Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.187$

$S = 1.033$

6199 reflections

296 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 5.43P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.263$ e Å^{-3}

$\Delta\rho_{min} = -0.292$ e Å^{-3}

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C1	1.805 (5)	S2—C14	1.800 (5)
S1—C3	1.861 (5)	S2—C16	1.861 (4)
O1—C2	1.423 (5)	O3—C15	1.420 (5)
O1—C3	1.426 (5)	O3—C16	1.437 (5)
O2—C11	1.421 (5)	O4—C24	1.425 (5)
C1—S1—C3	92.4 (2)	C14—S2—C16	92.0 (2)
C2—O1—C3	111.7 (4)	C15—O3—C16	111.6 (3)
C2—C1—S1	103.6 (4)	C15—C14—S2	104.1 (4)
O1—C3—S1	105.9 (3)	O3—C16—S2	105.9 (3)
C8—C3—S1	108.4 (3)	C21—C16—S2	108.7 (3)
C4—C3—S1	112.6 (3)	C17—C16—S2	113.2 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O4^i	0.82	1.89	2.693 (5)	166.4
O4—H4···O2^{ii}	0.82	1.85	2.655 (5)	166.9

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

The space group $P2_1/c$ was determined uniquely from the systematic absences. The H atoms were located from a difference map and were allowed to ride at geometrically idealized positions, with C—H and O—H distances of 0.95 and 0.82 Å, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL97*.

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Methyl N-(*tert*-Butoxycarbonyl)glycyl-L-valyl-L-tryptophanate

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Abstract

The title compound, $C_{24}H_{34}N_4O_6$, is an end-protected tripeptide and the peptide backbone adopts an extended conformation. The peptide units are *trans* and show significant deviations from planarity. The crystal packing enables neighbouring molecules to interact through an antiparallel β-sheet arrangement. An intramolecular hydrogen bond occurs between the peptide backbone carbonyl group and the N atom in the tryptophan side chain. An interesting feature of the packing is that the tryptophan side chain straddles both hydrophobic and hydrophilic environments.

Comment

The observed bond geometry of the title tripeptide, (I), agrees with expectations. All the peptide units are *trans* and show significant deviations from planarity. The conformation of the butoxycarbonyl (BOC) group, characterized by the torsion angles θ_0 (C1—O1—C0′—N1) and ω_0 (O1—C0′—N1—CA) is *trans–trans* (Benedetti *et al.*, 1980). The peptide chain backbone torsion angles are $\varphi_1 = 108.8 (5)$, $\psi_1 = 167.8 (4)$, $\omega_1 = 173.5 (4)$, $\varphi_2 = -106.4 (5)$, $\psi_2 = 115.3 (4)$, $\omega_2 = -169.6 (4)$, $\varphi_3 = -100.0 (5)$, $\psi_3 = -29.6 (6)$ and $\omega_3 = -176.0 (5)°$, and represent an extended

conformation, with a chain-repeat distance $(C1A\cdots C3A)$ of 6.095 (7) Å.

