# Crystal structure of tertiary butyloxycarbonyl-L-Ala-ΔPhe-ΔPhe-L-Ala-$OCH_3$, $C_{30}H_{36}N_4O_7$

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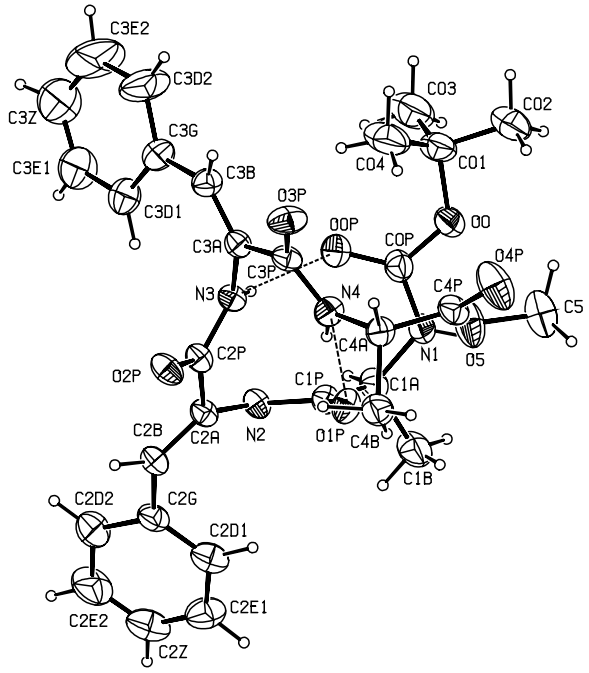


**Abstract**

$C_{30}H_{36}N_4O_7$, hexagonal, $P6_1$ (No. 169), $a$ = 15.132(5) Å, $c$ = 24.23(2) Å, $V$ = 4804.9 Å$^3$, $Z$ = 6, $R_{gt}(F)$ = 0.076, $wR_{ref}(F^2)$ = 0.223, $T$ = 293 K.

**Source of material**

The title peptide has been synthesised using the mixed anhydride coupling and the azalactone method according to [1] and [2] respectively. The peptide was crystallised from its solution in acetone-water mixture (4:1) by slow evaporation method.

**Experimental details**

The refinement was attempted in both space groups $P6_1$ and $P6_5$. However, the final progress was satisfactory in $P6_1$ space group only. The refined Flack parameter [3] was 0.1(3).

The position of the H atoms were determined geometrically, and several H positions were possible to be refined.

**Discussion**

The specific peptide structures can be designed with $\alpha,\beta$-dehydro-residues. A ΔPhe residue had been shown to adopt three conformations with values of torsion angles $\varphi,\psi$ centred at 80°,0°; –60°,–30° and –60°,140° [4]. However, a unit of two consecutive(ΔPhe-ΔPhe) residues restricts the conformation of individual ΔPhe residue to only one set of $\varphi,\psi$ values i.e. –60°,–30° or its enantiomer. In order to establish the latter, the structure of a designed peptide Boc-Ala-ΔPhe-ΔPhe-Ala-$OCH_3$ has been determined.

