(2S*,3R*,4S*,5R*)-3-(S*-1-Benzzyloxyethyl)-4-methyl-4-nitro-5-phenyl-proline methyl ester

Anthony Linden, Mirari Ayerbe, Ana Arrieta, Aizpea Zubia, Silvia Vivanco, Edurne Erquicia, Eneko Aldaba, Fernando P. Cossío and Begoña Lecea

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.
At 173 K, the five-membered ring of the title compound, C$_{22}$H$_{26}$N$_2$O$_5$, has an envelope conformation. The amine group is involved in both intramolecular and intermolecular hydrogen bonds, the latter linking the molecules into centrosymmetric dimers.

**Comment**

The title compound, (3c), is one of three diastereoisomeric products, (3a–c), obtained from the [3+2]-cycloaddition of the chiral nitroalkene (1) with the silver azomethine ylide derived from imine (2) (Ayerbe et al., 1998). Diastereoisomer (3a) could not be isolated; its absolute configuration was assumed by analogy with the compounds obtained in our previous work (Ayerbe et al., 1998). Compound (3b) did not give crystals that were suitable for X-ray diffraction. Its relative configuration was determined by NOE experiments. The minor diastereoisomer (3c) was successfully crystallized from ethanol and fully characterized.

The puckering parameters (Cremer & Pople, 1975) for the five-membered ring are: $q_2 = 0.463$ (2) Å and $\varphi_2 = 321.4$ (2)$^\circ$. The latter parameter is close to a value (324$^\circ$) that is appropriate for an envelope conformation. The envelope flap is formed by C5, which lies 0.699 (3) Å from the plane defined by atoms N1, C2, C3 and C4. This puckering causes significant contraction of the N1–C5–C4 angle (Table 1).

The amine group of the molecule forms long, weak bifurcated hydrogen bonds with the carbonyl-O atom of the ester substituent (Table 2). One interaction is intramolecular and completes a closed five-membered loop with a graph-set motif of $S(5)$ (Bernstein et al., 1995). The second is an intermolecular interaction with a neighbouring molecule, which is related to the original molecule by a centre of inversion. The intermolecular interactions thus link the molecules into hydrogen-bonded dimers which have a graph-set motif of $R_2^2(10)$.

**Experimental**

The title compound was prepared according to the procedure of Ayerbe et al. (1998). The reaction gave a mixture of three diastereoisomers, (3a–c), in the proportions 59:29:12, which were separated...
by flash chromatography (ethyl acetate/hexane, 1:10). Suitable crystals were obtained by evaporation of an ethanol solution (m.p. 454–455 K). Spectroscopic analysis: IR (KBr, cm⁻¹): 3328, 1722, 1535, 1381; ¹H NMR (CDCl₃, δ, p.p.m.): 7.31–7.14 (m, 10 H), 4.96 (s, 1 H), 4.59 (d, J = 11.5 Hz), 4.33 (d, J = 11.5 Hz), 3.81 (s, 3 H), 3.71 (m, 3 H), 2.52 (s, 1 H), 1.30 (d, J = 5.3 Hz), 1.26 (s, 3 H); ¹³C NMR (CDCl₃, δ, p.p.m.): 174.8, 137.6, 135.7, 128.6, 128.3, 128.2, 127.6, 127.5, 127.1, 112.3, 94.6, 73.7, 70.6, 70.1, 58.3, 57.0, 52.7, 17.0, 13.7; analysis, calculated for C₂₂H₂₆N₂O₅: C 66.30, H 6.59, N 7.03%; found: C 65.99, H 6.56, N 7.08%.

Crystal data

C₂₂H₂₆N₂O₅

Mr = 398.45

Monoclinic, P2₁/n

a = 9.245 (2) Å

b = 8.4082 (17) Å

C = 26.6330 (15) Å

β = 94.802 (11)°

V = 2063.1 (6) Å³

Z = 4

Data collection

Rigaku AFC-5R diffractometer

ω scans

Absorption correction: none

4719 independent reflections

2920 reflections with I > 2σ(I)

R$_{int}$ = 0.020

D = 1.283 Mg m⁻³

Mo Kα radiation

Cell parameters from 25 reflections

θ = 17.0–19.5°

μ = 0.09 mm⁻¹

T = 173 (1) K

Prism, colourless

0.50 × 0.32 × 0.22 mm

Refinement

Refinement on F²

$R(F² > 2σ(F²)) = 0.049$

$wR(F²) = 0.142$

S = 1.06

4719 reflections

269 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[σ²(F₀²) + (0.0528P)² + 0.4415P]$

where P = (F₀² + 2Fc²)/3

(Δ/σ)max = 0.001

Δρmax = 0.27 e Å⁻³

Δρmin = −0.19 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N1–C5</td>
<td>1.458 (3)</td>
<td>C2–C3</td>
<td>1.563 (2)</td>
</tr>
<tr>
<td>N1–C2</td>
<td>1.459 (3)</td>
<td>C3–C4</td>
<td>1.549 (3)</td>
</tr>
<tr>
<td>N2–C4</td>
<td>1.513 (3)</td>
<td>C4–C5</td>
<td>1.550 (2)</td>
</tr>
<tr>
<td>C5–N1–C2</td>
<td>107.02 (15)</td>
<td>C3–C4–C5</td>
<td>101.94 (14)</td>
</tr>
<tr>
<td>N1–C2–C3</td>
<td>105.08 (15)</td>
<td>N1–C5–C4</td>
<td>99.45 (16)</td>
</tr>
<tr>
<td>C2–C3–C4</td>
<td>103.10 (15)</td>
<td>C2–C3–C4</td>
<td>103.10 (15)</td>
</tr>
<tr>
<td>C5–N1–C2–C3</td>
<td>−29.00 (19)</td>
<td>C2–N1–C5–C4</td>
<td>46.76 (17)</td>
</tr>
<tr>
<td>N1–C2–C3–C4</td>
<td>−1.20 (18)</td>
<td>C3–C4–C5–N1</td>
<td>−45.43 (17)</td>
</tr>
</tbody>
</table>

Table 2

Hydrogen-bonding geometry (Å, °).

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D–H–A</td>
<td>D–H–H</td>
<td>H–A</td>
<td>D–A</td>
<td>D–H–A</td>
</tr>
<tr>
<td>N1–H1–O6</td>
<td>0.91 (2)</td>
<td>2.46 (2)</td>
<td>2.778 (2)</td>
<td>101.1 (16)</td>
</tr>
<tr>
<td>N1–H1–O6</td>
<td>0.91 (2)</td>
<td>2.39 (2)</td>
<td>3.278 (2)</td>
<td>164 (2)</td>
</tr>
</tbody>
</table>

All H atoms were initially located in a difference Fourier map. The methyl-H atoms were then constrained to an ideal
geometry with C—H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, but each group was allowed to rotate freely about its C—C bond. The position of the amine-H atom was refined freely along with an isotropic displacement parameter. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1991); cell refinement: MSC/AFC Diffractometer Control Software; data reduction: TEXSAN (Molecular Structure Corporation, 1999); program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2001).

References