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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71076 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR1005]

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Structure of Boc-Phe-D-Leu-OMe

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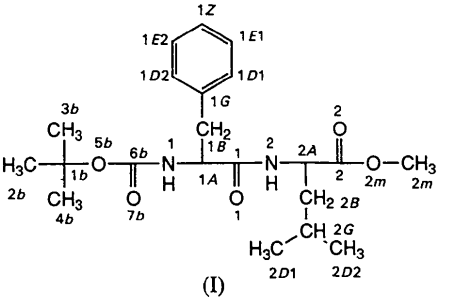
Abstract

The X-ray crystal structure analysis of *tert*-butoxycarbonyl-L-phenylalanyl-D-leucine methyl ester showed two crystallographically independent molecules, each of them taking a similar open conformation in which the *tert*-butoxycarbonyl group and D-leucine isobutyl side chain are located facing parallel to each other. In the crystal, these molecules are piled up alternately along the *b* axis and form an infinite sheet structure through four independent NH···O—C hydrogen bonds.

Comment

As one of a series of investigations into the relationship between the molecular conformation and the hydrophobicity/hydrophilicity of oligopeptides consisting of L-L, L-D or D-L sequences, the title peptide (I) was chemically synthesized and its molecular conformation determined by X-ray crystal analysis. The conformational study is also interesting in that this sequence constitutes a part of DADLE (H-Tyr-D-Ala-Gly-Phe-D-Leu-OH), an opioid peptide specific for the δ-receptor, and plays an important role in its activity (Zajac, Gacel, Petit, Dodey, Rossignol & Roques, 1983).



(I)

The atomic positional and equivalent isotropic thermal parameters are listed in Table 1. Table 2 lists some conformational torsion angles. There are two crystallographically independent molecules per asymmetric unit. Each of them, named molecules *A* and *B*, takes a similar open or extended conformation in

such a way that the φ and ψ angles of the Phe and Leu residues are in the allowed α_R and α_L regions, respectively. Fig. 1 shows the conformation of molecule *A*. It is characteristic that the N-terminal *tert*-butoxycarbonyl group is arranged side by side with the Leu isobutyl side chain in molecules *A* and *B*. Although the bonding parameters have relatively high e.s.d.'s because of the large thermal motion, especially for the terminal chains (0.005–0.02 Å for the bond lengths and 0.1–0.7° for the bond angles), their values are all in the accepted regions, and no notable abnormality was observed.

Molecules *A* and *B*, the whole conformations of which are related to each other by a rotation angle of about 90°, are alternately arranged along the *b* axis and form an infinite sheet structure through four independent hydrogen bonds (Fig. 2), *i.e.* N(1)(molecule *A*)···O(1)(molecule *B* at $2-x, y-\frac{1}{2}, 2-z$) = 2.898 (5); N(2)(molecule *A*)···O(1)(molecule*B* at $2-x, y-\frac{1}{2}, 2-z$) = 3.038 (5); N(1)(molecule*B*)···O(7*b*)(molecule *A*) = 3.009 (6); N(2)(molecule*B*)···O(1)(molecule *A*) = 2.931 (5) Å.

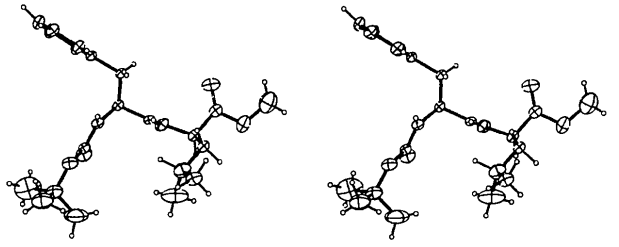


Fig. 1. Stereoscopic view of Boc-Phe-D-Leu-OMe, molecule *A*.

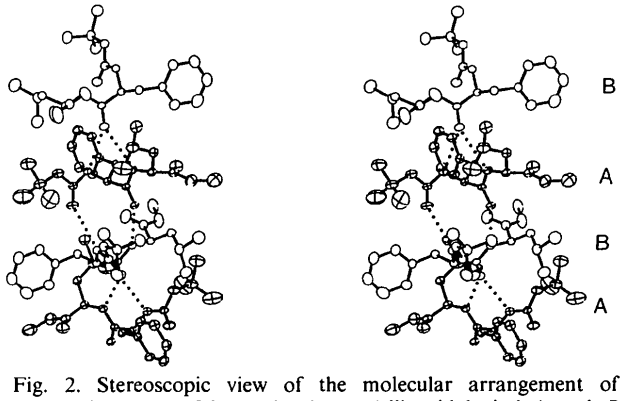


Fig. 2. Stereoscopic view of the molecular arrangement of Boc-Phe-D-Leu-OMe, molecules *A* (ellipsoidal circles) and *B* (open circles) along the *b* axis. The dotted lines represent hydrogen bonds.

