O5—C7—C6	111.6 (2)	O1—C18—N1	125.2 (2)
O5—C7—C8	106.7 (2)	O1—C18—O2	122.9 (2)
C6—C7—C8	112.1 (2)	N1—C18—O2	111.89 (15)
C7—C8—C9	112.6 (2)	O2—C19—C20	108.4 (2)
N1—C9—C10	101.87 (14)	C21—C20—C19	121.8 (2)
N1—C9—C8	111.8 (2)	C25—C20—C19	120.2 (2)
C10—C9—C8	114.1 (2)		

The Flack (1983) absolute structure parameters (χ) calculated on the 'inverted' structures assumed values of 1.0 (8) and 0.8 (7) for PTBEB and PTBEA, respectively. This implies that the assignment of the absolute configuration cannot rely on the value of this parameter. Instead, it is based on the knowledge of the absolute configuration of the chiral C atom in the starting pyroglutamic acid. The observed disorder in the structure of PTBEA concerns the two methylene groups of the proline ring. Several models for interpreting the disorder were tested and the final description implies the splitting of the C10 and C11 atoms into two groups (C10*A*/C10*B* and C11*A*/C11*B* with the corresponding H atoms). These C atoms were treated isotropically with a refined partial occupancy constraint and the related H atoms were kept at calculated positions. For PTBEA, all H-atom parameters were refined, except for atoms H10*A*, H10*B*, H10*C*, H10*D*, H11*A*, H11*B*, H11*C* and H11*D*. These atoms were kept at calculated positions with $U_{iso} = 1.2U_{eq}$ of the atom to which the H atom is bonded.

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

The authors gratefully acknowledge the provision of crystals by Professor C. Scolastico of the University of Milano, Italy.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1080). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 936–938

(*cis*-1-Cyclohexyl-6-methylene-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-yl)methyl 3,5-Dinitrobenzoate

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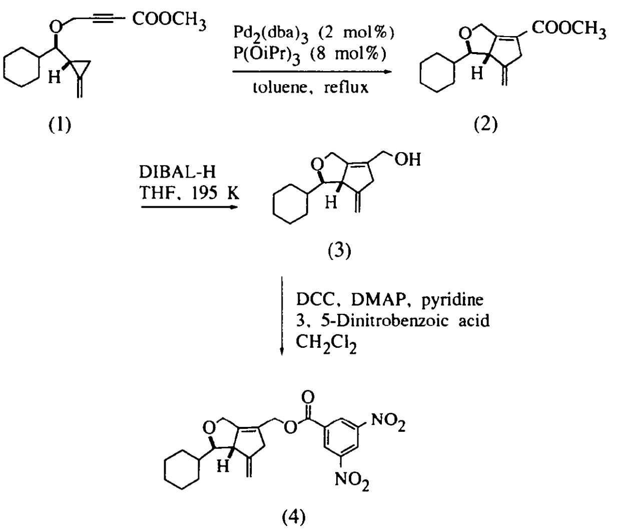
(*Received 8 November 1996; accepted 21 January 1997*)

Abstract

The structure determination of the title compound, $C_{22}H_{24}N_2O_7$, establishes the relative stereochemistry of the molecule.

Comment

Diastereomerically pure methylenecyclopropane, (1), undergoes intramolecular [3+2] cycloaddition in the presence of a Pd^0 catalyst. The stereochemistry on the methylenecyclopropane ring C atom was found to be retained during the process and the reaction was shown to be stereospecific (Lautens, Ren & Delanghe, 1994). The stereochemistry of the cycloadduct could not be easily determined by NMR spectroscopy.



$Pd_2(dba)_3$ = Pd_2(dibenzylideneacetone)$_3$
DIBAL-H = Diisobutylaluminium hydride
DCC = Dicylohexylcarbodiimide
DMAP = Dimethylaminopyridine

In order to establish the stereochemistry and assign the stereochemistry in the related cycloadducts, compound (2) was converted to the corresponding 3,5-dinitrobenzoate, (4), by the following sequence: DIBAL-H reduction of ester (2) gave the corresponding alcohol, (3), and esterification of the alcohol with 3,5-dinitrobenzoic acid yielded the desired ester, (4). The crystal structure of the 3,5-dinitrobenzoate reported herein established the relative stereochemistry of (4) as shown in Fig. 1.

