

1-*tert*-Butyl 2-methyl 4-(*R*)-hydroxy-pyrrolidine-1,2-(2*S*)-dicarboxylate

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Key indicators

Single-crystal X-ray study

$T = 160\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.030

wR factor = 0.075

Data-to-parameter ratio = 11.2

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

The title compound, $\text{C}_{11}\text{H}_{19}\text{NO}_5$, is a protected derivative of *trans*-4-hydroxy-*L*-proline. The pyrrolidine ring has a twisted conformation. The N atom has planar coordination and is conjugated with the attached ester group. The methyl ester substituent is pseudo-equatorial, while the hydroxy group is pseudo-axial and acts as a hydrogen-bond donor to a carbonyl O atom in an adjacent molecule, forming molecular chains.

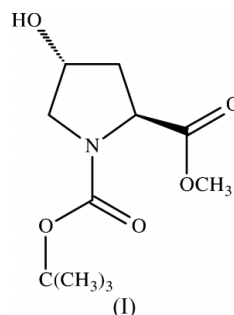
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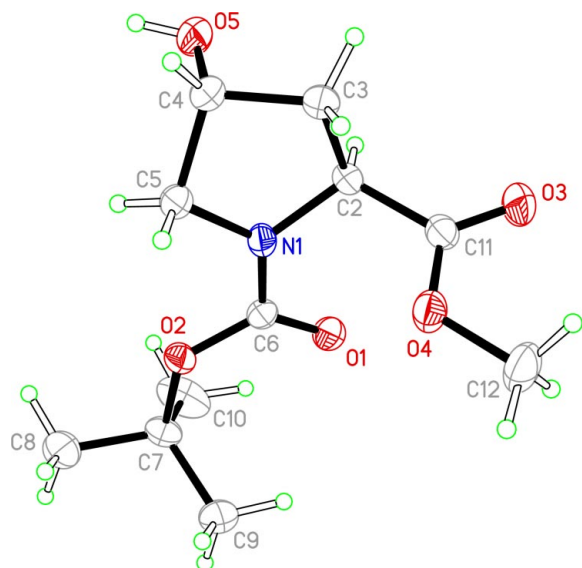
Comment

The title compound, (I), also known as (4*R*)-*N*-(*tert*-butoxy-carbonyl)-4-hydroxy-*L*-proline methyl ester, is a protected derivative of *trans*-4-hydroxy-*L*-proline and has been prepared as an intermediate in the synthesis of unnatural amino acids (Schumacher *et al.*, 1998; Deboves & Jackson, 1999). Although the compound has usually been reported as an oil (*e.g.* Abraham *et al.*, 1983; Jordis *et al.*, 1989; Kurokawa & Ohfune, 1993), and has been obtained in this form in many of our own experiments, it has also been prepared in crystalline form by others (Schumacher *et al.*, 1998) as well as ourselves. However, the crystal structure has not previously been determined and so we present it here.



The molecular structure of (I) is shown in Fig. 1 and the packing in Fig. 2. Bond lengths and angles are normal. The five-membered pyrrolidine ring has a twisted conformation, atoms C3 and C4 lying above and below the plane of the other three atoms. The bulky ester groups are pseudo-equatorial, and the 4-hydroxy group is pseudo-axial. A similar ring conformation has been found in the parent 4-hydroxyproline molecule, both in its enantiomerically pure form (Koetzle *et al.*, 1973) and in its racemic dihydrate (Shamala *et al.*, 1976). In contrast, the compound in which a 4-phenyl group replaces H in (I) has an envelope conformation, atom C4 being the flap (Tamaki *et al.*, 2001); this is presumably a consequence of the bulky extra substituent.

The torsion angles in Table 1 show that the N atom has planar coordination geometry and this is essentially coplanar


Figure 1

The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

with the attached ester group, as a result of conjugation. The effect of the conjugation can also be seen in the lengthening of the C6=O1 bond compared with C11=O3, whereas the single bonds C6–O2 and C11–O4 have insignificantly different lengths.

The molecule of (I) has only one classical hydrogen-bond donor, the hydroxy group. This donates to the carbonyl atom O1 of the N-bound ester group in an adjacent molecule (Table 2), forming chains along the *c* axis, each molecule being related to its neighbours in the chain by a screw-axis operation (Fig. 2). The hydrogen-bond formation presumably also contributes to the lengthening of C6=O1 relative to C11=O3.

