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Conformation and Structure of α-*tert*-Butyl *N*-(*N*-*tert*-Butoxycarbonyl-O^5-benzyl-α-L-glutamyl)-O^5-benzyl-L-glutamate, $C_{33}H_{44}N_2O_9$

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Abstract. $M_r = 612{\cdot}7$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}108$ (5), $b = 11{\cdot}528$ (3), $c = 28{\cdot}387$ (7) Å, $V = 3307{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}230$, D_m (flotation in aqueous KI) = 1·23 (2) Mg m^{-3}, Mo $K\alpha$ radiation ($\lambda K\alpha_1 = 0{\cdot}70926$, $\lambda K\alpha_2 = 0{\cdot}71354$ Å), $\mu = 0{\cdot}835$ mm^{-1}, $F(000) = 1312$, $T = 295$ K, $R = 0{\cdot}066$, $wR = 0{\cdot}060$ for 2066 observations. The fully blocked peptide adopts a β-sheet conformation with the side chains extended on opposite sides of the peptide backbone. The urethane and peptide bonds are in the *trans* configuration as are all the ester linkages. The side-chain conformations are unique compared to those of other structurally characterized glutamyl peptides.

Introduction. As part of a series of studies on the conformational and structural properties of linear peptides containing acidic amino acid residues we have prepared the title molecule by classical solution methods. It was of interest to compare the conformation of this fully blocked dipeptide with the structures of a series of unblocked glutamyl peptides which we have recently characterized (Eggleston, Valente & Hodgson, 1981*a*,*b*; Eggleston & Hodgson, 1982*a*,*b*,*c*, 1983*a*,*b*) to assess the conformational similarities and/or differences imposed by blocking the side chains and the peptide termini. In addition, we compare the conformation of the title molecule to that of a previously reported fully blocked diglutamyl peptide, *N*-Z-α-L-glutamyl-L-glutamic acid triethyl ester (Benedetti, DiBlasio, Pavone, Pedone, Germain & Goodman, 1979).

Experimental. Synthesis similar to the procedure reported previously by Rich, Lehrmann, Kawai, Goodman & Suttie (1981). Colorless rods grown by trituration of an ethyl acetate solution with *n*-heptane at 273 K. Crystal 0·4 × 0·2 × 0·2 mm. Enraf–Nonius CAD-4 diffractometer. Systematic absences $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd. Cell constants from a least-squares analysis of 25 reflections with $30° \le 2\theta$ (Mo) $\le 35°$ measured on the diffractometer. Intensity data collected in an ω–2θ scan mode, as suggested by peak shape analysis. 4285 independent reflections, $2\theta \le 55°$, $0 \le h \le 13$, $0 \le k \le 15$, $0 \le l \le 36$. Lorentz–polarization correction, no absorption correction. No systematic fluctuations in reflections $\bar{7},3,11$, 808, or $5,4,\bar{14}$ monitored at the beginning and every 3 h of exposure time (20 times). Programs in the CAD-4 structure determination package. Structure determined using *MULTAN*80 (Main *et al.*, 1980). *E* map revealed a 26-atom fragment of the molecule after deletion of 7 of the top 311 *E*'s of the type $h0l$ which were leading to poor origin definition (201, 204, 2,0,12, 4,0,10, 601, 6,0,15, 8,0,10); remainder of the non-hydrogen atoms located from a difference Fourier synthesis after two cycles of least-squares refinement on the initial fragment. Anisotropic full-matrix least-squares refinement (on *F*) of all 44 non-hydrogen atoms led to $wR = 0{\cdot}083$; weights $4F_o^2/\sigma^2(I)$. Subsequent difference Fourier maps revealed positions for all 44 H atoms; however, because of the paucity of data all H atoms were fixed at calculated positions with C(or N)–H 1·0 Å, with fixed isotropic temperature factors. Four final cycles of full-matrix least squares with the weighting scheme above and $\sigma(I)$ defined by Corfield, Doedens & Ibers (1967) with $p = 0{\cdot}04$, $wR = 0{\cdot}060$, $S = 1{\cdot}41$, 2066 observations with $I \ge 2\sigma(I)$ and 397 variables. No evidence for extinction. $(\Delta/\sigma)_{max} = 0{\cdot}06$. Final difference Fourier map contained no peak higher than 0·255 e Å^{-3}. A refinement cycle using all data with $I \ge 0{\cdot}01\sigma(I)$ gave R 0·100, wR 0·065.