In the title compound, the tetrapeptide adopts a conformation having two overlapping $\beta$-turns of types II and III' with torsion angles $\varphi_1$ = –61.6(6)°, $\psi_1$ = 132.2(4)°, $\varphi_2$ = 58.3(5)°, $\psi_2$ = 17.1(4)°, $\varphi_3$ = 72.2(4), $\psi_3$ = 12.3(5)°, and $\varphi_4$ = –103.1(5)°, $\psi_4$ = –45.6(6)°, respectively. The side chain of ΔPhe at position 2 is considerably non-planar with $\chi_2^1$ = 7.9(6)°, $\chi_2^{2,1}$ = 47.3(7)° and $\chi_2^{2,2}$ = 129.7(5)° whereas the second ΔPhe residue at position (i+3) with $\chi_3^1$ = 3.4(7)°, $\chi_3^{2,1}$ = 12.6(9)°, $\chi_3^{2,2}$ = –170.3(8)° is essentially planar. The stacking of the side chains of two ΔPhe residues seems to result in the non-planarity of one of them. Two intramolecular hydrogen bonds and two intermolecular hydrogen bonds were found.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colourless prism, size 0.3 × 0.4 × 0.5 mm |
| Wavelength: | Cu $K_\alpha$ radiation (1.54180 Å) |
| $\mu$: | 6.93 cm$^{-1}$ |
| Diffractometer, scan mode: | Enraf Nonius CAD4, $\omega/\theta$ |
| $2\theta_{max}$: | 149.38° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 6281, 5651 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 4602 |
| $N(param)_{refined}$: | 403 |
| Programs: | SHELXS-97 [5], SHELXL-97 [6] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(02A) | 6*a* | –0.0752 | 0.3279 | –0.1953 | 0.08 |
| H(02B) | 6*a* | –0.0785 | 0.3963 | –0.1476 | 0.08 |
| H(02C) | 6*a* | –0.1497 | 0.2775 | –0.1452 | 0.08 |
| H(03A) | 6*a* | 0.0490 | 0.2222 | –0.1159 | 0.08 |
| H(03B) | 6*a* | 0.0146 | 0.2257 | –0.1766 | 0.08 |
| H(03C) | 6*a* | –0.0675 | 0.1689 | –0.1305 | 0.08 |
| H(04A) | 6*a* | 0.0398 | 0.3142 | –0.0488 | 0.08 |
| H(04B) | 6*a* | –0.0756 | 0.2826 | –0.0542 | 0.08 |
| H(04C) | 6*a* | 0.0090 | 0.3981 | –0.0567 | 0.08 |
| H(1) | 6*a* | 0.2413 | 0.5396 | –0.1848 | 0.08 |
| H(1A) | 6*a* | 0.392(4) | 0.504(4) | –0.152(2) | 0.08 |
| H(1BA) | 6*a* | 0.4152 | 0.6138 | –0.2198 | 0.08 |
| H(1BB) | 6*a* | 0.5003 | 0.6647 | –0.1746 | 0.08 |
| H(1BC) | 6*a* | 0.4149 | 0.6943 | –0.1791 | 0.08 |
| H(2) | 6*a* | 0.460(4) | 0.551(4) | –0.067(2) | 0.08 |
| H(2B) | 6*a* | 0.561(3) | 0.648(3) | 0.066(2) | 0.08 |
| H(2DA) | 6*a* | 0.6204 | 0.7462 | –0.0655 | 0.08 |
| H(2DB) | 6*a* | 0.6976 | 0.5942 | 0.0389 | 0.08 |

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**Table 2.** Continued.

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(2EA) | 6*a* | 0.7779 | 0.8164 | –0.1053 | 0.08 |
| H(2EB) | 6*a* | 0.8547 | 0.6623 | –0.0077 | 0.08 |
| H(2Z) | 6*a* | 0.8880 | 0.7667 | –0.0801 | 0.08 |
| H(3) | 6*a* | 0.2746 | 0.4606 | –0.0106 | 0.08 |
| H(3B) | 6*a* | 0.070(4) | 0.356(4) | 0.087(2) | 0.08 |
| H(3DA) | 6*a* | 0.2932 | 0.3483 | 0.0537 | 0.08 |
| H(3EA) | 6*a* | 0.3138 | 0.2103 | 0.0653 | 0.08 |
| H(3EB) | 6*a* | 0.0277 | 0.0399 | 0.1039 | 0.08 |
| H(3Z) | 6*a* | 0.1892 | 0.0703 | 0.1086 | 0.08 |

**Table 2.** Continued.

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(3DB) | 6*a* | –0.0016 | 0.1846 | 0.1016 | 0.08 |
| H(4) | 6*a* | 0.2351 | 0.6133 | –0.0064 | 0.08 |
| H(4A) | 6*a* | 0.101(4) | 0.678(3) | 0.038(2) | 0.08 |
| H(4BA) | 6*a* | 0.266(4) | 0.782(4) | 0.052(2) | 0.08 |
| H(4BB) | 6*a* | 0.214(3) | 0.838(4) | 0.010(2) | 0.08 |
| H(4BC) | 6*a* | 0.290(4) | 0.799(4) | –0.019(2) | 0.08 |
| H(5C) | 6*a* | 0.1242 | 0.6389 | –0.1683 | 0.08 |
| H(5D) | 6*a* | 0.0894 | 0.7140 | –0.1461 | 0.08 |
| H(5A) | 6*a* | 0.0170 | 0.5959 | –0.1404 | 0.08 |

