

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(2*S,3*R**,4*S**,5*R**)-3-(*S**-1-Benzoyloxyethyl)-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.

(2*S,3*R**,4*S**,5*R**)-3-(*S**-1-Benzyloxyethyl)-4-methyl-4-nitro-5-phenylproline methyl ester**

Anthony Linden,^{a*} Mirari Ayerbe,^b Ana Arrieta,^b Aizpea Zubia,^b Silvia Vivanco,^b Edurne Erquicia,^b Eneko Aldaba,^b Fernando P. Cossío^{b†} and Begoña Lecea^c

^aInstitute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland, ^bKimika Fakultatea, Euskal Herriko Unibertsitatea, PK 1072, E-20080 San Sebastián-Donostia, Spain, and ^cFarmazi Fakultatea, Euskal Herriko Unibertsitatea, PK 450, E-01080 Vitoria-Gasteiz, Spain

† Additional correspondence author, email: qopcomof@sq.ehu.es.

Correspondence e-mail: alinden@oci.unizh.ch

Key indicators

Single-crystal X-ray study

T = 173 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.049

wR factor = 0.142

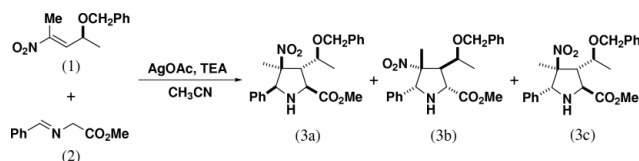
Data-to-parameter ratio = 17.5

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

At 173 K, the five-membered ring of the title compound, $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5$, 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, (3*c*), is one of three diastereoisomeric products, (3*a*–*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 (3*a*) could not be isolated; its absolute configuration was assumed by analogy with the compounds obtained in our previous work (Ayerbe *et al.*, 1998). Compound (3*b*) did not give crystals that were suitable for X-ray diffraction. Its relative configuration was determined by NOE experiments. The minor diastereoisomer (3*c*) was successfully crystallized from ethanol and fully characterized.



The puckering parameters (Cremer & Pople, 1975) for the five-membered ring are: $q_2 = 0.463 (2) \text{ \AA}$ and $\varphi_2 = 321.4 (2)^\circ$. The latter parameter is close to a value (324°) that is appropriate for an envelope conformation. The envelope flap is formed by C5, which lies $0.699 (3) \text{ \AA}$ 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, (3*a*–*c*), in the proportions 59:29:12, which were separated

Received 23 October 2001

Accepted 24 October 2001

Online 27 October 2001

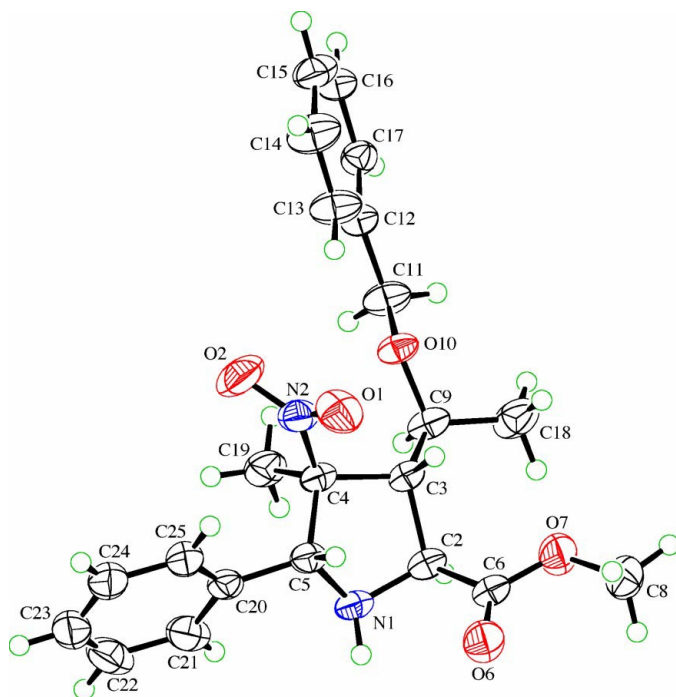


Figure 1
View of the molecule of (3c) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

