Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-(2-Hydroxynaphthylmethyl)-(*S*)-proline methyl ester

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.055
wR factor = 0.130
Data-to-parameter ratio = 13.5

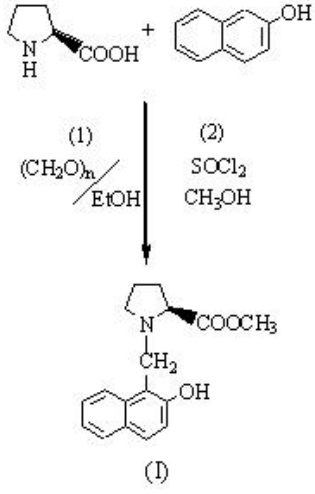
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{16}H_{17}NO_3$, a new derivative of L-proline, was synthesized *via* a Mannich reaction. The X-ray crystal analysis revealed that the pyrrolidine ring adopts an envelope conformation, with the N atom deviating by 0.515 (5) Å from the mean plane through the four C atoms. The 2-hydroxynaphthylmethyl moiety, which is *trans* to the methoxycarbonyl group, adopts a pseudo-equatorial direction.

Received 18 July 2003
Accepted 3 September 2003
Online 7 October 2003

Comment

In order to make a tridentate aminoalcohol for asymmetric Michael addition (Yamakoshi *et al.*, 1999; Sasai & Suzuki, 1993), *N*-(2-Hydroxynaphthylmethyl)-L-proline methyl ester, (I), was prepared *via* a Mannich reaction of L-proline, β-naphthol and formaldehyde, followed by esterification. Here we report on the synthesis and the crystal structure of the title compound, (I), which is useful for the preparation chiral amino alcohols. The original *S* configuration of the chiral center at C4 did not change during the preparation, as shown in Fig. 1. Selected bond distances and angles are given in Table 1. As a result of its relative flexibility, the proline ring can adopt different conformations (Stavropoulos *et al.*, 1989, Puliti *et al.*, 1996, 2000). Interestingly, here it adopts an envelope conformation, with atom N1 deviating by 0.515 (5) Å from the plane defined by atoms C1/C2/C3/C4. The 2-hydroxynaphthylmethyl group on N1 is *trans* to the methoxycarbonyl group and adopts a pseudo-equatorial direction. This makes the 2-hydroxynaphthylmethyl group *gauche* to the methoxycarbonyl group and atom H4, with a torsion angle C7—N1—C4—C5 of 78.7 (4)°.



(I)

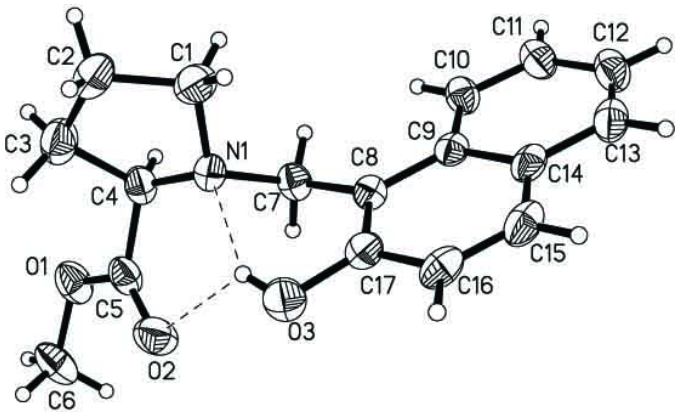


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Dashed lines indicate hydrogen bonds and H atoms are drawn as small spheres of arbitrary radius.

Conjugation between O1 and the carbonyl double bond C5═O2 is observed, as shown by the bond distances of 1.325 (4) and 1.450 (5) Å for bonds O1—C5 and O1—C6, respectively. These values are in accordance with those found in analogous compounds, *viz*. *N*-[2(*R*)-bromopropanoyl]-(2*S*)-proline methyl ester (Ingham & Lenman, 1995) and *N*-(*S*)-α-bromophenylacetyl-(*S*)-proline methyl ester (Smits *et al.*, 1986). The bond distance O3—C17 [1.370 (4) Å] is slightly longer than the corresponding distance of 1.357 (2) Å in 4-[(2-hydroxy-1-naphthyl)methyl]-2,2,5-triphenyl-1,3-dioxa-4-azonia-2-boratacyclopent-4-ene (Kliegel *et al.*, 2001). On the other hand, bond O3—C17 is shorter than O1—C6 [1.450 (5) Å] because of the π–π conjugation. The methylene and the hydroxyl groups bonded to the naphthalene backbone are essentially coplanar with the naphthalene plane, with displacements of 0.064 (1) and 0.034 (1) Å, respectively. The dihedral angle between the C1/C2/C3/C4 plane of the pyrrolidine ring and the naphthalene ring is 100.5 (8)°.

The conformation of (I) is stabilized by bifurcated intramolecular hydrogen bonds between hydroxyl O atom O3 and the ester carbonyl atom O2, and the pyrrolidone N atom N1 (see Table 2 for details). The hydroxyl H atom, H3, was observable in a Fourier difference synthesis, as a well defined, small, positive electron density peak. This intramolecular hydrogen bond induces atom N1 of the pyrrolidine ring to deviate from the plane defined by the other three atoms (C1, C4 and C7) attached to it.