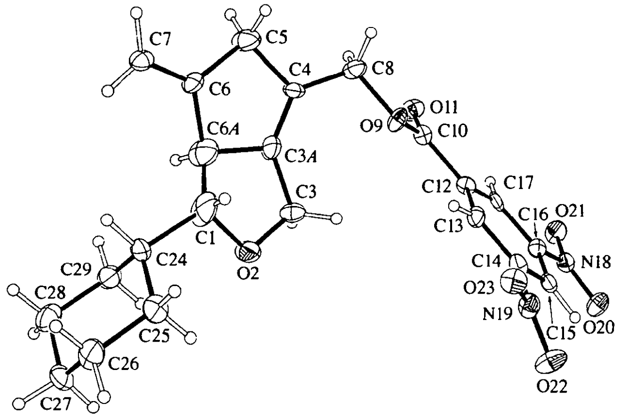


Fig. 1 View of the title molecule with the atomic labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as small spheres of arbitrary radii.

In (4), the fused five-membered rings both have envelope conformations (see Fig. 1). In the furan ring, atoms O2, C3, C3a and C6a form plane I [maximum deviation of 0.089 (5) Å for C3a], while C1 is 0.502 (19) Å from the plane. In the cyclopentene ring, atoms C6a, C3a, C4 and C5 form plane II [maximum deviation of 0.011 (6) Å for C3a], with C6 0.233 (15) Å from the plane. The angle between planes I and II is 16.8 (7) Å.

A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed only one other structure, namely, (5*S*)-2-[(1*R*,2*S*,3*R*,4*S*)-3-(2,2-dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]heptyl-2-oxy]-7-oxabicyclo[3.3.0]oct-1-en-3-one (Alvarez-Larena *et al.*, 1993), which contained the same system of fused five-membered rings found in (4).

Experimental

Ester (4) was crystallized from dichloromethane/pentane (1:1).

Crystal data

$C_{22}H_{24}N_2O_7$
$M_r = 428.43$
Monoclinic
$P2_1/c$
$a = 17.489\,(10)$ Å
$b = 5.415\,(4)$ Å
$c = 21.805\,(12)$ Å
$\beta = 95.08\,(2)°$
$V = 2057\,(2)$ Å^3
$Z = 4$
$D_x = 1.384$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 31 reflections
$\theta = 3.5–8.9°$
$\mu = 0.104$ mm^{-1}
$T = 178\,(2)$ K
Plate
0.12 × 0.10 × 0.05 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2718 measured reflections
2621 independent reflections
997 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.1138$

$\theta_{\rm max} = 22.5°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 5$
$l = -23 \rightarrow 23$
3 standard reflections every 97 reflections intensity decay: < 3%

Refinement

Refinement on F^2
$R(F) = 0.076$
$wR(F^2) = 0.104$
$S = 1.141$
2621 reflections
281 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.366$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.289$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.0010 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O2—C3	1.435 (7)	C3a—C3	1.466 (10)
O2—C1	1.478 (11)	C4—C8	1.476 (7)
C1—C6a	1.408 (9)	C4—C5	1.519 (10)
C6a—C3a	1.511 (9)	C5—C6	1.521 (8)
C6a—C6	1.535 (11)	C6—C7	1.300 (9)
C3a—C4	1.307 (9)		
C6a—C1—O2	103.1 (8)	O2—C3—C3a	104.3 (6)
C6a—C1—C24	121.8 (8)	C3a—C4—C8	129.2 (8)
O2—C1—C24	106.6 (8)	C3a—C4—C5	111.2 (6)
C1—C6a—C3a	103.1 (7)	C8—C4—C5	119.6 (7)
C1—C6a—C6	124.4 (11)	C4—C5—C6	102.2 (6)
C3a—C6a—C6	100.1 (7)	C7—C6—C5	124.7 (8)
C4—C3a—C3	139.2 (7)	C7—C6—C6a	125.8 (7)
C4—C3a—C6a	114.9 (8)	C5—C6—C6a	109.4 (7)
C3—C3a—C6a	105.6 (6)		