Experimental

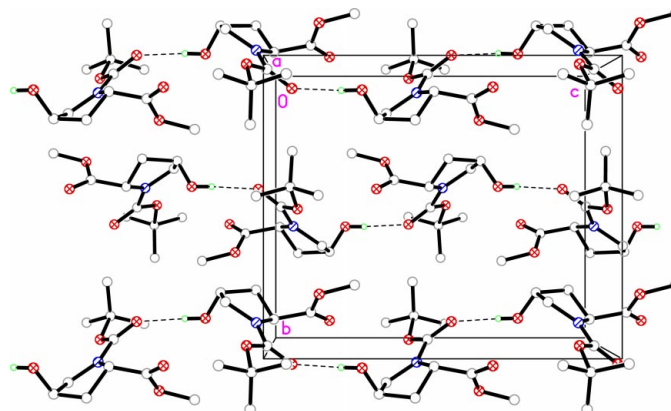
The title compound was prepared by the method of Schumacher *et al.* (1998), and was recrystallized by vapour diffusion of petroleum ether into a solution in toluene.

Crystal data

$C_{11}H_{19}NO_5$	Mo $K\alpha$ radiation
$M_r = 245.27$	Cell parameters from 4967 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 2.7\text{--}28.9^\circ$
$a = 9.1813 (10) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 10.7862 (12) \text{ \AA}$	$T = 160 (2) \text{ K}$
$c = 12.7242 (14) \text{ \AA}$	Plate, colourless
$V = 1260.1 (2) \text{ \AA}^3$	$0.53 \times 0.24 \times 0.09 \text{ mm}$
$Z = 4$	
$D_x = 1.293 \text{ Mg m}^{-3}$	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	1486 reflections with $I > 2\sigma(I)$
Thin-slice ω scans	$R_{\text{int}} = 0.028$
Absorption correction: none	$\theta_{\text{max}} = 28.9^\circ$
7889 measured reflections	$h = -11 \rightarrow 12$
1786 independent reflections	$k = -10 \rightarrow 14$
	$l = -16 \rightarrow 16$


Figure 2

The packing in (I), viewed down the *a* axis, showing hydrogen-bonded chains of molecules. H atoms have been omitted, except for the O–H group involved in hydrogen bonding.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.075$
 $S = 1.01$
 1786 reflections
 160 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL*
 (Sheldrick, 2001)
 Extinction coefficient: 0.021 (3)

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1–C2	1.463 (2)	C6–O2	1.3397 (19)
N1–C5	1.4738 (19)	C11–O3	1.198 (2)
N1–C6	1.341 (2)	C11–O4	1.333 (2)
C6–O1	1.2267 (19)		
C2–N1–C5	112.86 (12)	O1–C6–O2	126.14 (15)
C2–N1–C6	120.30 (13)	C2–C11–O3	123.01 (16)
C5–N1–C6	126.54 (13)	C2–C11–O4	112.39 (14)
N1–C6–O1	122.88 (14)	O3–C11–O4	124.47 (15)
N1–C6–O2	110.98 (13)		
C5–N1–C2–C3	10.55 (17)	C5–N1–C6–O1	174.16 (15)
C5–N1–C2–C11	130.59 (14)	C5–N1–C6–O2	−5.9 (2)
C6–N1–C2–C3	−175.32 (14)	N1–C6–O2–C7	175.30 (13)
C6–N1–C2–C11	−55.3 (2)	O1–C6–O2–C7	−4.8 (2)
N1–C2–C3–C4	−31.25 (15)	C6–O2–C7–C8	−172.30 (14)
C11–C2–C3–C4	−154.08 (14)	C6–O2–C7–C9	70.46 (18)
C2–C3–C4–C5	40.51 (16)	C6–O2–C7–C10	−54.8 (2)
C2–C3–C4–O5	−77.48 (15)	N1–C2–C11–O3	151.76 (17)
C2–N1–C5–C4	14.25 (18)	N1–C2–C11–O4	−32.2 (2)
C6–N1–C5–C4	−159.43 (15)	C3–C2–C11–O3	−92.81 (19)
C3–C4–C5–N1	−33.36 (16)	C3–C2–C11–O4	83.22 (17)
O5–C4–C5–N1	80.92 (16)	C2–C11–O4–C12	−177.28 (15)
C2–N1–C6–O1	0.9 (2)	O3–C11–O4–C12	−1.3 (2)
C2–N1–C6–O2	−179.20 (13)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O5–H5 \cdots O1 ⁱ	0.84	1.95	2.7831 (16)	171

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

H atoms were positioned geometrically and refined with a riding model (including free rotation about C–C and C–O bonds), with C–H = 0.98–1.00 and O–H = 0.84 Å, and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. In the absence of significant anomalous scattering effects, Friedel pairs were merged. The absolute configuration was assigned on the basis of that known for the starting material, a derivative of L-proline.

Data collection: *SMART* (Bruker, 2001); cell refinement: local programs; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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