

to be a rare case that two macrocyclic conformations can be structurally analysed in one crystal. The contact distances between the carbonyl-O atom and *ortho* protons of phenyl rings, which may be the important chiral sensors in the asymmetric epoxidation of olefins catalyzed by chiral ketones, vary from 4.08 (O1...H29) to 6.37 (O1...H33) for the conformer *A*, and from 4.75 (O7...H51) to 6.46 Å (O7...H43) for the conformer *B*.

Experimental

(2*S*,3*S*,9*S*,10*S*)-6,13-Dimethylene-2,3,9,10-tetraphenyl-1,4,8,11-tetraoxacyclotetradecane (1.51 g, 1.89 mmol) was ozonized at 195 K by passing an O₃/O₂ stream through until the solution was saturated with O₃. Excess O₃ was removed by the O₂ stream, and the triphenylphosphine (0.50 g, 1.89 mmol) was added portionwise to the reaction mixture. After stirring for 30–40 min at 195 K, the mixture was allowed to warm to room temperature, and the solvent was evaporated *in vacuo*. The product was purified chromatographically on silica gel (eluant ethyl acetate:hexane 2:1) and recrystallized from diethyl ether solution (yield 68%, m.p. 451–456 K).

Crystal data

C₃₄H₃₂O₆
M_r = 536.60
 Tetragonal
*P*4₃2₁2
a = 14.945 (2) Å
c = 39.572 (2) Å
V = 8838.5 (17) Å³
Z = 12
D_x = 1.210 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 7–14°
 μ = 0.082 mm⁻¹
T = 293 (2) K
 Octahedron
 0.65 × 0.50 × 0.40 mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: none
 4476 measured reflections
 4476 independent reflections
 2158 reflections with $I > 2\sigma(I)$

θ_{\max} = 24.97°
 h = 0 → 12
 k = 0 → 17
 l = 0 → 47
 3 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.150$
S = 0.999
 4476 reflections
 541 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.153 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.166 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected bond lengths (Å)

O1—C1	1.195 (6)	O6—C34	1.414 (6)
O2—C2	1.408 (6)	O6—C27	1.428 (6)
O2—C3	1.434 (6)	C1—C2	1.494 (7)

O3—C18	1.206 (6)	C1—C34	1.502 (7)
O4—C17	1.394 (5)	C3—C10	1.519 (7)
O4—C10	1.436 (5)	C17—C18	1.490 (7)
O5—C19	1.417 (5)	C18—C19	1.492 (7)
O5—C20	1.430 (5)	C20—C27	1.544 (6)

The absolute configuration of the structure was determined by the chemical used.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.2* (Hall *et al.*, 1994). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*b*). Molecular graphics: *ORTEPIII* (Johnson, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1289). Services for accessing these data are described at the back of the journal.

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Methyl 1-(*tert*-butoxycarbonyl-L-alanyl-L-leucylamino)cyclooctane-1-carboxylate

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Abstract

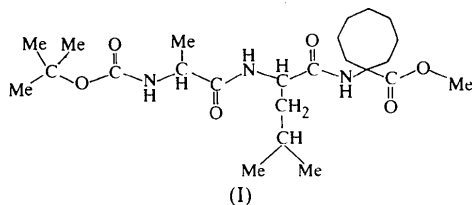
In the title compound, C₂₄H₃₃N₃O₆, an end-protected tripeptide, the peptide backbone adopts an incipient 3₁₀ helical conformation. The peptide units are *trans*

and show significant deviations from planarity. The tripeptide contains an intramolecular 4→1 hydrogen bond.

Comment

The C^α,α-disubstituted glycines used in the synthesis of peptides with restricted conformational flexibility have acquired increasing importance in the design of analogues of bioactive peptides (Toniolo & Benedetti, 1991). The use of 1-aminocycloalkane-1-carboxylic acid residues permits the introduction of completely hydrophobic side chains with limited conformational flexibility.

