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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1003). Services for accessing these data are described at the back of the journal.

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(7*R*,8*S*,10b*R*)-7,8-Dihydroxy-1,5,6,7,8,9,-10,10b-octahydro-3*H*-1,3-oxazolo[4,3-*a*]isoquinolin-3-one

KHALIL A. ABBOUD, GABOR BUTORA, STEPHEN P. FEARNLEY, ANDREW G. GUM, MICHELE R. STABILE AND TOMAS HUDLICKY

Department of Chemistry, University of Florida, PO Box 117200, Gainesville, Florida 32611-7200, USA. E-mail: abboud@chem.ufl.edu

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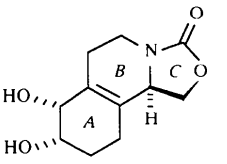
Abstract

The title compound, $C_{11}H_{15}NO_4$, was synthesized as an intermediate in a synthesis of the morphine skeleton. The two six-membered rings adopt $^4H_3$ half-chair conformations. The five-membered ring is in an envelope (*E*) conformation. Chains of the molecules hydrogen bonded through the allylic hydroxyl and carbonyl groups extend along the *b* axis. These chains are cross-linked along the [101] direction by hydrogen bonds between the adjacent secondary OH group and the allylic O atom [allylic O···O(x, $1+y$, z) 2.836 (2) Å, O—H···O 133 (2)°; secondary hydroxyl O···O($\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$) 2.751 (2) Å, O—H···O 174 (2)°].

Comment

In the past 40 years, numerous total syntheses of morphine have been published [for a recent review see Hudlicky *et al.* (1996), and references therein]. We recently reported a chemo-enzymatic synthesis of the morphine skeleton in which the title compound, (1), was synthesized in one of the intermediate steps (Butora *et al.*, 1996). Attempts have been made to relate the absolute stereochemistry at C10b to either C7 or C8 using standard spectroscopic techniques. Careful coupling-constant analysis (^{1}H NMR, various solvents) suggested the absolute stereochemistry shown below. Although nuclear Overhauser enhancement experiments seemed to support these conclusions, final proof was sought from a single-crystal X-ray structure determination. As the absolute stereochemistry at C7 and C8 is set enzymatically (Stabile *et al.*, 1995), this also provided proof of the absolute stereochemistry of (1) as shown.



(1)

The bond lengths and angles in (1) are in good agreement with counterparts observed in other organic compounds (Allen *et al.*, 1987). The molecules of (1) have two six-membered rings fused through the C6a=C10a double bond, which has the only zero-value endocyclic torsion angle in either ring. The planar geometry around the double bond forces the ring conformations to deviate from a more stable chair conformation. Consequently, rings *A* and *B* adopt half-chair conformations which may be described as $^4H_3$ according to Boeyens (1978) terminology. Ring *A* has C8 and C9 at distances of −0.465 (3) and 0.294 (3) Å, respectively, from the plane of C6a, C7, C10a and C10, while N4 and C5 are at distances of −0.340 (3) and 0.303 (4) Å, respectively, from the plane of C6, C6a, C10a and C10b. Ring *C* adopts an envelope conformation with C10b occupying the flap position at a distance of 0.382 (3) Å from the plane of C1, O2, C3 and N4.

Each molecule of (1) is involved in two intermolecular hydrogen bonds. One hydrogen bond between O7—H7 and O1 results in a chain of molecules extending

along the *b* axis. The second hydrogen bond, between O8—H8 and O7, cross-links the chains along the [101] direction.

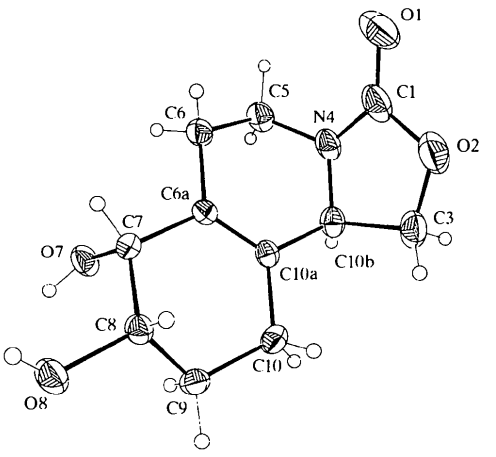


Fig. 1. The molecular structure of (1) showing the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level.