(I)
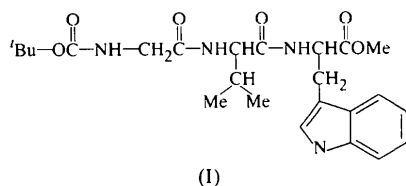
Successive peptide chains related by the crystallographic 2_1 screw axis parallel to the a axis form an infinite ribbon of antiparallel β-strands interacting through characteristic inter-chain hydrogen bonds involving peptide amino and carbonyl groups. The valyl side chain adopts the conformation $g^- t$ [$\chi_1 = -47.6$ (6) and $\chi_2 = -170.6$ (4)°]. The tryptophan side chain adopts $\chi_1 = -67.9$ (5) and $\chi_2 = 77.5$ (7)°, in contrast to that observed in Trp–Gly–Gly dihydrate (Subramanian & Sahayamary, 1989), where $\chi_1 = -171.6$ and $\chi_2 = 101.0°$. The N atom of the imidazole ring in tryptophan forms an intramolecular N—H$\cdots$O hydrogen bond with atom OO$'$ of the urethane moiety [N4$\cdots$OO$'$ 2.917 (6), H$\cdots$O 2.10 Å and N4—H$\cdots$OO$'$ 159°]. This tripeptide sequence occurs only rarely in proteins, as for example in carboxypeptidase (Rees et al., 1983) and cytochrome C551 (Matsuura et al., 1982), where they display an α-helical conformation. In the present case, the molecular conformation is β-sheet.
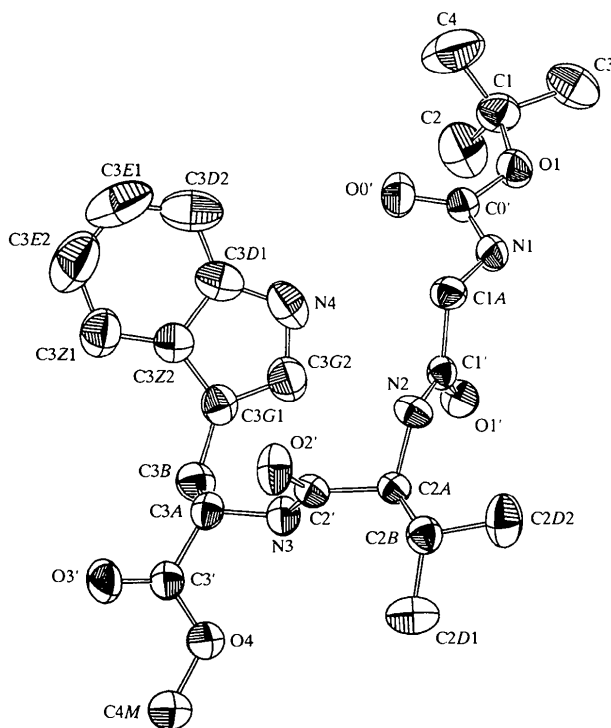
The crystal packing produces alternating layers of non-polar and polar regions perpendicular to the c axis (Fig. 2). The non-polar layers are formed essentially by the hydrophobic moieties of the BOC group, valyl and tryptophan side chains, while the polar regions consist of the peptide moieties. The crystal packing makes the side chain of the tryptophan occupy the interspace between the hydrophobic and hydrophilic environments. One side of the tryptophan ring is exposed to the cluster of hydrophobic groups (such as BOC and the valyl side chain) constituting the non-polar layer, while the other side is exposed to polar groups.
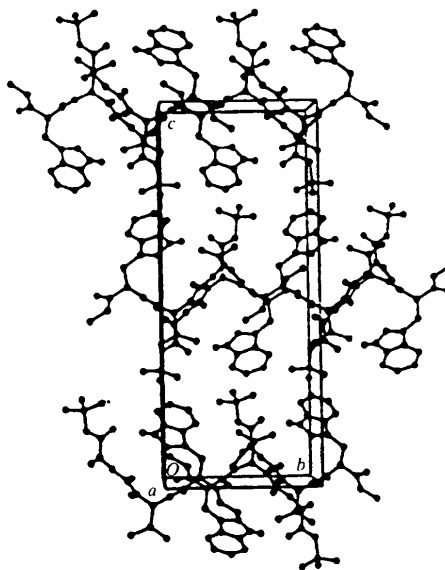

Fig. 2. Packing of the molecule down a axis, with the c axis vertical (PLUTO; Motherwell & Clegg, 1978).

Experimental

The title tripeptide was synthesized by the solution-phase method using tert-BOC as the N-protecting group. Coupling reactions were carried out by the dicyclohexyl carbodiimide/1-hydroxybenzotriazole method. The final peptide was purified by silica-gel column chromatography and characterized by spectroscopic methods (Konig & Geiger, 1970). Crystals were obtained by slow evaporation of a methanol/water solution at room temperature.

