

## 17a-Allyl-17a-aza-D-homoandrost-4-en-3-one

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## Key indicators

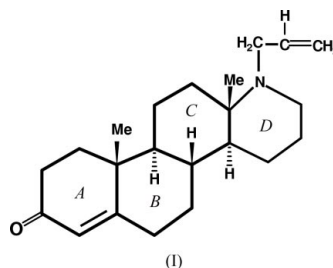
Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
R factor = 0.046  
wR factor = 0.119  
Data-to-parameter ratio = 8.8

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

The title compound,  $\text{C}_{22}\text{H}_{33}\text{NO}$ , a homoandrost-4-ene, is composed of four six-membered rings. Ring A adopts a  $1\alpha$ -sofa conformation, while the other rings adopt chair conformations. The crystal structure is stabilized by weak intermolecular  $\text{C}-\text{H}\cdots\text{O}$  interactions and van der Waals forces.

## Comment

The X-ray investigation of the title compound, (I), was undertaken as part of a study on the structure and conformation of new synthetic steroid derivatives (Hema *et al.*, 2002; Vasuki *et al.*, 2001; Vasuki Parthasarathi, Ramamurthi, Dubey & Jindal, 2002*a,b,c*; Vasuki, Parthasarathi, Ramamurthi, Jindal & Dubey, 2002; Vasuki, Thamotharan *et al.*, 2002*a,b*). Compound (I), consisting of four six-membered fused rings, is a steroid with the normal  $8\beta$ ,  $9\alpha$ ,  $10\beta$ ,  $13\beta$  and  $14\alpha$  configuration. We are particularly interested to study the conformational flexibility of the steroid, resulting from the substitution of the allyl moiety at position 17*a*.

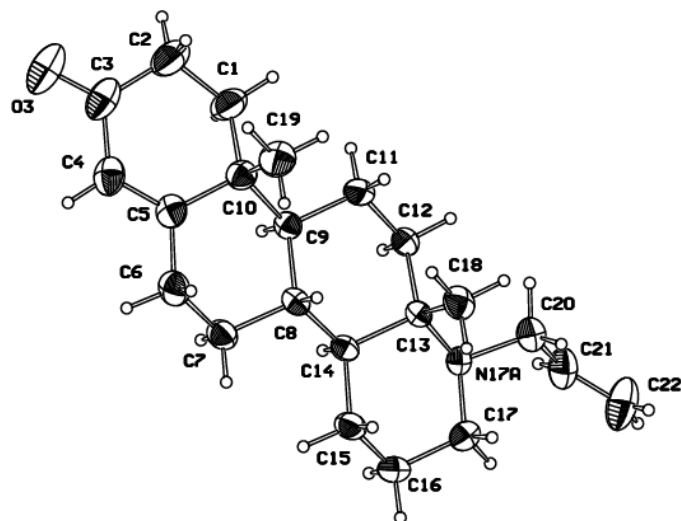


In (I), ring A adopts a sofa conformation, with atom C1 in the  $\alpha$ -position, as is evident from the deviation of C1 by  $0.571(4) \text{ \AA}$  from the mean C2/C3/C4/C5/C10 plane. Rings B and C adopt slightly distorted chair conformations, with Cremer & Pople (1975) puckering parameters  $Q = 0.538(5) \text{ \AA}$ ,  $\theta = 10.4(5)^\circ$  and  $\varphi = 188.1(7)^\circ$  for ring B, and  $Q = 0.561(5) \text{ \AA}$ ,  $\theta = 9.1(5)^\circ$  and  $\varphi = 241.7(8)^\circ$  for ring C. Ring D adopts a normal chair conformation, with  $Q = 0.564(5) \text{ \AA}$ ,  $\theta = 1.8(5)^\circ$  and  $\varphi = 98.4(6)^\circ$ . The allyl group at N17A shows a  $\beta$ -orientation. The C13–N17A–C20–C21 torsion angle is  $-163.9(3)^\circ$ ; thus, the allyl moiety is (–)antiperiplanar with respect to the C13–N17A bond. The B/C and C/D ring junctions are all *trans*. The widening of the exocyclic angle C13–N17A–C20 [ $113.3(2)^\circ$ ] may be due to steric interaction between atoms H12A and H20B ( $\text{H12A}\cdots\text{H20B} = 1.99 \text{ \AA}$ ). The C2–C3 ( $\text{Csp}^3-\text{Csp}^2$ ) bond distance of  $1.490(6) \text{ \AA}$  is comparable with the reported value of  $1.489(5) \text{ \AA}$  in a related structure (Vasuki *et al.*, 2002), which also shows a  $1\alpha$ -sofa conformation for ring A. The C4–C5 ( $\text{Csp}^2-\text{Csp}^2$ ) distance of  $1.340(5) \text{ \AA}$  confirms the localization of a double bond at

