Stabile, M. R., Hudlicky, T., Meisels, M. L., Butora, G., Gum, A. G., Fearnley, S. P., Thorpe, A. J. & Ellis, M. R. (1995). *Chirality*, 7, 556–559.

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N-Benzyl-*N*-(*tert*-butyloxycarbonyl)-glycine, an *N*-Substituted Glycine (Peptoid) Monomer

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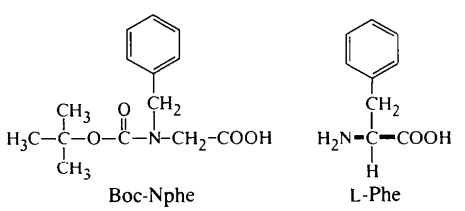
Abstract

The title compound, $C_{14}H_{19}NO_4$, an amino acid mimic, was crystallized from ethyl acetate solution in a centrosymmetric space group. The distance between the side chain and the backbone was shorter than usually found in amino acids. The positional shift from α-carbon to nitrogen produced no significant steric hindrance between the side chain and the *tert*-butyl group.

Comment

Peptoids, amino acid mimics, have a basic *N*-substituted glycine unit and were designed as a new series of potentially bioactive compounds (Simon *et al.*, 1992; Zuckermann *et al.*, 1992). The side chains or functional groups are bonded to the α-N atom, unlike the usual side chain, which is bound to the α-C atom. The chemical structure is similar to that of a β-amino acid and, therefore, metabolic stability, reduction of conformational constraint by chirality and a wide variability of functional groups are expected (Figliozzi *et al.*, 1996). Relative to polypeptides, polypeptoids have their side chains shifted by one position along the backbone. A monomer derivative, *N*-benzyl-*N*-(*tert*-butyloxycarbonyl)glycine (Boc–Nphe), was crystallized from ethyl acetate solution in the centrosymmetric space group $P2_1/a$.



The N1—C1*B* bond length is 1.456 (4) Å. As expected, this linkage is shorter than a Cα—Cβ bond length (1.54 Å). In comparison with the corresponding phenylalanine derivative, the benzyl group is spatially closer to the *tert*-butyl group by one covalent bond. No steric hindrance, however, was found in the title compound. The O5*BT*—C6*BT*—N1—C1*A* torsion angle, which corresponds to the ω angle of a peptide bond, has a value of 177.4 (3)° and is in the *trans* region. Although the O5*BT*—C6*BT*—N1—C1*B* torsion angle in the peptoid is −1.3 (3)°, no significant contact was found between the benzyl and *tert*-butyl groups. In packing, the molecules of Boc–Nphe form hydrogen-bonded dimers of O1*T*···O1 distance 2.622 (3) Å [O1*T*—H1*T* 0.819 (3), H1*T*···O1 1.807 (3) Å and O1*T*—H1*T*···O1 172.8 (2)°] across a center of symmetry at $-x$, $-y$, $-z+1$.

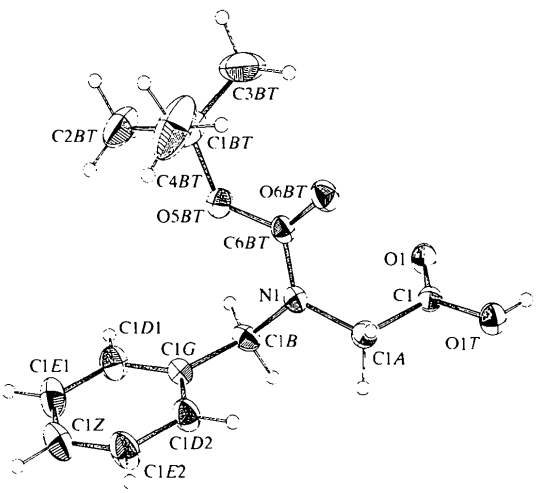


Fig. 1. A view of the title compound with displacement ellipsoids drawn at the 50% probability level.

Experimental

The synthesis of the title compound was carried out according to Simon *et al.* (1992). A Schiff base was formed by mixing glyoxylic acid and benzylamine (molar ratio 1:1) in MeOH, and was hydrolyzed on Pd–carbon. The product was extracted with ethyl acetate (AcOEt) and aqueous $NaHCO_3$, and was then reacted with di-*tert*-butyl dicarbonate in dioxane/aqueous NaOH solution. The reaction mixture was extracted with AcOEt and aqueous $KHSO_4$. The AcOEt extract was condensed and the residue crystallized over a period of 2–3 d without any solvent.