Experimental

Crystal data

$C_{21}H_{32}N_2O_5$
M_r = 392.49
Monoclinic
$P2_1$
a = 10.922 (3) Å
b = 18.858 (5) Å
c = 11.701 (4) Å
β = 104.60 (3)°
V = 2332 (1) Å^3
Z = 4
D_x = 1.118 Mg m^{-3}
D_m = 1.103 (5) Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 21–27°
μ = 0.615 mm^{-1}
T = 293 K
Plates
0.4 × 0.2 × 0.1 mm
Transparent

Data collection

Rigaku AFC-5 diffractometer
ω-2θ scans
Absorption correction: none
4346 measured reflections
4114 independent reflections
3558 observed reflections [$I > 0.0$]
R_{int} = 0.025
θ_{max} = 65.21°
h = 0 → 12
k = −22 → 0
l = −13 → 13
4 standard reflections monitored every 100 reflections
intensity variation: 3%

Refinement

Refinement on F
Final R = 0.053
wR = 0.057
S = 1.505
3558 reflections
761 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ = 0.36
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Molecule *A*				
C(1*b*)	0.6544 (7)	0.8498	1.1638 (8)	0.100 (5)
C(2*b*)	0.6230 (9)	0.7776 (5)	1.191 (1)	0.147 (8)
C(3*b*)	0.556 (1)	0.879 (1)	1.058 (2)	0.25 (2)
C(4*b*)	0.662 (2)	0.8955 (8)	1.272 (2)	0.25 (2)
O(5*b*)	0.7772 (4)	0.8423 (2)	1.1362 (4)	0.086 (3)
C(6*b*)	0.8365 (5)	0.8966 (3)	1.1021 (4)	0.057 (3)
O(7*b*)	0.8067 (5)	0.9569 (2)	1.1017 (5)	0.094 (3)
N(1)	0.9457 (4)	0.8736 (2)	1.0778 (4)	0.061 (2)
C(1*A*)	1.0196 (4)	0.9225 (3)	1.0236 (4)	0.052 (2)
C(1*B*)	1.1562 (4)	0.8974 (3)	1.0478 (4)	0.055 (2)
C(1*G*)	1.2258 (5)	0.8918 (3)	1.1779 (4)	0.060 (3)
C(1*D*1)	1.2628 (6)	0.8280 (3)	1.2282 (5)	0.071 (3)
C(1*E*1)	1.3307 (6)	0.8218 (4)	1.3443 (6)	0.082 (4)
C(1*Z*)	1.3608 (7)	0.8829 (5)	1.4108 (5)	0.086 (4)
C(1*E*2)	1.3272 (7)	0.9457 (4)	1.3647 (6)	0.086 (4)
C(1*D*2)	1.2549 (6)	0.9525 (3)	1.2467 (5)	0.072 (3)
C(1)	0.9628 (4)	0.9279 (3)	0.8897 (4)	0.049 (2)
O(1)	0.9392 (3)	0.9858 (2)	0.8421 (3)	0.062 (2)
N(2)	0.9489 (4)	0.8673 (2)	0.8304 (4)	0.059 (2)
C(2*A*)	0.9088 (5)	0.8655 (3)	0.7026 (5)	0.062 (3)
C(2*B*)	0.8687 (5)	0.7918 (3)	0.6545 (5)	0.067 (3)
C(2*G*)	0.7721 (8)	0.7538 (5)	0.7058 (9)	0.111 (6)
C(2*D*1)	0.661 (1)	0.7971 (8)	0.707 (2)	0.20 (1)
C(2*D*2)	0.7448 (8)	0.6808 (5)	0.6528 (8)	0.107 (6)
C(2)	1.0116 (6)	0.8898 (3)	0.6486 (6)	0.071 (3)
O(2)	1.1206 (5)	0.8942 (4)	0.6962 (6)	0.119 (4)
O(2*m*)	0.9611 (6)	0.9048 (4)	0.5314 (5)	0.118 (4)
C(2*m*)	1.052 (2)	0.9226 (7)	0.462 (1)	0.17 (1)

