ter each cycle. Most of the calculations were performed on an IBM 3090 computer at the Universidade Federal de Santa Catarina. Data collection, cell refinement and data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELX*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HA1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl *N*,*N*-Diallyl-*O*-*tert*-butyltyrosyl-α-aminoisobutyrl-α-aminoisobutyrate, $C_{28}H_{43}N_3O_5$

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Abstract

In this N- and C-protected tripeptide the nine backbone atoms are essentially planar and fully extended except for N1 and C3′ which lie below the plane and are folded in towards it. The tyrosine side chain extends away from the opposite side of the plane. There is one $(N—H)_i\cdots(O=C)_i$ intramolecular hydrogen bond and a weak $(N—H)_{i+2}\cdots(O=C)_i$ intermolecular hydrogen bond [where (i) = 2].

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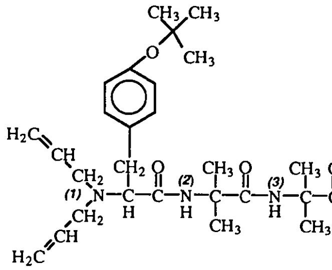
Comment

N,*N*-Diallylenkephalin analogs have been shown to have activity as δ-selective opiate antagonists (Thornber *et al.*, 1986). The title compound, (I), was synthesized at the Research Triangle Institute, North Carolina, as part of a program designed to study the relative antagonist activity within this family of compounds.



(I)

The shape of the peptide backbone is defined by the following torsion angles: ψ_1 = 20.6 (6), ω_2 = −172.2 (5), φ_2 = 179.2 (5), ψ_2 = 172.2 (5), ω_3 = 176.2 (4) and φ_3 = −54.7 (6)°. The tyrosyl side chain extends away from the main peptide backbone, χ_1 = −144.1°, and is rotated about the C1β—C1γ bond such that the aromatic ring is approximately *gauche* to the plane formed by backbone atoms C1α-C3α with the angle between the two planes being 41.5°. The hydrogen-bond parameters, N···O, H···O and N—H···O are 2.566, 2.091 Å and 113.6°, respectively, for the intramolecular N2···O2 hydrogen bond, and 3.242, 2.531 Å and 139.5°, respectively, for the weak intermolecular N3···O1 hydrogen bond. There are no other intermolecular approaches less than van der Waals separations. The *tert*-butyl group on O1ζ is disordered with a ratio of 4:1 for the high to low occupancy.

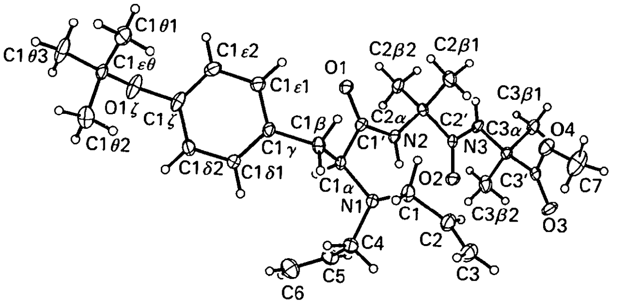


Fig. 1. Structure of the tripeptide showing 20% probability displacement ellipsoids. The disordered *tert*-butyl group on C1εθ is not shown.

Experimental

Crystal data

$C_{28}H_{43}N_3O_5$ Cu *K*α radiation
M_r = 501.65 λ = 1.54178 Å

Orthorhombic
$P2_12_12_1$
$a = 9.570$ (2) Å
$b = 10.613$ (2) Å
$c = 28.920$ (6) Å
$V = 2937.3$ (10) Å^3
$Z = 4$
$D_x = 1.134$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 18.6$–$26.5°$
$\mu = 0.592$ mm^{-1}
$T = 233$ (2) K
Plate
0.62 × 0.36 × 0.08 mm
Colorless
Crystal source: evaporation from methanol/ethylene glycol

Data collection

Siemens *R3m/V* four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: face
$T_{\min} = 0.672$, $T_{\max} = 0.943$
2243 measured reflections
2216 independent reflections
1638 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0248$
$\theta_{\max} = 56.06°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 31$
3 standard reflections monitored every 97 reflections intensity variation: constant within 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0540$
$wR(F^2) = 0.1241$
$S = 1.120$
2216 reflections
339 parameters
H atoms refined as riding
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 0.1717P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.041$

$\Delta\rho_{\max} = 0.243$ e Å^{-3}
$\Delta\rho_{\min} = -0.215$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1994)
Extinction coefficient: 0.0009 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