Experimental

N-(2-Hydroxynaphthylmethyl)-L-proline: Formaldehyde solution (37%, 20 ml) was added dropwise to a stirred solution of β-naphthol (2.66 g, 18.4 mmol) and L-proline (2.12 g, 18.4 mmol) in EtOH (40 ml). The mixture was then stirred at room temperature for 3.5 h, concentrated under reduced pressure, and finally cooled in the refrigerator. The solid product was filtered and recrystallized from EtOH. Yield: 4.52 g (90.4%); m.p.: 455–457 K; IR (KBr) 3219 (*w*), 3038 (*m*), 1739 (*s*), 1620 (*s*), 1335 (*m*), 826 (*s*), 759 (*s*) cm^{-1}; ^1H NMR (CD_3OD) *d* 7.16–8.23 (*m*, 6H), 4.85 (*s*, 2H, covered by CD_3OD), 4.06 (*q*, *J* = 6.0, 1H), 3.37 (*m*, 2H), 2.15–2.53 (*m*, 2H), 2.15 (*m*, 2H) p.p.m. Analysis for $C_{16}H_{17}NO_3$, calculated: C 70.85, H 6.27, N 5.17%; found: C 70.81, H 6.31, N 5.16%.

N-[(2-Hydroxynaphthyl)methyl]-L-proline methyl ester: To a solution of *N*-(2-Hydroxynaphthylmethyl)-L-proline (4.52 g, 16.6 mmol) in MeOH (35 ml) cooled to 268 K, $SOCl_2$ (3 ml, 31.1 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for a further 0.5 h and then refluxed for 4.5 h. The reaction mixture was washed with a saturated Na_2CO_3 solution (30 ml) and extracted with ethyl acetate (3 × 30 ml). The organic phase was washed with brine (2 × 20 ml) and dried with Na_2SO_4 and finally concentrated in vacuo. The residue was recrystallized from EtOH giving crystals of (I). Yield: 2.89 g (81.5%); m.p.: 406–408 K; IR (KBr) 3264 (*w*), 3042 (*m*), 1740 (*s*), 1619 (*s*), 1335 (*m*), 1131(*s*), 828 (*s*), 758 (*s*) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) 7.13–7.86 (*m*, 6H), 4.27–4.37 (*q*, *J* = 14.0, 2H), 3.76 (*s*, 3H), 3.47–3.51 (*m*, *J* = 6.8, 6.4, 1H), 3.13–3.14 (*m*, 2H), 2.43–2.45 (*m*, 2H), 2.00–2.06 (*m*, 2H) p.p.m. Analysis for $C_{17}H_{19}NO_3$, calculated: C 70.58, H 6.67, N 4.91%; found: C 71.57, H 6.70, N 4.89%. Crystals suitable for X-ray crystallography were obtained as colourless rods by slow evaporation from acetonitrile/cyclohexane.

Crystal data

$C_{17}H_{19}NO_3$	Mo *Kα* radiation
M_r = 285.33	Cell parameters from 744 reflections
Orthorhombic, $P2_12_12_1$	θ = 2.3–19.7°
a = 9.427 (6) Å	μ = 0.09 mm^{-1}
b = 11.692 (7) Å	*T* = 293 (2) K
c = 13.501 (8) Å	Column, colourless
V = 1488.0 (15) $Å^3$	0.40 × 0.35 × 0.10 mm
Z = 4	
D_x = 1.274 Mg m^{-3}	

Data collection

Bruker *SMART* CCD area-detector diffractometer	2585 independent reflections
φ and ω scans	1420 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	R_{int} = 0.058
T_{min} = 0.966, T_{max} = 0.991	θ_{max} = 25.0°
5521 measured reflections	*h* = −5 → 11
	k = −12 → 13
	l = −15 → 16

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0458P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.055	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.130	$\Delta\rho_{max}$ = 0.20 e $Å^{-3}$
S = 0.99	$\Delta\rho_{min}$ = −0.18 e $Å^{-3}$
2585 reflections	Absolute structure: Flack (1983)
191 parameters	Flack parameter = −1 (2)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.325 (4)	N1—C4	1.448 (4)
O1—C6	1.450 (5)	N1—C1	1.463 (5)
O2—C5	1.193 (4)	N1—C7	1.464 (4)
O3—C17	1.370 (4)	C4—C5	1.488 (5)
C5—O1—C6	116.6 (3)	O2—C5—C4	125.2 (4)
C4—N1—C1	106.1 (3)	O1—C5—C4	111.4 (3)
O2—C5—O1	123.3 (4)		
C4—N1—C1—C2	36.1 (4)	C6—O1—C5—O2	−2.3 (6)
C7—N1—C4—C5	78.7 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2	0.850	2.470	3.080 (4)	130.0
O3—H3···N1	0.850	1.960	2.709 (4)	147.0

The H atoms were introduced in calculated positions as riding atoms, with C—H bond lengths of 0.93–0.97 Å, and O—H = 0.85 Å; displacement parameters were set equal to 1.2(CH-aromatic and CH_2) and 1.5(CH_3 and O3 hydroxyl H atom) times U_{eq}(parent C atom) .

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997) and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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