Repeated crystallizations of (4) yielded only very small plates and many unsuccessful attempts were made to mount a crystal for data collection before a suitable crystal was found. The crystal which was used for data collection was the best available but it diffracted very weakly. As a consequence of this weak diffraction, data were only collected to a maximum θ of 22.5° [only 38% of these data had $I > 2\sigma(I)$]. Although we did not collect data to 25° in θ as recommended (Notes for Authors of *Acta Crystallographica Section C*) and our final *R* factor for observed data was 0.076 (which may be considered to be on the high side), the results of this crystal structure determination are adequate to establish the stereochemistry of the title molecule.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

This research was supported by the Natural Science and Engineering Research Council (NSERC) of Canada, the A. P. Sloan Foundation, the Merck Frosst Center for Therapeutic Research, Bio-Mega, Eli Lilly Grantee Program and the University of Toronto.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1257). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 938–940

3β,4β-Epoxy-5β-androstan-17-one

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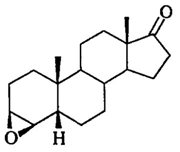
(*Received 10 December 1996; accepted 3 February 1997*)

Abstract

The title compound, $C_{19}H_{28}O_2$, has the configuration of a 5β epimer with an epoxy O atom at 3β,4β. The asymmetric unit contains two molecules with almost identical geometry. Cohesion of the crystal can be attributed to weak intermolecular C—H···O and van der Waals interactions.

Comment

As part of our study of steroids obtained as intermediate products during the synthesis of formestane (Tavares da Silva, Sá e Melo & Campos Neves, 1996), an irreversible aromatase inhibitor which has been shown to be very effective in the treatment of breast cancer, the crystal structure of 3β,4β-epoxy-5β-androstan-17-one, (I), was determined by X-ray diffraction analysis.



(I)

The unit cell contains two symmetry-independent molecules, *A* and *B*, with almost identical geometry, and one of these (molecule *A*) is illustrated in Fig. 1. The angle between the least-squares planes defined by rings *B*, *C* and *D* of the two molecules is 59.88 (6)°.

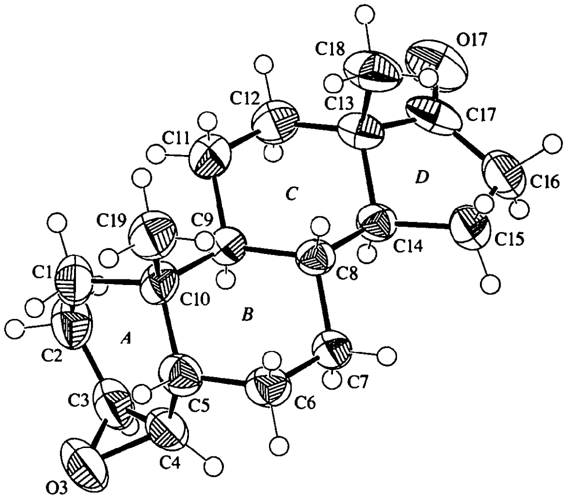


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound (molecule *A*). Displacement ellipsoids are drawn at the 50% probability level except for H atoms, which were given arbitrary radii.

Following Kálman, Argay, Scharfenberg-Pfeiffer, Höhne & Ribár (1991), who studied the isostructuralism of several structures, a test of similarity between the two non-symmetry-related molecules was performed through calculation of the factor

$$I_B^n = \{1 - [(\Sigma \Delta R_i/R)/n]^{0.5}\} \times 100$$

where the sum extends over the nR_i equivalent distances (or angles) of the two molecules. The values obtained are I_B^{25} (distances) = 99.4%, I_B^{23} (valency angles) = 99.5%.

From the X-ray analysis, a β configuration for this epimer was evident, with a *cis* junction between rings *A* and *B*. The values of the bowing angles are 81.53 (9)° (molecule *A*) and 81.97 (9)° (molecule *B*). The corresponding distances between terminal O atoms were found to be 8.929 (4) and 8.904 (4) Å and the values for the pseudo-torsion angles C19—C10—C13—C18 are 1.1 (3) and 2.7 (3)°, respectively. The bond lengths, bond angles and conformational details of these molecules are very similar to those found for the α epimer (Paixão *et al.*, 1997). Ring *A* is strongly distorted from