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

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
C1	0.6214 (7)	0.6033 (5)	0.0670 (2)	0.047 (2)
C2	0.7146 (7)	0.4960 (6)	0.0582 (2)	0.055 (2)
C3	0.7337 (7)	0.4406 (6)	0.0182 (2)	0.066 (2)
C4	0.7958 (7)	0.7705 (6)	0.0561 (2)	0.047 (2)
C5	0.9044 (7)	0.8418 (7)	0.0810 (2)	0.058 (2)
C6	0.9367 (8)	0.9588 (7)	0.0749 (3)	0.079 (2)
N1	0.6978 (5)	0.7095 (4)	0.0880 (1)	0.0366 (1)
C1α	0.6049 (6)	0.7981 (5)	0.1121 (2)	0.036 (1)
C1$'$	0.5607 (6)	0.7454 (5)	0.1593 (2)	0.034 (1)
O1	0.4553 (4)	0.7863 (4)	0.1790 (1)	0.050 (1)
C1β	0.4770 (6)	0.8434 (5)	0.0837 (2)	0.042 (2)
C1γ	0.4336 (6)	0.9797 (5)	0.0916 (2)	0.037 (1)
C1δ1	0.5055 (7)	1.0779 (5)	0.0719 (2)	0.045 (2)
C1δ2	0.4643 (7)	1.2013 (6)	0.0783 (2)	0.052 (2)
C1ζ	0.3462 (7)	1.2277 (6)	0.1039 (2)	0.047 (2)
O1ζ	0.3076 (5)	1.3509 (4)	0.1131 (2)	0.072 (2)
C1ϵ2	0.2728 (7)	1.1305 (6)	0.1244 (2)	0.053 (2)
C1ϵ1	0.3180 (6)	1.0075 (6)	0.1177 (2)	0.048 (2)
C1$\epsilon\theta$	0.2000 (5)	1.4090 (4)	0.0858 (2)	0.0476 (1)
C1θ1	0.0697 (6)	1.3282 (6)	0.0810 (3)	0.067 (3)
C1θ2	0.2651 (8)	1.4342 (7)	0.0390 (2)	0.067 (3)
C1θ3	0.1687 (9)	1.5302 (6)	0.1114 (3)	0.087 (4)
C1θ4	0.2450 (40)	1.5366 (17)	0.0670 (11)	0.136 (21)
C1θ5	0.1157 (31)	1.4254 (35)	0.1300 (7)	0.094 (14)
C1θ6	0.1156 (33)	1.3375 (30)	0.0498 (9)	0.120 (19)
N2	0.6435 (5)	0.6568 (4)	0.1758 (1)	0.038 (1)
C2α	0.6240 (6)	0.5767 (5)	0.2168 (2)	0.034 (1)
C2$'$	0.7548 (6)	0.4916 (5)	0.2172 (2)	0.036 (1)
O2	0.8375 (4)	0.4915 (4)	0.1847 (1)	0.054 (1)
C2β1	0.4955 (6)	0.4933 (6)	0.2109 (2)	0.055 (2)
C2β2	0.6143 (7)	0.6551 (5)	0.2606 (2)	0.045 (1)
N3	0.7747 (5)	0.4177 (4)	0.2543 (1)	0.036 (1)
C3α	0.8911 (6)	0.3291 (5)	0.2560 (2)	0.035 (1)
C3$'$	0.8857 (7)	0.2438 (5)	0.2136 (2)	0.039 (1)
O3	0.9867 (5)	0.2020 (4)	0.1941 (1)	0.064 (1)
C3β1	0.8726 (7)	0.2438 (5)	0.2981 (2)	0.049 (2)
C3β2	1.0310 (7)	0.3960 (6)	0.2591 (2)	0.062 (2)
O4	0.7543 (5)	0.2129 (4)	0.2034 (1)	0.056 (1)
C7	0.7350 (10)	0.1293 (7)	0.1646 (3)	0.105 (3)

Table 2. *Selected geometric parameters* (Å, °)

