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16-(2-Pyridylmethylene)-androst-4-ene-3,17-dione

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The title compound, $C_{25}H_{29}NO_2$, crystallizes in the triclinic space group $P1$ with two crystallographically independent molecules in the unit cell. These two molecules differ in the orientation of the pyridyl rings with respect to the steroid nucleus, and also in the conformation of the five-membered rings.

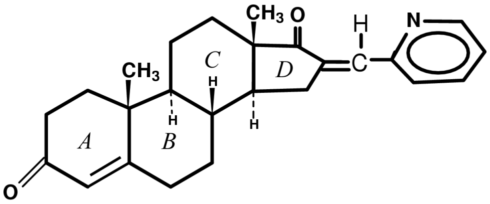
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.102
Data-to-parameter ratio = 8.2

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

Comment

The X-ray investigation of the title compound, (I), was undertaken as a part of our study on the structure and conformation of new synthetic steroid derivatives (Vasuki *et al.*, 2001; Vasuki, Parthasarathi, Ramamurthi, Jindal & Dubey, 2002; Vasuki, Parthasarathi, Ramamurthi, Dubey & Jindal, 2002). The activity of steroid hormones depends upon a number of factors, including solubility, motility, transport, metabolism and complementarity of fit between hormone and receptor (Duax *et al.*, 1979). We are particularly interested in the study of the influence of structural modification upon the overall geometry and conformation of the steroid nucleus. Compound (I), an androgen derivative, is a steroid with the normal 8β,9α,10β,13β,14α configuration.



(I)

The crystal structure of the title compound contains two crystallographically independent molecules in the $P1$ unit cell, which is unusual for a steroid nucleus (Andrade *et al.*, 1999). The conformation of both molecules in the unit cell is nearly the same, except for a variation in the conformation of the five-membered ring and in the orientation of the pyridyl ring with respect to the steroid nucleus. In molecule 1, ring A is slightly distorted towards an envelope conformation, with puckering parameters Q = 0.456 (3) Å, θ = 55.8 (4)° and φ = 15.7 (4)° (Cremer & Pople, 1975), whereas, in molecule 2, it adopts an envelope conformation [Q = 0.441 (3) Å, θ = 59.1 (4)° and φ = 2.9 (4)°]. Rings B and C adopt chair conformations in both molecules. The five-membered ring D exhibits a distorted 14α-envelope conformation in molecule 1, with pseudo rotational parameters Δ = 17.6° and φ_m = 42.9 (1)° (Altona *et al.*, 1968); in molecule 2, ring D adopts a distorted 13β, 14α-half-chair conformation [Δ = 9.5° and φ_m = 45.1 (1)°]. The dihedral angle between the plane of the pyri-

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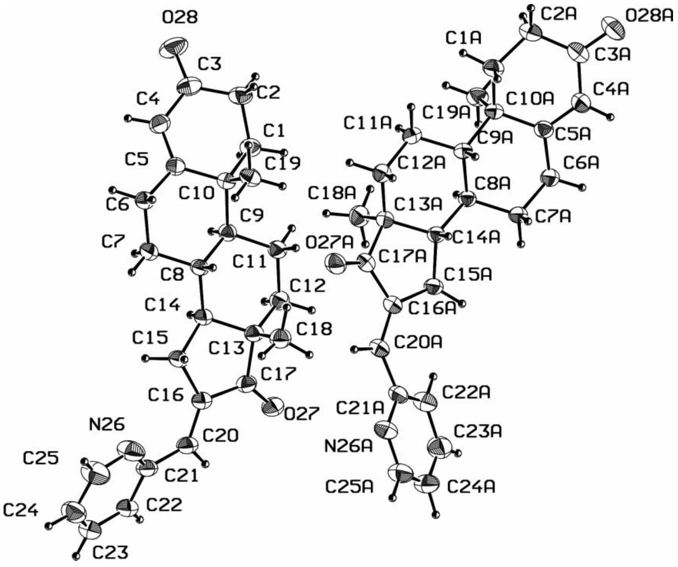

Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

dine ring and the average molecular plane comprising rings *A*, *B*, *C* and *D* is 46.09 (1)° [42.55 (1)°]. The geometry of the rings is *trans* at the *B*/*C* and *C*/*D* ring junctions in both molecules.