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)

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and additional bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39280 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
O(1)	0·6171 (4)	0·7461 (4)	1·1586 (1)	3·8 (1)
O_1'	0·7991 (4)	0·7216 (4)	1·0013 (2)	3·8 (1)
O(2)	0·4523 (4)	0·6510 (5)	1·1205 (2)	5·5 (1)
O_2''	0·6100 (4)	0·9003 (4)	0·8527 (1)	4·2 (1)
O_2'	0·4512 (4)	0·8050 (4)	0·8924 (1)	4·3 (1)
$O_1^{\varepsilon 1}$	0·7090 (4)	0·2980 (4)	1·0068 (2)	5·5 (1)
$O_1^{\varepsilon 2}$	0·8593 (4)	0·3057 (3)	1·0651 (2)	3·9 (1)
$O_2^{\varepsilon 1}$	0·6715 (5)	0·9622 (4)	1·0440 (2)	5·9 (1)
$O_2^{\varepsilon 2}$	0·4768 (5)	1·0477 (5)	1·0296 (2)	6·0 (1)
N_1	0·6427 (4)	0·6960 (4)	1·0842 (2)	2·8 (1)
N_2	0·6040 (5)	0·7704 (4)	0·9673 (2)	2·8 (1)
C_1'	0·6765 (6)	0·7191 (5)	1·0009 (2)	2·6 (1)
C_1^{α}	0·7619 (6)	0·3515 (5)	1·0366 (2)	3·6 (1)
C_1^{β}	0·6100 (6)	0·5229 (5)	1·0314 (2)	2·8 (1)
C_1^{γ}	0·7408 (6)	0·4755 (5)	1·0493 (2)	3·7 (1)
C_1^{δ}	0·5985 (5)	0·6565 (5)	1·0380 (2)	2·4 (1)
C(1)	0·5465 (6)	0·7515 (6)	1·2035 (2)	4·0 (2)
C_2^{γ}	0·6232 (7)	1·0324 (5)	0·9656 (2)	3·9 (2)
C_2^{α}	0·6649 (6)	0·8331 (5)	0·9284 (2)	2·9 (1)
C_2^{δ}	0·5949 (7)	1·0077 (5)	1·0164 (2)	4·1 (2)
C_2'	0·5633 (6)	0·8436 (5)	0·8893 (2)	3·2 (1)
C_2^{β}	0·7205 (6)	0·9505 (5)	0·9429 (2)	3·0 (1)
C(2)	0·6388 (8)	0·8200 (8)	1·2340 (3)	7·0 (2)
C(3)	0·4160 (7)	0·8168 (7)	1·1985 (3)	5·9 (2)
C(4)	0·5272 (8)	0·6317 (7)	1·2232 (2)	6·0 (2)
C(5)	0·5625 (6)	0·6951 (5)	1·1214 (2)	3·3 (1)
C(6)	0·9002 (7)	0·1890 (5)	1·0531 (3)	4·6 (2)
C(7)	0·9839 (6)	0·1434 (6)	1·0930 (2)	4·0 (2)
C(8)	1·0645 (7)	0·2136 (6)	1·1200 (2)	4·4 (2)
C(9)	1·1431 (7)	0·1662 (7)	1·1556 (3)	5·9 (2)
C(10)	1·1437 (9)	0·0517 (7)	1·1638 (3)	6·9 (2)
C(11)	1·064 (1)	−0·0192 (6)	1·1377 (3)	8·1 (3)
C(12)	0·9839 (9)	0·0263 (6)	1·1025 (3)	6·2 (2)
C(13)	0·4438 (8)	1·0379 (8)	1·0791 (3)	6·8 (2)
C(14)	0·5028 (8)	1·1320 (6)	1·1076 (2)	5·3 (2)
C(15)	0·4514 (8)	1·2431 (7)	1·1057 (3)	6·2 (2)
C(16)	0·5042 (9)	1·3318 (7)	1·1322 (3)	7·5 (2)
C(17)	0·6137 (8)	1·3103 (8)	1·1583 (3)	7·7 (2)
C(18)	0·6689 (8)	1·2027 (8)	1·1604 (3)	7·0 (2)
C(19)	0·6137 (8)	1·1128 (8)	1·1348 (3)	6·5 (2)
C(20)	0·5346 (6)	0·9147 (6)	0·8082 (2)	4·2 (2)
C(21)	0·4081 (8)	0·9819 (7)	0·8180 (3)	6·2 (2)
C(22)	0·6267 (8)	0·9883 (8)	0·7794 (3)	6·9 (2)
C(23)	0·5100 (9)	0·7988 (7)	0·7864 (2)	6·0 (2)