**Table 3.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| C(01) | 6*a* | –0.0013(4) | 0.3226(4) | –0.1254(3) | 0.085(3) | 0.096(3) | 0.101(4) | 0.016(2) | –0.008(2) | –0.014(3) |
| C(02) | 6*a* | –0.0838(5) | 0.3319(6) | –0.1562(4) | 0.079(3) | 0.145(6) | 0.152(6) | 0.034(3) | –0.015(3) | –0.016(5) |
| C(03) | 6*a* | –0.0013(7) | 0.2263(7) | –0.1383(5) | 0.118(5) | 0.136(6) | 0.21(1) | 0.033(4) | –0.039(6) | –0.025(6) |
| C(04) | 6*a* | –0.0076(6) | 0.3300(8) | –0.0663(4) | 0.093(4) | 0.195(8) | 0.118(5) | –0.004(4) | 0.008(3) | –0.001(5) |
| O(0) | 6*a* | 0.0931(2) | 0.4092(3) | –0.1480(1) | 0.067(2) | 0.117(2) | 0.094(2) | 0.033(2) | –0.007(1) | 0.013(2) |
| C(0P) | 6*a* | 0.1856(3) | 0.4375(4) | –0.1294(2) | 0.082(2) | 0.104(3) | 0.068(2) | 0.047(2) | –0.004(2) | 0.002(2) |
| O(0P) | 6*a* | 0.2044(3) | 0.3960(3) | –0.0908(1) | 0.096(2) | 0.099(2) | 0.078(2) | 0.045(2) | –0.006(2) | 0.004(2) |
| N(1) | 6*a* | 0.2576(2) | 0.5140(3) | –0.1576(2) | 0.065(2) | 0.104(2) | 0.079(2) | 0.038(2) | –0.002(1) | 0.019(2) |
| C(1A) | 6*a* | 0.3644(3) | 0.5557(4) | –0.1431(2) | 0.070(2) | 0.117(3) | 0.073(2) | 0.052(2) | 0.004(2) | 0.007(2) |
| C(1B) | 6*a* | 0.4296(4) | 0.6397(7) | –0.1828(2) | 0.071(3) | 0.196(7) | 0.086(3) | 0.045(3) | 0.014(2) | 0.023(4) |
| C(1P) | 6*a* | 0.3832(3) | 0.5983(3) | –0.0848(2) | 0.062(2) | 0.087(2) | 0.072(2) | 0.045(2) | 0.011(2) | 0.010(2) |
| O(1P) | 6*a* | 0.3507(2) | 0.6525(2) | –0.0676(1) | 0.095(2) | 0.105(2) | 0.091(2) | 0.076(2) | 0.014(1) | 0.016(2) |
| N(2) | 6*a* | 0.4366(2) | 0.5689(2) | –0.0524(1) | 0.058(1) | 0.081(2) | 0.070(2) | 0.045(1) | –0.002(1) | –0.011(1) |
| C(2A) | 6*a* | 0.4561(2) | 0.5948(3) | 0.0034(2) | 0.057(2) | 0.065(2) | 0.080(2) | 0.037(1) | –0.005(1) | –0.010(2) |
| C(2B) | 6*a* | 0.5471(3) | 0.6356(3) | 0.0267(2) | 0.058(2) | 0.082(2) | 0.078(2) | 0.037(2) | –0.008(2) | –0.008(2) |
| C(2G) | 6*a* | 0.6440(3) | 0.6717(3) | –0.0052(2) | 0.057(2) | 0.080(2) | 0.107(3) | 0.031(2) | –0.004(2) | –0.005(2) |
| C(2D1) | 6*a* | 0.6683(4) | 0.7312(4) | –0.0510(3) | 0.072(2) | 0.101(3) | 0.127(4) | 0.035(2) | 0.002(3) | –0.013(3) |
| C(2D2) | 6*a* | 0.7129(4) | 0.6404(5) | 0.0102(3) | 0.079(3) | 0.141(5) | 0.144(5) | 0.068(3) | 0.002(3) | 0.013(4) |
| C(2E1) | 6*a* | 0.7612(5) | 0.7699(5) | –0.0765(3) | 0.097(3) | 0.105(4) | 0.141(5) | 0.043(3) | 0.033(3) | 0.017(3) |
| C(2E2) | 6*a* | 0.8068(5) | 0.6802(8) | –0.0187(5) | 0.076(3) | 0.166(7) | 0.207(9) | 0.072(4) | –0.001(4) | 0.001(6) |
