, R., FOURME, R., ANDRÉ, D. & RENAUD, M. (1973). *Acta Cryst.* B**29**, 131–138.

SAVONA, G., PATERNOSTRO, M. P. PIOZZI, F., HANSON, J. R. HITCHCOCK, P. B. & THOMAS, S. A. (1978). *J. Chem. Soc. Perkin Trans.* 1, pp. 643–646.

SHELDRICK, G. M. (1981). *Nicolet SHELXTL Operations Manual*, revision 3. Nicolet XRD Corporation, Cupertino, California.

Acta Cryst. (1987). C**43**, 1567–1569

Conformation and Structure of a Blocked Gla Residue: *N*-Benzyloxycarbonyl-(γ,γ-di-*tert*-butyl)-L-carboxyglutamic Acid α-Methyl Ester

BY YOSHINOBU YOKOMORI,* DAVID W. DEERFIELD II, RICHARD G. HISKEY AND DEREK J. HODGSON†

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, *USA*

(*Received* 9 *October* 1986; *accepted* 10 *February* 1987)

Abstract. γ,γ-Di-*tert*-butyl α-methyl *N*-benzyloxycarbonyl-L-carboxyglutamate, $C_{23}H_{33}NO_8$, M_r = 451·4, orthorhombic, $P2_12_12_1$, a = 14·234 (3), b = 19·671 (5), c = 8·929 (5) Å, V = 2500 (2) Å^3, Z = 4, D_x = 1·200, D_m (flotation in aqueous NaBr) = 1·16 (3) Mg m^{-3}, Mo $K\alpha$ radiation ($\lambda K\alpha_1$ = 0·70926, $\lambda K\alpha_2$ = 0·71354 Å), μ = 0·0975 mm^{-1}, $F(000)$ = 968, T = 295 K, R = 0·042, wR = 0·043 for 1348 observations. The molecule is extended, with C′ *trans* to Cγ and Cα *trans* to C^{δ}_{1}. There is an intermolecular hydrogen bond between the NH group and the carboxyl oxygen of a neighboring benzyloxycarbonyl group.

Introduction. The presence of γ-carboxyglutamic acid (Gla) residues in a variety of proteins is well established (Stenflo, Fernlund, Egan & Roepstorff, 1974; Hauschka, Lian & Gallop, 1975; Price, Otsuka, Poser, Kristaponis & Raman, 1976; Jackson & Nemerson, 1980). Both low- and high-resolution crystal structures of fragment 1 of prothrombin, which contains ten Gla residues, have been published, but unfortunately the extensive disorder in the metal-binding region of the protein leaves the Gla residues unresolved (Olsson, Andersen, Lindqvist, Sjolin, Magnusson, Petersen & Sottrup-Jensen, 1982; Park & Tulinsky, 1986). In view of the biological significance of species containing Gla residues, it is surprising that the only crystallographic studies reported to date are those of the free amino acid (Satyshur & Rao, 1979), its ammonium salt (Satyshur, Rao, Stenflo & Suttie, 1979), and our own study of a blocked Gla-Gly dipeptide, Z-Gla(*O*-^{t}Bu)$_2$-GlyOEt (Valente, Hiskey & Hodgson, 1979) (Z = benzyloxycarbonyl). The present study of Z-Gla(*O*-^{t}Bu)$_2$OMe was undertaken in order to compare the conformation of this fully blocked Gla residue with the structures of both the unblocked and blocked residues noted above, and with those unblocked glutamyl (Glu) peptides (Eggleston & Hodgson, 1983, and references therein) and their blocked analogues (Benedetti, DiBlasio, Pavone, Pedone, Germain & Goodman, 1979; Eggleston & Hodgson, 1984).

Experimental. Colorless rods by slow evaporation of an aqueous methanol solution at room temperature. Crystal 0·3 × 0·3 × 0·9 mm. Enraf–Nonius CAD-4 diffractometer. Systematic absences $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd. Cell constants by least squares using 25 reflections with $23 \le 2\theta(\text{Mo}) \le 32°$ measured on the diffractometer. Intensity data collected in an ω–2θ scan mode, as suggested by peak-shape analysis. 1975 independent reflections, $2\theta \le 44°$, $0 \le h \le 15$, $0 \le k \le 20$, $0 \le l \le 9$. Lorentz–polarization correction, no absorption correction. No systematic fluctuations in $\bar{9}\bar{9}1$, $\bar{5}\bar{7}3$, 275 monitored at the beginning and every 3 h of exposure time (20 times). Programs in CAD-4 *Structure Determination Package* (Enraf–Nonius, 1979); atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Structure determined using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). E map revealed a 26-atom fragment of the molecule after several trials; remainder of the non-hydrogen atoms located from a difference Fourier synthesis after three cycles of least-squares refinement on the initial fragment. Anisotropic full-matrix least-squares refinement (on F) of all 32 non-hydrogen atoms led to wR = 0·148; weights $4F_o^2/\sigma^2(I)$. Subsequent difference Fourier maps revealed positions for all 33 H atoms; however, because of the paucity of data all H atoms were fixed at calculated positions (with C–H = 0·95 and N–H = 0·87 Å) with fixed isotropic

* Permanent address: Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239, Japan.