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**Figure 1**  
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

this position. The mean  $Csp^3-Csp^3$  bond length in (I) is calculated as 1.528 (2) Å. However, the C10–C9 ( $Csp^3-Csp^3$ ) distance of 1.559 (4) Å has the largest deviation from the mean value. A similar larger value for this bond has been observed in some related structures, e.g. 1.567 (2) (Duax & Norton, 1975), 1.559 (3) (Paixão *et al.*, 1998), 1.564 (3) (Vasuki *et al.*, 2002a), and 1.560 (3) and 1.556 (3) Å in two independent molecules (Vasuki, Thamocharan *et al.*, 2002b). The C3···C16 distance of 8.98 Å, which is a measure of the length of the steroid nucleus, indicates that the molecule is in a completely extended form (Karle, 1970). The pseudo-torsion angle C19–C10···C13–C18 in (I) is 0.4 (3)°. A short intermolecular C–H···O contact is observed between atoms C6 and O3<sup>i</sup>, with an H6B···O3<sup>i</sup> distance of 2.59 Å [symmetry code: (i)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ]. The structure is stabilized by van der Waals interactions.

## Experimental

The title compound was prepared by refluxing 17a-aza-D-homoandrost-4-en-3-one (1 g, 3.48 mmol), allyl bromide (1 ml) and dry methylketone (50 ml) for 15 min, and then adding anhydrous potassium carbonate (1 g). The reaction mixture was refluxed for 4 h with continuous stirring. The resulting slurry was filtered and the solvent was removed under reduced pressure. The residue obtained was crystallized from *n*-hexane to afford crystals of (I) (0.85 g, 74.63%; m.p.: 403–408 K).

### Crystal data

$C_{22}H_{33}NO$	Mo $K\alpha$ radiation
$M_r = 327.49$	Cell parameters from 25 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 10-15^\circ$
$a = 7.358$ (2) Å	$\mu = 0.07$ mm <sup>-1</sup>
$b = 12.635$ (2) Å	$T = 293$ (2) K
$c = 20.596$ (10) Å	Plate, green
$V = 1914.8$ (12) Å <sup>3</sup>	0.20 × 0.17 × 0.17 mm
$Z = 4$	
$D_x = 1.136$ Mg m <sup>-3</sup>	

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ -2 $\theta$  scans  
Absorption correction: none  
1992 measured reflections  
1910 independent reflections  
1228 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.027$

$\theta_{max} = 25.0^\circ$   
 $h = 0 \rightarrow 8$   
 $k = -4 \rightarrow 15$   
 $l = -7 \rightarrow 24$   
2 standard reflections  
frequency: 120 min  
intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.120$   
 $S = 1.03$   
1910 reflections  
217 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 0.1373P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.12$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.15$  e Å<sup>-3</sup>

All H atoms were placed geometrically and refined using a riding model, with C–H = 0.93–0.98 Å and  $U_{iso}(H) = 1.5U_{eq}(C)$  for methyl H atoms and  $1.2U_{eq}(C)$  for all other H atoms. The absolute configuration was assigned to correspond with that of the known chiral centres in a starting molecules, namely 17a-aza-D-homoandrost-4-en-3-one. Friedel pairs were not merged.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: MolEN (Fair, 1990); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ZORTEP97 (Zsolnai, 1997); software used to prepare material for publication: SHELXL97.

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