The C17—C16—C20—C21 torsion angle of 174.8 (2)° [177.9 (2)°] indicates that the 2-pyridyl ring has an *E* configuration with respect to the carbonyl group at position 17. The C15—C16—C20 exocyclic angle of 130.6 (2)° in molecule 1 is significantly greater than the normal value. This might be a consequence of repulsion between the lone pair of electrons on N26 and H15*B* attached to C15 (N26···H15*B* = 2.85 Å). In the case of molecule 2, the C15*A*—C16*A*—C20*A* exocyclic angle of 132.5 (2)° is also significantly greater than the normal value. This may be due to the steric repulsion between the atoms H15*C* and H22*A* (H15*C*···H22*A* = 2.49 Å). The torsion angle H20—C20—C21—N26 in molecule 1 is 154.9°, whereas the corresponding torsion angle in molecule 2 is −18.3°. This indicates that the pyridyl ring has been rotated about the C20*A*—C21*A* bond in molecule 2. The pseudo-torsion angle C19—C10···C13—C18 is observed to be −1.08 (2)° [1.49 (2)°]. The C4—C5 (Csp^2—Csp^2) distance of 1.342 (3) Å [1.341 (3) Å] confirms the localization of a double bond at this position (Vasuki *et al.*, 2002). The C8—C14—C15 angle of 120.1 (2)° [121.2 (1)°] and C14—C13—C17 angle of 100.5 (2)° [99.3 (2)°] are close to the expected values of 121.2° and 101.4°, respectively (Duax & Norton, 1975). The crystal structure is stabilized by van der Waals interactions.

Experimental

The title compound was prepared by dissolving 17-oxo-16-(2-pyridylmethylene)androst-5-en-3β-ol (1 g, 2.65 mmol) in dry toluene (150 ml) by refluxing and then adding cyclohexanone (10 ml). Traces of moisture were removed by azeotropic distillation. The distillation was continued at a slow rate during dropwise addition of a solution of aluminium isopropoxide (1 g) in dry toluene. The reaction mixture was refluxed for 4 h and left overnight. The next day, the solvent was removed by steam distillation. The solid thus obtained was filtered, dried and crystallized from methanol to afford crystals of (I) (yield 0.8 g, 90.48%, m.p. 461–463 K).

Crystal data

$C_{25}H_{29}NO_2$
M_r = 375.49
Triclinic, *P*1
a = 6.991 (1) Å
b = 11.674 (2) Å
c = 13.528 (2) Å
α = 79.327 (10)°
β = 76.866 (13)°
γ = 78.438 (14)°
V = 1042.0 (3) Å^3

Z = 2
D_x = 1.197 Mg m^{-3}
Cu *K*α radiation
Cell parameters from 25 reflections
θ = 20–30°
μ = 0.59 mm^{-1}
T = 293 (2) K
Plate, white
0.50 × 0.40 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.759, $T_{\max}$ = 0.917
4136 measured reflections
4136 independent reflections

3938 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 68.0°
$h = 0 \rightarrow 8$
$k = -13 \rightarrow 14$
$l = -15 \rightarrow 16$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.102
S = 0.93
4136 reflections
506 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0837P)^2 + 0.0801P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\min}$ = −0.15 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0121 (11)

All H atoms were geometrically fixed and refined using a riding model, with C—H = 0.93–0.98 Å and $U_{\rm iso}$ (H) = 1.5 $U_{\rm eq}$(C) for methyl H and 1.2 $U_{\rm eq}$(C) for all others. The molecule was assigned an absolute configuration on the basis of the known chirality of the starting material used in the synthesis of the compound (Vasuki *et al.*, 2001); the Flack (1983) parameter was not used.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *DIRDIF*99 (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP*97 (Zsolnai, 1997); software used to prepare material for publication: *SHELXL*97.

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