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, ν cm^{-1}): 3328, 1722, 1535, 1381; ^1H NMR (CDCl_3 , δ , p.p.m.): 7.31–7.14 (*m*, 10 H), 4.96 (*s_b*, 1 H), 4.59 (*d*, 1 H, $J = 11.5$ Hz), 4.33 (*d*, 1 H, $J = 11.5$ Hz), 3.81 (*s*, 3 H), 3.71 (*m*, 3 H), 2.52 (*s*, 1 H), 1.30 (*d*, 3 H, $J = 5.3$ Hz), 1.26 (*s*, 3 H); ^{13}C NMR (CDCl_3 , 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 $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5$: C 66.30, H 6.59, N 7.03%; found: C 65.99, H 6.56, N 7.08%.

Crystal data

$\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_5$	$D_x = 1.283 \text{ Mg m}^{-3}$
$M_r = 398.45$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 9.245$ (2) Å	$\theta = 17.0$ – 19.5°
$b = 8.4082$ (17) Å	$\mu = 0.09 \text{ mm}^{-1}$
$c = 26.6330$ (15) Å	$T = 173$ (1) K
$\beta = 94.802$ (11) $^\circ$	Prism, colourless
$V = 2063.1$ (6) Å 3	$0.50 \times 0.32 \times 0.22 \text{ mm}$
$Z = 4$	

Data collection

Rigaku AFC-5R diffractometer	$\theta_{\text{max}} = 27.5^\circ$
ω scans	$h = 0 \rightarrow 12$
Absorption correction: none	$k = 0 \rightarrow 10$
5348 measured reflections	$l = -34 \rightarrow 34$
4719 independent reflections	3 standard reflections
2920 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.020$	intensity decay: none

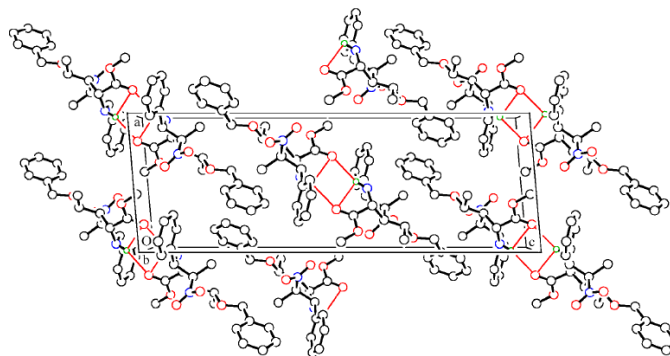


Figure 2
The molecular packing of (3c) viewed along the *b* axis. H atoms bonded to C atoms have been omitted for clarity. Red lines indicate the hydrogen bonding interactions.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.142$
 $S = 1.06$
 4719 reflections
 269 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.4415P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$

Table 1

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

N1—C5	1.458 (3)	C2—C3	1.563 (2)
N1—C2	1.459 (3)	C3—C4	1.549 (3)
N2—C4	1.513 (3)	C4—C5	1.550 (2)
C5—N1—C2	107.02 (15)	C3—C4—C5	101.94 (14)
N1—C2—C3	105.08 (16)	N1—C5—C4	99.45 (16)
C2—C3—C4	103.10 (15)		
C5—N1—C2—C3	−29.00 (19)	C2—N1—C5—C4	46.76 (17)
N1—C2—C3—C4	−1.20 (18)	C3—C4—C5—N1	−45.43 (17)
C2—C3—C4—C5	28.37 (18)		

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O6	0.91 (2)	2.46 (2)	2.778 (2)	101.1 (16)
N1—H1 \cdots O6 ⁱ	0.91 (2)	2.39 (2)	3.278 (2)	164 (2)

Symmetry code: (i) $2 - x, 1 - y, -z$.

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 $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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

- Ayerbe, M., Arrieta, A., Cossío, F. P. & Linden, A. (1998). *J. Org. Chem.* **63**, 1795–1805.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2001). *PLATON*. University of Utrecht, The Netherlands.