† Author to whom correspondence should be addressed.

0108-2701/87/081567-03$01.50

temperature factors ($B = 5{\cdot}0$ Å^2). Final cycle of full-matrix least squares [with the weighting scheme above and $\sigma(I)$ defined by Corfield, Doedens & Ibers (1967) with $p = 0{\cdot}02$] gave $R = 0{\cdot}042$, $wR = 0{\cdot}043$, $S = 2{\cdot}18$, using 1348 observations with $I \geq 3\sigma$ and 259 variables. No evidence for extinction. $(\Delta/\sigma)_{max} = 0{\cdot}05$. Final difference Fourier map contained no peak higher than 0·065 e Å^{-3}.

Table 1. *Positional and equivalent isotropic thermal parameters*

	x	y	z	U_{eq}(Å^2)
O''	0·6155 (2)	0·4343 (1)	1·0228 (3)	0·066 (2)
$O_1^{\varepsilon 2}$	0·7445 (2)	0·7338 (1)	0·6231 (3)	0·053 (2)
$O_2^{\varepsilon 2}$	0·8467 (2)	0·6815 (2)	0·8985 (3)	0·054 (2)
O'	0·5054 (2)	0·4921 (2)	0·9045 (4)	0·090 (2)
$O_1^{\varepsilon 1}$	0·5912 (2)	0·7196 (2)	0·6763 (4)	0·071 (2)
$O_2^{\varepsilon 1}$	0·7138 (2)	0·6914 (2)	1·0311 (3)	0·070 (2)
O(1)	0·8684 (2)	0·4458 (2)	0·7878 (3)	0·061 (2)
O(2)	0·8312 (2)	0·4779 (2)	1·0215 (3)	0·056 (2)
N	0·7362 (2)	0·5015 (2)	0·8246 (3)	0·041 (2)
C(17)	0·5490 (3)	0·3830 (3)	1·0646 (6)	0·071 (3)
C'	0·5842 (3)	0·4858 (2)	0·9434 (4)	0·048 (3)
Cα	0·6632 (3)	0·5350 (2)	0·9092 (4)	0·041 (2)
Cβ	0·6273 (3)	0·5987 (2)	0·8299 (5)	0·048 (3)
Cγ	0·7067 (3)	0·6456 (2)	0·7850 (5)	0·043 (2)
C_1^{δ}	0·6720 (3)	0·7034 (2)	0·6900 (5)	0·049 (3)
C(13)	0·7341 (3)	0·7956 (2)	0·5319 (5)	0·057 (3)
C(16)	0·6711 (4)	0·7806 (3)	0·3985 (6)	0·071 (3)
C(15)	0·6957 (4)	0·8520 (3)	0·6244 (6)	0·084 (4)
C(14)	0·8335 (4)	0·8102 (3)	0·4855 (6)	0·087 (4)
C_2^{δ}	0·7561 (3)	0·6755 (2)	0·9211 (5)	0·049 (3)
C(9)	0·9091 (3)	0·7127 (3)	1·0127 (5)	0·066 (3)
C(12)	0·8806 (4)	0·7840 (3)	1·0416 (6)	0·091 (4)
C(11)	0·9093 (4)	0·6694 (3)	1·1501 (6)	0·085 (4)
C(10)	1·0035 (4)	0·7103 (4)	0·9378 (6)	0·100 (4)
C(8)	0·8121 (3)	0·4756 (2)	0·8884 (5)	0·048 (3)
C(7)	0·9529 (3)	0·4129 (3)	0·8453 (6)	0·073 (3)
C(1)	1·0336 (3)	0·4598 (2)	0·8621 (5)	0·064 (3)
C(2)	1·0540 (3)	0·4900 (3)	0·9971 (6)	0·084 (4)
C(3)	1·1293 (4)	0·5325 (3)	1·0113 (8)	0·120 (5)
C(4)	1·1826 (4)	0·5438 (3)	0·8848 (11)	0·138 (5)
C(5)	1·1675 (5)	0·5152 (4)	0·7545 (8)	0·159 (5)
C(6)	1·0909 (4)	0·4742 (3)	0·7436 (6)	0·097 (4)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