* $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

as far as possible. Principal bond lengths and angles are listed in Table 2. The bond lengths within the Boc group are very similar to the average lengths for this blocking group recently compiled (Benedetti, Pedone, Toniolo, Nemethy, Pottles & Scheraga, 1980). There are three notable variations from these averages in the bond angles involving the urethane bond. Thus, the O(1)–C(5)–N(1) angle [111·9 (5)°] is 2° wider than the average for *trans* Boc groups while the O(2)–C(5)–N(1) angle [122·8 (6)°] and the C(1)–O(1)–C(5) angle [120·6 (5)°] are both 1° compressed from the computed averages for these urethane linkages. Bond lengths and angles within the peptide linkage are quite similar to averages compiled for this molecular fragment (Benedetti, 1977; Eggleston, 1983); however, there are exceptions involving C_1^{α}. The C_1^{α}–C_1^{β} bond of 1·556 (8) Å is lengthened by nearly 0·02 Å over the normally observed sp^3–sp^3 C–C distance while the C_1^{α}–C_1' distance of 1·502 (7) Å is approximately 0·02 Å shorter than the normally observed value of 1·522 Å. This shortening in the C_1^{α}–C_1' bond is accompanied by lengthening of approximately 0·01 Å each in the C_1'–O_1' and C_1'–N_2 bonds and may reflect some 'leakage' of electron density out of the amide linkage towards C_1^{α}. Such delocalization of electron density over the entire peptide backbone has been proposed before (Chakrabarti, Venkatesan, Singh & Rao, 1981); however, an extensive statistical analysis of the crystallographic data in support of this concept has not been undertaken. The observed lengthening in the C_1^{α}–C_1^{β} bond may in part facilitate the adoption of an unusual torsion angle (see below) about this bond by reducing non-bonded interactions between these two atoms and their substituents. In all other respects, the bond distances in this peptide appear normal. Other than the normally observed widening about C^{β} in the two glutamyl side chains (Eggleston, 1983) from the classical tetrahedral values [C_1^{α}–C_1^{β}–C_1^{γ} = 112·4 (5)°; C_2^{α}–C_2^{β}–C_2^{γ} = 115·6 (5)°] the bond angles also appear quite normal.