All peptide units are *trans* and show significant deviations from planarity. The conformation of the butoxycarbonyl (boc) group of (I), characterized by the torsion angles $\theta_0 = \text{C1—O1—C0'—N1}$ and $\omega_0 = \text{O1—C0'—N1—CA}$ is *trans-trans* (Benedetti *et al.*, 1980). The peptide chain backbone torsion angles are $\varphi_1 = -64.0(3)$, $\psi_1 = -25.2(3)$, $\omega_1 = 177.6(2)$, $\varphi_2 = -60.1(3)$, $\psi_2 = -40.2(3)$, $\omega_2 = -173.4(2)$ and $\varphi_3 = 53.8(4)$, $\psi_3 = 38.3(4)$, $\omega_3 = 179.1(2)^\circ$ and represent an incipient right-handed 3₁₀ helical structure.



The achiral residue Ac⁸c (1-aminocyclooctane-1-carboxylic acid) has been reported to show preference for both right- and left-handed helical conformations. In the present structure, (I), it is found to adopt a left-handed 3₁₀ helical conformation (Benedetti, 1994). The side-chain conformation of this residue is *tg*⁻.

The side chain of leucine has $\chi_1 = 177.9(2)$, $\chi_{21} = 66.3(5)$, $\chi_{22} = -168.0(4)^\circ$ representing a *t(g⁺t)* conformation which is moderately favoured (Benedetti *et al.*, 1983). The endocyclic torsion angles relating the cyclooctyl ring to the peptide chain, N3—C3A—C3B1—C3G1 and N3—C3A—C3B2—C3G2 are 175.5(3) and $-61.8(5)^\circ$, respectively, as observed in cyclooctane ring systems. All other endocyclic bond angles have values higher than those expected for a regular tetrahedral carbon angle. The Ac⁸c ring is in twist boat-chair conformation. The cycloalkane ring is appreciably distorted, resembling a chiral intermediate in the pseudo-rotational pathway from the boat-chair to the twisted-boat-chair conformation (Anet, 1974; Dunitz, 1967; Hendrickson, 1967). The Ac⁸c ring is nearly perpendicular to the adjacent peptide unit, the dihedral angle being 84.1(2)°. N3 (Ac⁸c) and O0' (boc group) are connected by a 4→1 hydrogen bond (Venkatachalam, 1968; Toniolo, 1980; Rose *et al.*, 1985).

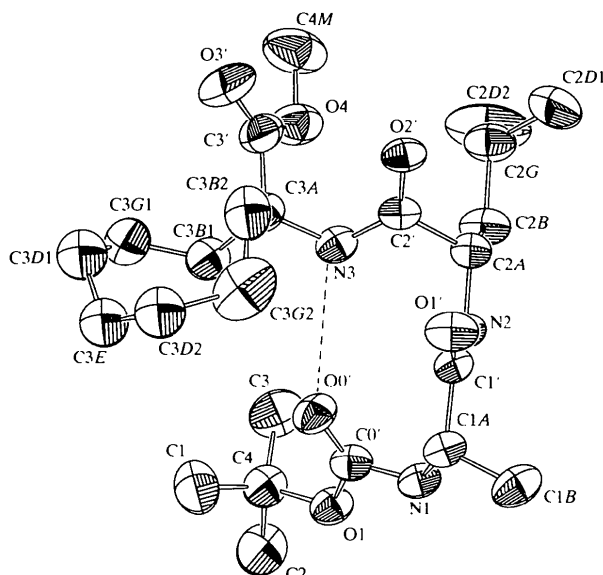


Fig. 1. View showing 30% probability displacement ellipsoids and the atom-numbering scheme in the molecular structure. Dashed line represents the 4→1 hydrogen bond. Only the disordered atoms with the higher occupancy are shown.

Experimental

The crystals were obtained by slow evaporation of a methanol/water solution at room temperature.