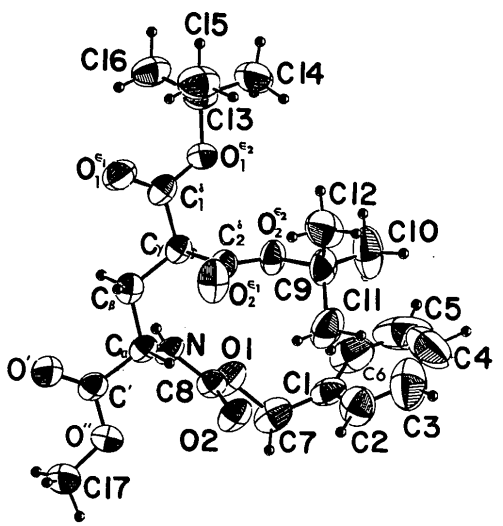

Fig. 1. View of a single molecule of Z-Gla(O-^{t}Bu)$_2$OMe. Thermal ellipsoids are at the 40% probability level; H atoms are shown as spheres of arbitrary size.

Discussion. The positional parameters, along with their standard deviations as estimated from the inverse matrix, are listed in Table 1.* The structure of a single molecule is shown in Fig. 1; the notation used in the labeling of the atoms is that adopted by the IUPAC–IUB Commission on Biochemical Nomenclature (1970) as far as possible.

Principal bond lengths and angles are available as supplementary material (see deposition footnote). The bond lengths within the *tert*-butyl groups and the benzyloxycarbonyl group are very similar to the average values reported for these groups in recent compilations (Benedetti *et al.*, 1979; Eggleston & Hodgson, 1984; Blessing & Smith, 1982; Antolini, Menabue, Saladini, Sola, Battaglia & Bonamartini Corradi, 1984). The Z group assumes the partially extended form, with approximately linear torsion angles around C(8)–N [O(1)–C(8)–N–Cα = 178·6°] and O(1)–C(8) [C(7)–O(1)–C(8)–N = −177·8°] but a folded angle of −86·0° around C(7)–O(1) [C(1)–C(7)–O(1)–C(8)]. This partially extended structure has been observed elsewhere (de Kock & Romers, 1981), but is less common than the fully extended form in which all three angles approximate 180° (Coiro, Mazza & Mignucci, 1974; Blessing & Smith, 1982; Antolini *et al.*, 1984).

Significant torsion angles are listed in Table 2. The molecule assumes an extended conformation with C′ *trans* to Cγ and Cα *trans* to C_1^{δ}. This is in contrast to the structure of unblocked L-Gla, where N is *trans* to Cγ while C′ is (necessarily) *gauche* to both O′ [N–Cα–C′–O′ = 119·4°] and Cγ [N–Cα–Cβ–Cγ = −51·5°]. The χ angles are in extended conformations which are comparable to those in free Gla and those in a variety of Glu-containing peptides (Benedetti *et al.*, 1979; Eggleston & Hodgson, 1984). The torsion angle ψ around C′–Cα [N–Cα–C′–O″] is 60·2° rather than the expected value of approximately 0°. It is noteworthy that in free Gla and in its ammonium salt non-zero values of ψ were also observed (Satyshur & Rao, 1979; Satyshur *et al.*, 1979), but in both cases these carboxyl groups are involved in hydrogen bonding; in the present case, atoms O′ and O″ do not participate in hydrogen bonding.

The molecular packing is shown in Fig. 2. The only available donor, N, participates in a hydrogen bond to O(2) of a neighboring Z group, with N···O, H···O distances and N–H···O angle of 2·900 (5), 2·06 Å and 154°, respectively.

* Lists of bond lengths and bond angles, structure amplitudes, H-atom positional parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43785 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected torsional angles* (°)

Atoms	Designation*	Angle
N–Cα–C′–O″	ψ	60·2
C(8)–N–Cα–C′	φ	−96·3
C′–Cα–Cβ–Cγ		−175·7
N–Cα–Cβ–Cγ	χ^1	−51·5
Cα–Cβ–Cγ–C_1^δ	$\chi^{2,1}$	172·7
Cα–Cβ–Cγ–C_2^δ	$\chi^{2,2}$	−66·4
Cβ–Cγ–C_1^δ–$O_1^{\varepsilon 1}$	$\chi^{3,1,1}$	14·8
Cβ–Cγ–C_1^δ–$O_1^{\varepsilon 2}$	$\chi^{3,1,2}$	−165·1
Cβ–Cγ–C_2^δ–$O_2^{\varepsilon 1}$	$\chi^{3,2,1}$	−37·4
Cβ–Cγ–C_2^δ–$O_2^{\varepsilon 2}$	$\chi^{3,2,1}$	143·6

* IUPAC–IUB Commission on Biochemical Nomenclature (1970).