A complete list of the torsion angles in this peptide has been deposited. The values of θ^1 (−178·3°) and ω_0(−173·2°) for the Boc group are consistent with the *trans–trans* conformation typical of almost all structures containing a secondary N in the urethane linkage (Benedetti, Pedone, Toniolo, Nemethy, Pottles & Scheraga, 1980). The principal peptide torsion angles φ_1 = 152·0°, ψ_1 = 128·5°, ω = −179·1° and φ_2 = 160·8° reflect the extended β-sheet structure which this

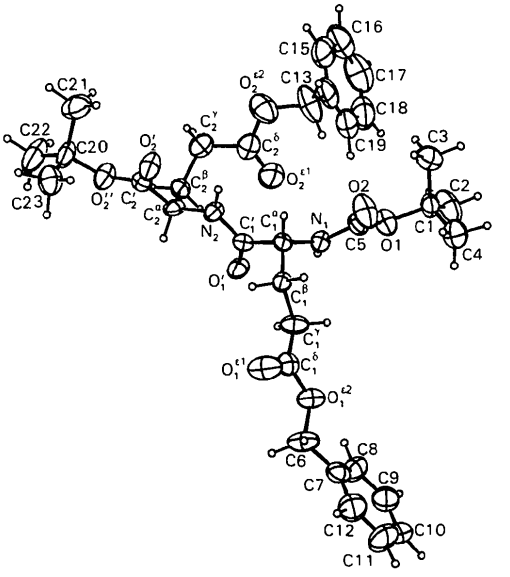

Fig. 1. View of a single molecule of the title compound showing atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, but H atoms are shown as small spheres of arbitrary size.

Table 2. *Principal bond lengths* (Å) *and angles* (°)

C(1)–C(2)	1·498 (9)	C(1)–C(3)	1·526 (9)	C(1)–C(4)	1·503 (9)
C(1)–O(1)	1·463 (7)	O(1)–C(5)	1·329 (7)	O(2)–C(5)	1·225 (7)
N(1)–C(5)	1·331 (7)	N(1)–C_1^{α}	1·457 (6)	C_1^{α}–C_1^{β}	1·556 (8)
C_1^{α}–C_1'	1·502 (7)	C_1^{β}–C_1^{γ}	1·518 (7)	C_1^{γ}–C_1^{δ}	1·489 (8)
C_1^{δ}–$O_1^{\varepsilon 1}$	1·176 (7)	C_1^{δ}–$O_1^{\varepsilon 2}$	1·378 (7)	N_2–C_2^{α}	1·457 (7)
C_2^{α}–C_2^{β}	1·522 (8)	C_2^{α}–C_2'	1·516 (8)	C_2^{β}–C_2^{γ}	1·508 (8)
C_2^{γ}–C_2^{δ}	1·496 (8)	C_2^{δ}–$O_2^{\varepsilon 1}$	1·220 (7)	C_2^{δ}–$O_2^{\varepsilon 2}$	1·334 (8)
$O_2^{\varepsilon 2}$–C(13)	1·449 (8)	C(13)–C(14)	1·478 (10)	C(14)–C(15)	1·383 (11)
C(14)–C(19)	1·380 (10)	C(15)–C(16)	1·373 (11)	C(16)–C(17)	1·354 (13)
C(17)–C(18)	1·361 (13)	C(18)–C(19)	1·383 (12)	$O_1^{\varepsilon 2}$–C(6)	1·448 (7)
C(6)–C(7)	1·509 (9)	C(7)–C(8)	1·379 (9)	C(7)–C(12)	1·377 (9)
C(8)–C(9)	1·398 (9)	C(9)–C(10)	1·341 (11)	C(10)–C(11)	1·368 (12)
C(11)–C(12)	1·387 (11)	C_1'–O_1'	1·239 (6)	C_1'–N_2	1·340 (7)
C_2'–O_2'	1·220 (7)	C_2'–O_2''	1·316 (6)	O_2''–C(20)	1·485 (7)
C(20)–C(21)	1·520 (9)	C(20)–C(22)	1·502 (9)	C(20)–C(23)	1·493 (9)
C(1)–O(1)–C(5)	120·6 (5)	O(1)–C(1)–C(2)	102·8 (5)	O(1)–C(1)–C(3)	111·2 (5)
O(1)–C(1)–C(4)	110·4 (5)	O(1)–C(5)–N(1)	111·9 (5)	O(2)–C(5)–N(1)	122·8 (6)
O(1)–C(5)–O(2)	125·2 (6)	C_2^{α}–N_2–C_1'	121·9 (5)	$O_2^{\varepsilon 2}$–C(13)–C(14)	112·3 (6)
C_1^{α}–N_1–C(5)	121·6 (5)	$O_1^{\varepsilon 2}$–C(6)–C(7)	107·9 (5)	O_2'–C_2'–O_2''	124·8 (6)
C_2^{α}–C_2'–O_2'	123·2 (6)	C_2^{α}–C_2'–O_2''	112·0 (6)	C_2'–O_2''–C(20)	122·9 (5)
$O_2^{\varepsilon 1}$–C_2^{δ}–$O_2^{\varepsilon 2}$	122·4 (7)	C_2^{γ}–C_2^{δ}–$O_2^{\varepsilon 2}$	112·2 (6)	C_2^{γ}–C_2^{δ}–$O_2^{\varepsilon 1}$	125·4 (7)
C_2^{δ}–$O_2^{\varepsilon 2}$–C(13)	116·9 (6)	C_2^{β}–C_2^{γ}–C_2^{δ}	114·6 (5)	C_2^{α}–C_2^{β}–C_2^{γ}	115·6 (5)
C_2^{β}–C_2^{α}–C_2'	112·2 (5)	N_2–C_2^{α}–C_2^{β}	113·0 (5)	N_2–C_2^{α}–C_2'	108·0 (5)
O_1'–C_1'–N_2	122·9 (5)	C_1^{α}–C_1'–N_2	115·2 (5)	C_1^{α}–C_1'–O_1'	121·9 (5)
C_1^{γ}–C_1^{δ}–$O_2^{\varepsilon 2}$	109·1 (6)	C_1^{γ}–C_1^{δ}–$C_1^{\varepsilon 1}$	127·8 (6)	$O_1^{\varepsilon 1}$–C_1^{δ}–$O_1^{\varepsilon 2}$	123·1 (6)
C_1^{δ}–$O_1^{\varepsilon 2}$–O(6)	115·0 (5)	C_1^{β}–C_1^{γ}–C_1^{δ}	112·9 (5)	C_1^{α}–C_1^{β}–C_1^{γ}	112·4 (5)
C_1^{β}–C_1^{α}–C_1'	110·6 (4)	N_1–C_1^{α}–C_1'	108·7 (4)	N_1–C_1^{α}–C_1^{β}	113·3 (4)
O_2''–C(20)–C(21)	109·5 (5)	O_2''–C(20)–C(22)	102·0 (5)	O_2''–C(20)–C(23)	109·8 (5)