Experimental

The synthesis of (1) has been reported previously (Butora *et al.*, 1996). Colorless blocks of (1) were obtained by slow evaporation of an ethyl acetate solution.

Crystal data

$C_{11}H_{15}NO_4$
M_r = 225.24
Orthorhombic
$P2_12_12_1$
a = 8.519 (2) Å
b = 9.315 (2) Å
c = 13.429 (3) Å
V = 1065.7 (4) Å^3
Z = 4
D_x = 1.404 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 10–11°
μ = 0.107 mm^{-1}
T = 298 (2) K
Block
0.38 × 0.34 × 0.31 mm
Colorless

Data collection

Siemens *P3/PC* diffractometer
ω scans
Absorption correction: by integration based on measured crystal faces (*SHELXTL5*; Sheldrick, 1995)
T_{min} = 0.963, T_{max} = 0.972
2745 measured reflections
1224 independent reflections
1115 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 27.5°
h = −11 → 11
k = 0 → 12
l = 0 → 17
4 standard reflections
every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.078
S = 1.06
2447 reflections
154 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 0.4538P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXTL5*
Extinction coefficient: 0.034 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.209 (3)	N4—C10b	1.453 (2)
C1—O2	1.351 (3)	N4—C5	1.457 (2)
C1—N4	1.352 (3)	C7—O7	1.442 (2)
O2—C3	1.440 (3)	C8—O8	1.426 (2)
O1—C1—O2	122.5 (2)	C1—N4—C10b	110.8 (2)
O1—C1—N4	127.8 (2)	C1—N4—C5	121.1 (2)
O2—C1—N4	109.7 (2)	C10b—N4—C5	117.36 (14)
C1—O2—C3	109.0 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7···O1^i	0.81 (3)	2.22 (3)	2.836 (2)	133 (2)
O8—H8···O7^{ii}	0.83 (2)	1.93 (2)	2.751 (2)	174 (2)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.

Friedel pairs were used in an attempt to determine the absolute configuration, but refinement of the Flack (1983) parameter was inconclusive. The hydroxyl H atoms were refined without constraints, while the rest of the H atoms were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.98 and 0.97 Å were used for tertiary and secondary C atoms, respectively. The displacement parameters of the H atoms were set at $1.2U_{eq}$ of the parent C.

Data collection: *P3/PC* (Siemens, 1993). Cell refinement: *P3/PC*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL5* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL5*. Molecular graphics: *SHELXTL5*. Software used to prepare material for publication: *SHELXTL5*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1088). Services for accessing these data are described at the back of the journal.

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

MITSUNOBU DOI, KAZUE KINOSHITA, AKIKO ASANO, RYUJI YONEDA, TAKUSHI KURIHARA AND TOSHIMASA ISHIDA

Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 569-1094, Japan. E-mail: doit@oysun01.oups.ac.jp

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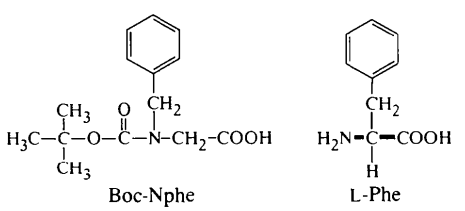
Abstract

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 $-x$, $-y$, $-z+1$.

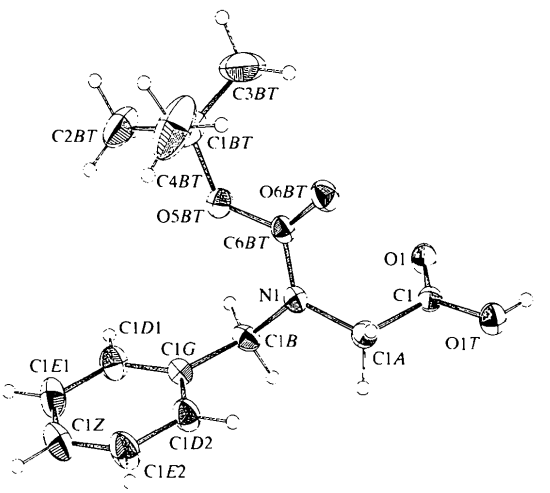


Fig. 1. A view of the title compound with displacement ellipsoids drawn at the 50% probability level.

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