Molecule *B*				
C(1*b*)	0.5296 (4)	1.0365 (3)	0.7188 (4)	0.070 (3)
C(2*b*)	0.6143 (6)	1.0254 (4)	0.6371 (5)	0.100 (5)
C(3*b*)	0.4374 (5)	1.0972 (4)	0.6805 (5)	0.103 (5)
C(4*b*)	0.4597 (6)	0.9694 (4)	0.7321 (5)	0.112 (5)
O(5*b*)	0.6120 (3)	1.0473 (2)	0.8394 (3)	0.063 (2)
C(6*b*)	0.6809 (4)	1.1057 (3)	0.8664 (4)	0.056 (3)
O(7*b*)	0.6755 (3)	1.1587 (2)	0.8089 (3)	0.078 (2)
N(1)	0.7631 (3)	1.0971 (2)	0.9754 (3)	0.047 (2)
C(1*A*)	0.8344 (4)	1.1581 (2)	1.0321 (3)	0.047 (2)
C(1*B*)	0.8871 (4)	1.1410 (3)	1.1654 (4)	0.057 (3)
C(1*G*)	0.7913 (4)	1.1512 (3)	1.2353 (4)	0.059 (3)
C(1*D*1)	0.7341 (5)	1.0924 (4)	1.2726 (4)	0.081 (4)
C(1*E*1)	0.6478 (7)	1.0997 (5)	1.3394 (5)	0.103 (5)
C(1*Z*)	0.6223 (6)	1.1638 (5)	1.3768 (5)	0.104 (5)
C(1*E*2)	0.6708 (7)	1.2234 (5)	1.3407 (7)	0.122 (6)
C(1*D*2)	0.7617 (5)	1.2169 (3)	1.2685 (5)	0.084 (4)
C(1)	0.9476 (4)	1.1790 (2)	0.9841 (4)	0.047 (2)
O(1)	0.9926 (3)	1.2381 (2)	1.0101 (3)	0.065 (2)
N(2)	0.9889 (3)	1.1335 (2)	0.9175 (3)	0.052 (2)
C(2*A*)	1.1047 (4)	1.1462 (2)	0.8823 (4)	0.050 (3)
C(2*B*)	1.0992 (4)	1.1154 (3)	0.7602 (4)	0.060 (3)
C(2*G*)	0.9926 (4)	1.1448 (3)	0.6641 (4)	0.074 (3)
C(2*D*1)	0.9902 (7)	1.1039 (5)	0.5503 (5)	0.128 (6)
C(2*D*2)	0.9962 (7)	1.2225 (4)	0.6469 (6)	0.118 (6)
C(2)	1.2160 (5)	1.1172 (3)	0.9775 (4)	0.067 (3)
O(2)	1.2033 (4)	1.0865 (3)	1.0645 (4)	0.120 (4)
O(2*m*)	1.3224 (3)	1.1270 (3)	0.9554 (3)	0.114 (3)
C(2*m*)	1.4356 (5)	1.1045 (6)	1.0446 (5)	0.128 (6)

Table 2. *Selected torsion angles* (°) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
Phe φ*	−80.4 (4)	−77.2 (4)
ψ	−55.6 (4)	−14.9 (4)
ω	−173.5 (5)	−171.9 (4)
χ^1	−59.4 (4)	−80.8 (4)
χ^2	−68.0 (5)	−78.2 (5)
Leu φ	72.8 (5)	87.4 (4)
ψ†	17.3 (7)	2.5 (5)
ω‡	−174.0 (8)	176.7 (4)
χ^1	51.6 (6)	58.7 (4)
χ^2	−178.1 (8)	−174.1 (5)

* C(6*b*)—N(1)—C(1*A*)—C(1).
† N(2)—C(2*A*)—C(2)—O(2).
‡ C(2*A*)—C(2)—O(2*m*)—C(2*m*).

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). During the last stage of refinement all H atoms were placed at assumed positions (C—H = 1.08 and N—H = 0.97 Å, $U = 1.2 \times U_{eq}$ of associated non-H atoms) and refined. Refinement was by full-matrix least-squares methods using *SHELX*76 (Sheldrick, 1976). The *y* coordinate of atom C(1*b*) of molecule *A* was fixed during the refinement. The molecular conformation was drawn by the *ORTEP* program (Johnson, 1971).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71109 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1034]

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Structure of Boc-Phe-D-Leu-Thr-OMe

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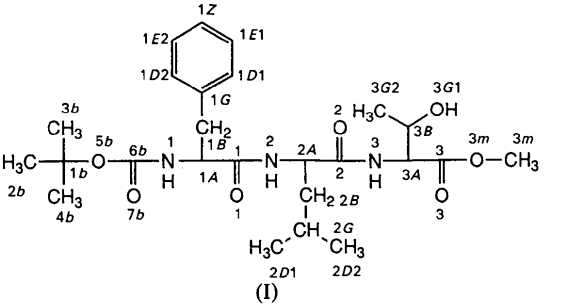
Abstract

The X-ray crystal structure analysis shows that *tert*-butoxycarbonyl-L-phenylalanyl-D-leucine-L-threonine methyl ester takes an open conformation in which the *tert*-butoxycarbonyl group is located face-to-face with the D-leucine isobutyl side chain. In the crystal, the molecules, translated by twofold screw symmetry, form an infinite sheet structure through four independent hydrogen bonds.

Comment

As one of a series of investigations into the relationship between the molecular conformation and the hydrophobicity/hydrophilicity of oligopeptides consisting of L-L, L-D or D-L sequences, the title peptide (I) was chemically synthesized and its molecular conformation determined by X-ray crystal analysis. The conformational study is also interesting in determining whether or not the conformational characteristic observed in the related Boc-Phe-D-Leu-OMe peptide (Doi, In, Ikuma, Inoue & Ishida, 1993), *i.e.* the face-to-face alignment between the *tert*-butoxycarbonyl and D-leucine isobutyl side groups, is maintained.



(I)