peptide adopts with a *trans* peptide bond. With the value of φ_2 near 180° the terminal carboxyl group is nearly coplanar with the peptide bond. The torsion angles for both glutamyl side chains are unique amongst structurally characterized glutamyl residues. The combination of $\chi_1^1 = -44{\cdot}5°$ and $\chi_1^2 = 171{\cdot}1°$ is fundamentally the same as the conformation for the first glutamyl residue of another fully blocked Glu-Glu peptide, Z-α-L-glutamyl-L-glutamic acid triethyl ester (Benedetti, DiBlasio, Pavone, Pedone, Germain & Goodman, 1979). The value of χ_1^1, however, is fully 15° away from the ideal *gauche* value of −60° and thus reflects some considerable adjustment within the side chain at the expense of unfavorable non-bonded interactions between the H atoms at C_1^{β} and other atoms of this molecule. Such distortion in χ^1 values is not normally observed in glutamyl peptides; however, a distortion of the opposite sense occurs in the structure of α-L-glutamylglycine (Eggleston, Valente & Hodgson, 1981*b*) where the χ^1 value of +72° is 12° away from the ideal value of +60°. The conformation of the second glutamyl side chain in the title molecule, which contrasts to that of the first residue, is *gauche–gauche* as described by the values of χ_2^1 (−56·6°) and χ_2^2 (78·8°). The χ^1 value for this side chain is much closer to the ideal value of −60° but the χ^2 value is fully 18° away from the ideal value of +60°. This conformation is distinct from the *trans–trans* conformation adopted by the second glutamyl residue of the other blocked Glu-Glu peptide and from the conformation adopted by the second glutamyl residue of unblocked Glu-Glu (Eggleston & Hodgson, 1982*b*). Moreover, this is the first structural documentation for this particular combination of χ^1 and χ^2 values for the glutamyl side chain. A similar, though more highly distorted, conformation about the C_2^{α}–C_2^{β} bond ($\chi^2 = -131°$) in the side chain of the second glutamyl residue of the totally unblocked Glu-Glu peptide was observed.