Crystal data

C₂₄H₃₃N₃O₆
M_r = 459.53
 Monoclinic
*P*2₁
a = 11.375(3) Å
b = 10.438(3) Å
c = 12.577(4) Å
 β = 115.80(2)°
V = 1344.4(7) Å³
Z = 2
D_x = 1.135 Mg m⁻³
D_m not measured

Data collection

Siemens R3m/V diffractometer
 ω scans
 Absorption correction: none
 2835 measured reflections
 2696 independent reflections
 2513 reflections with $I > 2\sigma(I)$

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.068
 $wR(F^2) = 0.186$

Mo *K* α radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 5-22^\circ$
 $\mu = 0.082$ mm⁻¹
T = 293(2) K
 Needle
 0.30 × 0.19 × 0.10 mm
 Colourless

*R*_{int} = 0.022
 $\theta_{\text{max}} = 25.67^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 12$
 $l = -15 \rightarrow 13$
 2 standard reflections every 98 reflections
 intensity decay: <2%

$w = 1/[\sigma^2(F_o^2) + (0.1412P)^2 + 0.1578P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.091$
2684 reflections
286 parameters
H-atom parameters
constrained

$(\Delta/\sigma)_{\max} = 0.015$
 $\Delta\rho_{\max} = 0.368 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.245 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected torsion angles ($^{\circ}$)

O1—C0'—N1—C1A	−169.7 (2)
C1—O1—C0'—N1	−169.5 (2)
C0'—N1—C1A—C1'	−64.0 (3)
N1—C1A—C1'—N2	−25.2 (3)
C1A—C1'—N2—C2A	177.6 (2)
C1'—N2—C2A—C2'	−60.1 (3)
N2—C2A—C2B—C2G	177.9 (2)
C2A—C2B—C2G—C2D1	66.3 (5)
C2A—C2B—C2G—C2D2	−168.0 (4)
N2—C2A—C2'—N3	−40.2 (3)
C2A—C2'—N3—C3A	−173.4 (2)
C2'—N3—C3A—C3'	53.8 (4)
N3—C3A—C3'—O4	38.3 (4)
C3A—C3'—O4—C4M	179.1 (2)
N3—C3A—C3B1—C3G1	175.5 (3)
N3—C3A—C3B2—C3G2	−61.8 (5)

Three of the cyclooctane ring atoms (C3D1, C3D2 and C3E) showed positional disorder, a feature not unexpected in an eight-membered ring. This was modelled in terms of two unequal sites of occupancies 0.6 and 0.4. The disordered atoms were allowed to refine with isotropic displacement parameters (Mukhopadhyay *et al.*, 1998). All the H atoms (except the disordered atoms) were geometrically fixed and allowed to ride on the corresponding non-H atoms. Two of the cyclooctane ring distances were restrained.

Data collection: *P3 Software* (Siemens, 1991). Cell refinement: *P3 Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). 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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Trichloro[(Z)-2-chloro-1,2-diphenylvinyl]-tellurium(IV)

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Abstract

In the title structure, [Te(C₁₄H₁₀Cl)Cl₃] or C₁₄H₁₀Cl₄Te, the Te atom is in a pseudo-trigonal bipyramidal configuration, with the lone pair of electrons, a vinyl-C atom and a Cl atom occupying the equatorial positions and the other two Cl atoms occupying the axial positions. Distances and angles are: Te—Cl 2.280 (2), 2.463 (5) and 2.469 (5), and Te—C 2.132 (7) Å; Cl—Te—Cl 174.15 (12), 87.9 (2) and 89.4 (2), and Cl—Te—C 86.8 (5), 88.4 (5) and 97.8 (2) $^{\circ}$.

Comment

Vinyllic tellurides are emerging as important synthetic reagents (Comasseto *et al.*, 1997). The most popular method of preparing such reagents consists of the addition of nucleophilic tellurium to acetylenes (Comasseto, 1993). The addition of electrophilic tellurium to acetylenes as a method of accessing vinyllic tellurides has been studied much less (Comasseto *et al.*, 1997). Recently, we developed a method of preparing tri- and tetrasubstituted vinyllic tellurides by means of the addi-