| C(2Z) | 6*a* | 0.8268(5) | 0.7423(6) | –0.0611(4) | 0.080(3) | 0.112(4) | 0.168(6) | 0.036(3) | 0.006(4) | –0.026(5) |
| C(2P) | 6*a* | 0.3638(2) | 0.5612(3) | 0.0403(2) | 0.059(2) | 0.072(2) | 0.072(2) | 0.043(2) | –0.004(1) | –0.012(2) |
| O(2P) | 6*a* | 0.3713(2) | 0.5994(2) | 0.0858(1) | 0.067(1) | 0.104(2) | 0.078(2) | 0.042(1) | –0.009(1) | –0.029(1) |
| N(3) | 6*a* | 0.2749(2) | 0.4890(2) | 0.0202(1) | 0.056(1) | 0.066(1) | 0.070(2) | 0.034(1) | 0.002(1) | –0.007(1) |
| C(3A) | 6*a* | 0.1798(3) | 0.4564(3) | 0.0478(2) | 0.059(2) | 0.072(2) | 0.071(2) | 0.037(2) | –0.002(1) | –0.003(1) |
| C(3B) | 6*a* | 0.1237(3) | 0.3656(3) | 0.0701(2) | 0.073(2) | 0.073(2) | 0.087(2) | 0.036(2) | 0.007(2) | 0.004(2) |
| C(3G) | 6*a* | 0.1425(4) | 0.2801(4) | 0.0756(3) | 0.106(3) | 0.073(2) | 0.119(4) | 0.044(2) | –0.006(3) | 0.010(2) |
| C(3D1) | 6*a* | 0.2386(5) | 0.2870(5) | 0.0660(3) | 0.119(4) | 0.103(3) | 0.129(4) | 0.068(3) | –0.009(3) | 0.010(3) |
| C(3E1) | 6*a* | 0.2521(8) | 0.2062(7) | 0.0743(5) | 0.156(6) | 0.115(5) | 0.26(1) | 0.097(5) | –0.035(7) | 0.011(6) |
| C(3E2) | 6*a* | 0.082(2) | 0.1056(7) | 0.099(1) | 0.27(2) | 0.072(4) | 0.60(4) | 0.036(7) | –0.07(2) | 0.09(1) |
| C(3Z) | 6*a* | 0.176(1) | 0.1205(9) | 0.0956(7) | 0.20(1) | 0.124(7) | 0.29(2) | 0.102(8) | –0.05(1) | –0.006(8) |
| C(3D2) | 6*a* | 0.0614(7) | 0.1911(5) | 0.0934(6) | 0.142(6) | 0.078(3) | 0.31(2) | 0.046(4) | 0.039(7) | 0.048(6) |
| C(3P) | 6*a* | 0.1407(2) | 0.5301(3) | 0.0469(2) | 0.049(1) | 0.068(2) | 0.083(2) | 0.028(1) | 0.005(1) | –0.006(2) |
| O(3P) | 6*a* | 0.0689(2) | 0.5159(2) | 0.0764(2) | 0.069(2) | 0.087(2) | 0.139(3) | 0.040(1) | 0.042(2) | 0.013(2) |
| N(4) | 6*a* | 0.1852(2) | 0.6074(2) | 0.0133(1) | 0.069(2) | 0.079(2) | 0.091(2) | 0.050(2) | 0.014(2) | 0.009(2) |
| C(4A) | 6*a* | 0.1548(3) | 0.6845(3) | 0.0072(2) | 0.071(2) | 0.072(2) | 0.090(2) | 0.047(2) | 0.004(2) | 0.003(2) |
| C(4B) | 6*a* | 0.2479(4) | 0.7914(4) | 0.0084(3) | 0.094(3) | 0.081(3) | 0.112(4) | 0.043(2) | –0.015(3) | –0.006(2) |
| C(4P) | 6*a* | 0.0940(3) | 0.6699(3) | –0.0444(2) | 0.061(2) | 0.082(2) | 0.110(3) | 0.045(2) | –0.004(2) | –0.005(2) |
| O(4P) | 6*a* | 0.0201(4) | 0.6797(5) | –0.0472(2) | 0.115(3) | 0.233(6) | 0.154(4) | 0.129(4) | –0.025(3) | –0.040(4) |
| O(5) | 6*a* | 0.1311(3) | 0.6523(5) | –0.0869(2) | 0.124(3) | 0.223(5) | 0.092(2) | 0.128(4) | –0.006(2) | –0.005(3) |
| C(5) | 6*a* | 0.0867(7) | 0.6501(8) | –0.1398(3) | 0.145(5) | 0.194(8) | 0.117(4) | 0.114(6) | –0.035(4) | –0.021(5) |

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