The conformations of all the ester linkages are, as expected, *trans* with respect to the side chain while the C=O bonds of all the ester linkages are synplanar with respect to their C–O counterparts (Dunitz & Strickler, 1968). The phenyl groups of the benzyl ester moieties are planar.

There appears to be weak hydrogen bonding in the crystals involving both available amide H atoms. Thus, the N-terminal nitrogen, N_1, is a donor towards the C-terminal carboxyl oxygen, O_2', of a screw-related molecule with an $N_1\cdots O_2'$ separation of 3·188 (5) Å, an $HN_1\cdots O_2'$ separation of 2·29 Å and an angle at H of 147 (2)°. The peptide-bond nitrogen, N_2, is a donor to the peptide-bond carbonyl oxygen, O_1', of a screw-related molecule with an $N_2\cdots O_1'$ separation of 3·210 (6) Å, an $HN_2\cdots O_1'$ separation of 2·27 Å and an angle at H of 157 (2)°.

Using solid-state and solution NMR studies as well as theoretical force-field calculations we are in the process of assessing the influence of the crystal lattice environment on the unusual χ_1^1 and χ_2^2 torsion angles observed in the blocked diglutamyl peptide.

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Triméthyl-1,3,6 Diphényl-4,5 Oxa-9 Diaza-2,7 Tricyclo[3.3.1.$0^{2,4}$]nonan-one-8, $C_{21}H_{22}N_2O_2$

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Abstract. $M_r = 334{\cdot}4$, monoclinic, $P2_1/c$, $a = 11{\cdot}669\ (2)$, $b = 15{\cdot}338\ (4)$, $c = 13{\cdot}596\ (4)$ Å, $\beta = 133{\cdot}75\ (2)°$, $V = 1758\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ Mg m^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1{\cdot}5424$ Å, $\mu = 0{\cdot}66$ mm^{-1}, $F(000) = 712$, $T = 295$ K, $R = 0{\cdot}035$ for 1834 unique reflections. The molecule resulting from the condensation of two molecules of 2-methyl-3-phenylazirine with one molecule of ethyl lactate has a tricyclic structure. In spite of the presence of six asymmetric centers, only one diastereoisomer, corresponding to the lowest steric hindrance, is formed.

Introduction. Le composé a été obtenu par condensation de deux molécules de méthyl-2 phényl-3 azirine avec une molécule de lactate d'éthyle (Alvernhe, Laurent, Masroua & Diab, 1983). Il est remarquable qu'un seul diastéréoisomère soit obtenu. La spectrométrie de masse et la RMN ^{1}H n'ont pas permis d'en établir la structure de façon non équivoque.

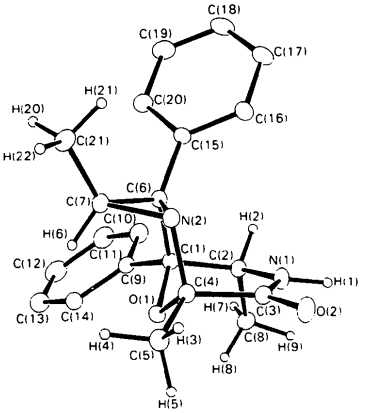

Fig. 1. Vue schématique en perspective de la molécule (par simplification, les atomes d'hydrogène des phényles ne sont pas représentés).

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