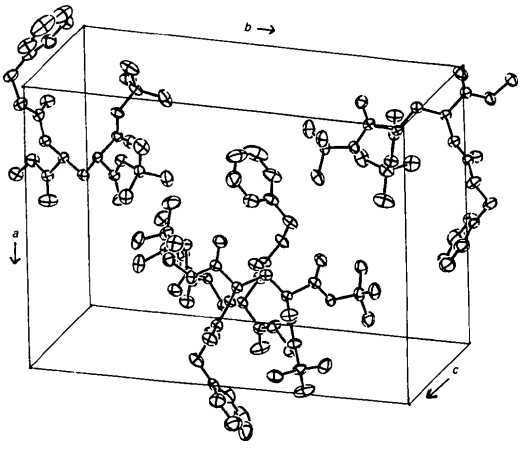

Fig. 2. The packing of the Z-Gla(O-^{t}Bu)$_2$OMe molecules in the cell. The crystallographic axial directions are shown on the figure.

References

ANTOLINI, L., MENABUE, L., SALADINI, M., SOLA, M., BATTAGLIA, L. P. & BONAMARTINI CORRADI, A. (1984). *Inorg. Chim. Acta,* **93**, 61–66.

BENEDETTI, E., DIBLASIO, B., PAVONE, V., PEDONE, C., GERMAIN, G. & GOODMAN, M. (1979). *Biopolymers,* **18**, 517–522.

BLESSING, R. H. & SMITH, G. D. (1982). *Acta Cryst.* B**38**, 1203–1207.

COIRO, M., MAZZA, F. & MIGNUCCI, G. (1974). *Acta Cryst.* B**30**, 2607–2613.

CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

EGGLESTON, D. S. & HODGSON, D. J. (1983). *Acta Cryst.* C**39**, 75–78.

EGGLESTON, D. S. & HODGSON, D. J. (1984). *Acta Cryst.* C**40**, 1201–1204.

Enraf–Nonius (1979). *Structure Determination Package.* Enraf–Nonius, Delft.

HAUSCHKA, P. V., LIAN, J. & GALLOP, P. M. (1975). *Proc. Natl Acad. Sci. (USA),* **72**, 3925–3929.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.

JACKSON, C. M. & NEMERSON, Y. (1980). *Annu. Rev. Biochem.* **49**, 765–811.

KOCK, A. J. DE & ROMERS, C. (1981). *Cryst. Struct. Commun.* **10**, 745–750.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

OLSSON, G., ANDERSEN, L., LINDQVIST, O., SJOLIN, L., MAGNUSSON, S., PETERSEN, T. E. & SOTTRUP-JENSEN, L. (1982). *FEBS Lett.* **145**, 317–322.

PARK, C. H. & TULINSKY, A. (1986). *Biochemistry,* **25**, 3977–3982.

PRICE, P. A., OTSUKA, A. S., POSER, J. W., KRISTAPONIS, J. & RAMAN, N. (1976). *Proc. Natl Acad. Sci. USA,* **73**, 1447–1451.

SATYSHUR, K. & RAO, S. T. (1979). *Acta Cryst.* B**35**, 2260–2263.

SATYSHUR, K., RAO, S. T., STENFLO, J. & SUTTIE, J. W. (1979). *Acta Cryst.* B**35**, 1493–1496.

STENFLO, J., FERNLUND, P., EGAN, W. & ROEPSTORFF, P. (1974). *Proc. Natl Acad. Sci. USA,* **71**, 2730–2733.

VALENTE, E. J., HISKEY, R. G. & HODGSON, D. J. (1979). *Biochim. Biophys. Acta,* **579**, 466–468.

Acta Cryst. (1987). C**43**, 1569–1571

Structure of a Novel $C_{11}H_{12}N_2O_3$ Cage Molecule

BY WILLIAM H. WATSON*

Department of Chemistry, Texas Christian University, Box 32908, *Fort Worth, Texas* 76129, *USA*

AND ALAN P. MARCHAND* AND PARITOSH R. DAVE

Department of Chemistry, North Texas State University, Box 5068, *Denton, Texas* 76203, *USA*

(*Received* 5 *December* 1986; *accepted* 16 *March* 1987)

Abstract. *N*-Hydroxy-3-nitro-4-azahexacyclo-[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane, $C_{11}H_{12}N_2O_3$, M_r = 220·23, monoclinic, P_1/c, a = 9·924 (7), b = 9·839 (7), c = 10·287 (7) Å, β = 93·40 (6)°, V = 1003 (1) Å^3, Z = 4, D_x = 1·458 g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ = 9·1 cm^{-1}, $F(000)$ = 464, T = 300 K,

* Authors to whom correspondence should be addressed.

0108-2701/87/081569-03$01.50