Crystal data

$C_{14}H_{19}NO_4$
M_r = 265.30

Cu $K\alpha$ radiation
λ = 1.54180 Å

Monoclinic	Cell parameters from 20 reflections
$P2_1/a$	θ = 19.80–20.03°
a = 13.323 (2) Å	μ = 0.713 mm^{-1}
b = 7.8005 (9) Å	T = 293 (2) K
c = 15.324 (2) Å	Block
β = 110.499 (8)°	0.6 × 0.4 × 0.1 mm
V = 1491.7 (3) Å^3	Colorless
Z = 4	
D_x = 1.181 Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-5*R* diffractometer	R_{int} = 0.018
$2\theta-\omega$ scans	θ_{max} = 63.18°
Absorption correction: none	$h = 0 \rightarrow 15$
2533 measured reflections	$k = -9 \rightarrow 0$
2413 independent reflections	$l = -17 \rightarrow 16$
1783 reflections with $I > 2\sigma(I)$	3 standard reflections every 100 reflections
	intensity decay: −0.7%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.068	$\Delta\rho_{max}$ = 0.281 e Å^{-3}
$wR(F^2)$ = 0.183	$\Delta\rho_{min}$ = −0.458 e Å^{-3}
S = 1.176	Extinction correction: *SHELXL*93
2365 reflections	Extinction coefficient: 0.0038 (8)
176 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.1062P)^2 + 0.6150P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Scan widths were (1.628 + 0.3tanθ)° in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statics were consistent with centrosymmetric space group $P2_1/a$. Intensities were measured to the mechanical limit of the diffractometer; the θ_{max} was set approximately at 65°. H atoms were calculated at idealized positions and refined with fixed isotropic displacement parameters (U_{iso} = 1.2U_{eq} for the associated C atom or 1.5U_{eq} for methyl C atoms).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1067). Services for accessing these data are described at the back of the journal.

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Figliozzi, G. M., Goldsmith, R., Ng, S. C., Banville, S. C. & Zuckermann, R. N. (1996). *Methods Enzymol.* **267**, 437–447.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Simon, R. J., Kania, R. S., Zuckermann, R. N., Huebner, V. D., Jewell, D. A., Banville, S., Ng, S., Wang, L., Rosenberg, S., Marlowe, C. K., Spellmeyer, D. C., Tan, R., Frankel, A. D., Santi, D. V., Cohen, F. E. & Bartlett, P. A. (1992). *Proc. Natl Acad. Sci. USA*, **89**, 9367–9371.

Zuckermann, R. N., Kerr, J. M., Kent, S. B. H. & Moos, W. H. (1992). *J. Am. Chem. Soc.* **114**, 10646–10647.

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9-Deoxy-15-hydroxy- and 9-Deoxy-19-hydroxycotylenol†

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Abstract

The title analogs (both $C_{21}H_{34}O_4$) of cotylenol, a plant-growth regulator, both have a chair–sofa eight-membered ring, which has been recognized as important for the biological activity of this class of compounds.

Comment

Cotylenol, (I) (Sassa *et al.*, 1975), is a common aglycon of cotylenins and is known to have potent plant hormone-like activity, similar to fusicoccin. Since the binding protein of fusicoccin has recently been identified as a member of the 14–3–3 proteins (Korthout & De Boer, 1994), these fusicoccane diterpenoids have at-

† Alternative nomenclature: (1*R*,3a*S*,4*R*,5*S*,9a*R*)-1,2,3,3a,4,5,6,8,9,9a-decahydro-7-(1-hydroxy-1-methylethyl)-1-(methoxymethyl)-4,9a-dimethyldicyclopenta[*a*,*d*]cyclooctene-1,5-diol and (1*R*,3a*S*,4*R*,5*S*,9a*R*)-1,2,3,3a,4,5,6,8,9,9a-decahydro-7-[(*S*)-2-hydroxy-1-methylethyl]-1-(methoxymethyl)-4,9a-dimethyldicyclopenta[*a*,*d*]cyclooctene-1,5-diol.