C1—N1	1.474 (7)	C1$\epsilon\theta$—C1θ3	1.513 (8)
C1—C2	1.470 (8)	C1$\epsilon\theta$—C1θ2	1.514 (8)
C2—C3	1.310 (8)	C1$\epsilon\theta$—C1θ1	1.520 (8)
C4—N1	1.466 (7)	C1$\epsilon\theta$—C1θ6	1.520 (23)
C4—C5	1.474 (8)	C1$\epsilon\theta$—C1θ5	1.522 (24)
C5—C6	1.292 (9)	C1$\epsilon\theta$—C1θ4	1.522 (30)
N1—C1α	1.471 (6)	N2—C2α	1.470 (6)
C1α—C1$'$	1.536 (7)	C2α—C2β1	1.525 (8)
C1α—C1β	1.552 (7)	C2α—C2β2	1.519 (7)
C1$'$—O1	1.236 (6)	C2α—C2$'$	1.543 (7)
C1$'$—N2	1.320 (6)	C2$'$—O2	1.229 (6)
C1β—C1γ	1.522 (8)	C2$'$—N3	1.343 (6)
C1γ—C1ϵ1	1.370 (8)	N3—C3α	1.459 (6)
C1γ—C1δ1	1.373 (8)	C3α—C3β2	1.518 (8)
C1δ1—C1δ2	1.380 (8)	C3α—C3β1	1.529 (7)
C1δ2—C1ζ	1.380 (8)	C3α—C3$'$	1.523 (7)
C1ζ—C1ϵ2	1.381 (9)	C3$'$—O3	1.205 (7)
C1ζ—O1ζ	1.384 (7)	C3$'$—O4	1.333 (7)
O1ζ—C1$\epsilon\theta$	1.436 (6)	O4—C7	1.442 (7)
C1ϵ2—C1ϵ1	1.389 (8)		
N1—C1—C2	111.3 (5)	C1θ3—C1$\epsilon\theta$—C1θ1	111.2 (3)
C3—C2—C1	125.8 (6)	C1θ2—C1$\epsilon\theta$—C1θ1	110.8 (3)
N1—C4—C5	111.7 (5)	O1ζ—C1$\epsilon\theta$—C1θ6	122.9 (15)
C6—C5—C4	126.5 (7)	O1ζ—C1$\epsilon\theta$—C1θ5	88.1 (10)
C1α—N1—C4	113.8 (4)	C1θ6—C1$\epsilon\theta$—C1θ5	110.5 (3)
C1α—N1—C1	112.6 (4)	O1ζ—C1$\epsilon\theta$—C1θ4	112.1 (10)
C4—N1—C1	113.3 (4)	C1θ6—C1$\epsilon\theta$—C1θ4	110.5 (3)
N1—C1α—C1$'$	110.9 (4)	C1θ5—C1$\epsilon\theta$—C1θ4	110.4 (3)
N1—C1α—C1β	115.0 (4)	C1$'$—N2—C2α	128.8 (5)
C1$'$—C1α—C1β	111.6 (5)	N2—C2α—C2β1	110.4 (4)
O1—C1$'$—N2	125.1 (5)	N2—C2α—C2β2	111.3 (4)
O1—C1$'$—C1α	120.4 (5)	C2β1—C2α—C2β2	111.3 (5)
N2—C1$'$—C1α	114.6 (5)	N2—C2α—C2$'$	103.9 (4)
C1γ—C1β—C1α	115.4 (5)	C2β1—C2α—C2$'$	108.4 (4)
C1ϵ1—C1γ—C1δ1	118.0 (5)	C2β2—C2α—C2$'$	111.3 (4)
C1ϵ1—C1γ—C1β	120.5 (5)	O2—C2$'$—N3	121.3 (5)
C1δ1—C1γ—C1β	121.4 (5)	O2—C2$'$—C2α	121.1 (5)
C1γ—C1δ1—C1δ2	121.4 (6)	N3—C2$'$—C2α	117.6 (5)
C1ζ—C1δ2—C1δ1	120.0 (6)	C2$'$—N3—C3α	120.8 (4)
C1δ2—C1ζ—C1ϵ2	119.6 (5)	N3—C3α—C3β2	111.9 (4)
C1δ2—C1ζ—O1ζ	120.9 (6)	N3—C3α—C3β1	108.6 (4)
C1ϵ2—C1ζ—O1ζ	119.2 (6)	C3β2—C3α—C3β1	109.4 (5)
C1ζ—O1ζ—C1$\epsilon\theta$	119.4 (4)	N3—C3α—C3$'$	109.3 (4)
C1ζ—C1ϵ2—C1ϵ1	118.9 (6)	C3β2—C3α—C3$'$	110.9 (5)
C1γ—C1ϵ1—C1ϵ2	122.0 (6)	C3β1—C3α—C3$'$	106.6 (4)
O1ζ—C1$\epsilon\theta$—C1θ3	103.8 (4)	O3—C3$'$—O4	124.1 (5)
O1ζ—C1$\epsilon\theta$—C1θ2	105.7 (5)	O3—C3$'$—C3α	124.7 (6)
C1θ3—C1$\epsilon\theta$—C1θ2	111.6 (3)	O4—C3$'$—C3α	111.0 (5)
O1ζ—C1$\epsilon\theta$—C1θ1	113.3 (4)	C3$'$—O4—C7	116.5 (6)