Fig. 1. Perspective view of the title molecule, with displacement ellipsoids shown at the 30% probability level.

Crystal data

$C_{24}H_{34}N_4O_6$	Cu $K\alpha$ radiation
$M_r = 474.55$	$\lambda = 1.5418$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 9.022$ (1) Å	$\theta = 5$–20°
$b = 11.052$ (1) Å	$\mu = 0.709$ mm^{-1}
$c = 26.580$ (3) Å	$T = 293$ (2) K
$V = 2650.3$ (3) Å^3	Parallelepiped
$Z = 4$	0.42 × 0.30 × 0.20 mm
$D_x = 1.189$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 65°$
	$h = 0 \rightarrow 10$
$\omega/2\theta$ scans	$k = 0 \rightarrow 12$
Absorption correction: none	$l = 0 \rightarrow 31$
2554 measured reflections	3 standard reflections
2544 independent reflections	every 100 reflections
2189 reflections with	frequency: 60 min
$I > 2\sigma(I)$	intensity decay: $<2\%$
R_{int} not available (see below)	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.004$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$\Delta\rho_{max} = 0.194$ e Å^{-3}
$wR(F^2) = 0.178$	$\Delta\rho_{min} = -0.231$ e Å^{-3}
$S = 0.913$	Extinction correction: none
2542 reflections	Scattering factors from
307 parameters	*International Tables for*
H atoms riding	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected torsion angles (°)*

C1—O1—C0'—N1	178.8 (5)
O1—C0'—N1—C1A	172.7 (4)
C0'—N1—C1A—C1'	108.8 (5)
N1—C1A—C1'—N2	167.8 (4)
C1A—C1'—N2—C2A	173.5 (4)
C1'—N2—C2A—C2'	−106.4 (5)
N2—C2A—C2B—C2D1	−170.6 (4)
N2—C2A—C2B—C2D2	−47.6 (6)
N2—C2A—C2'—N3	115.3 (4)
C2A—C2'—N3—C3A	−169.6 (4)
C2'—N3—C3A—C3'	−100.0 (5)
N3—C3A—C3B—C3G1	−67.9 (5)
C3A—C3B—C3G1—C3G2	77.5 (7)
N3—C3A—C3'—O4	−29.6 (6)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N4—H1N4···O0'	0.86	2.10	2.917 (6)	159
N1—H1N1···O2'^{i}	0.86	2.11	2.937 (6)	161
N2—H1N2···O1'^{ii}	0.86	2.05	2.899 (5)	171
N3—H1N3···O3'^{iii}	0.86	2.16	3.010 (5)	171

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

The title structure was solved by direct methods and refined by full-matrix anisotropic least squares assuming all H atoms riding in calculated positions with fixed isotropic U's. The data collection was not continued beyond $\theta_{max} = 65°$ due to the large number of too-weak reflections, and also because of the sudden failure in the encoders of the goniometer device. R_{int} was not available since the data collection and processing were carried out by a fees-for-service organization which sent only *hkl*, F_o and $\sigma(F_o)$, and deleted the files before *Acta Crystallographica Section C*'s requirements regarding R_{int} became known. Since we used the *TWIN* option, the Flack parameter was suppressed.

Data collection: *SDP* (Frenz, 1978). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL93* and *PARST* (Nardelli, 1983, 1995).

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4-(Dimethylaminomethylene)-2-(2-nitrophenyl)oxazol-5(4H)-one

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Abstract

The crystal structure of the title compound, $C_{12}H_{11}N_3O_4$, has been determined as part of a study of the luminescent activity of oxazolin-5-ones [Singh & Singh (1994). *Indian J. Chem.* **33B**, 232–235]. The dihedral angle between the 2-oxazoline (4,5-dihydrooxazole) and phenyl rings is 12.48 (8)°. A conjugation effect is observed in the dimethylaminomethylene moiety.