Data collection, cell refinement, data reduction, structure solution and preparation of graphics were performed using *SHELXTL-Plus* (Sheldrick, 1992). The structure was refined and the material prepared for publication with *SHELXL93* (Sheldrick, 1994).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71812 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BK1005]

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Nitrilotriacetic Acid, $C_6H_9NO_6$

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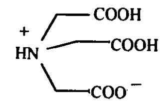
Abstract

Nitrilotriacetic acid participates as a multidentate ligand in many metal chelation compounds of Al, B, Bi, Ca, Co, Cr, Cu, Fe, Mo, Nd, Ni, Pb, Ti, W, Zn and Zr. The structure of this popular ligand has been refined and compared with that of calcium nitrilotriacetate dihydrate [Whitlow (1972). *Acta Cryst.* B**28**, 1914–1919], which is another structure where this ligand is not affected by chelation.

Comment

The structure of nitrilotriacetic acid, which exists in the zwitterionic form (I) in the crystal, has been published previously (Stanford, 1967); it was described as well as possible on the basis of visually estimated photographic data (R = 0.093). As part of our continuing studies of amide derivatives of nitrilotriacetic acid and their chelation complexes with metals (Smith, Sucheck & Pinkerton, 1992; Smith, Cramer, Sucheck & Skrzypczak-Jankun, 1992; Skrzypczak-Jankun & Smith, 1994*a*,*b*), we have reexamined this ligand and report here the structure refined to a higher degree of accuracy.



(I)

Nitrilotriacetic acid (NTA) or its derivatives are present in many complex structures in which a metal atom is bonded to several atoms of the polydentate complexing agent. However, only a few structures of unchelated acid, anion or NTA derivatives are known: nitrilotriacetic acid (Stanford, 1967); calcium nitrilotriacetate dihydrate (Whitlow, 1972); 2,2′,2″-nitrilotriethanol (Mootz, Brodalla & Wiebcke, 1989); *N*-methylnitrilotriacetamide (Skrzypczak-Jankun & Smith, 1994*a*). In the last two of these structures, the central N atom is not protonated and the N—C bonds are shorter (1.467 and 1.463 Å, respectively) and the C—N—C angles smaller (110.7 and 110.9°, respectively) than in the protonated compounds. In CaNTA.2H_2O, five of the six NTA O atoms are bound to metal ions, but each O atom is joined to a different Ca ion, so that the NTA zwitterion is *not* the chelating ligand, but part of a three-dimensional ionic network similar to that seen in NTA itself. The structure described in this paper agrees very well with that observed in CaNTA.2H_2O [mean values for N—C and C—N—C: 1.500 (2) Å and 113.0 (7)°, respectively, in NTA, and 1.496 (5) Å and 112.0 (15)°, respec-

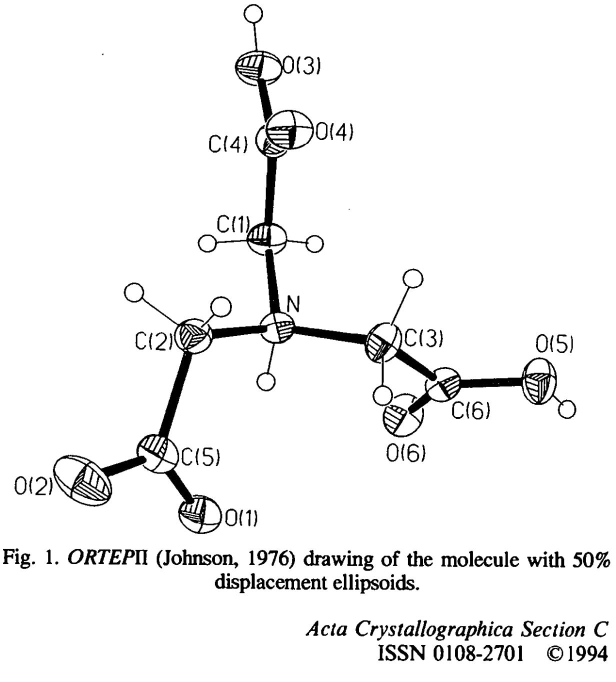


Fig. 1. *ORTEPII* (Johnson, 1976) drawing of the molecule with 50% displacement ellipsoids.

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