

4-(3,17-Dioxoandro-4-en-16-yl-
idenemethyl)benzonitrileG. Vasuki,^a V. Parthasarathi,^{a*} K. Ramamurthi,^a
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Received 29 October 2001

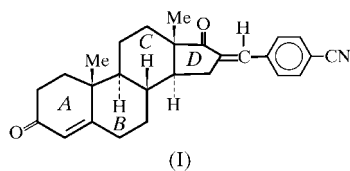
Accepted 2 January 2002

Online 20 February 2002

The title compound, C₂₇H₂₉NO₂, has the outer six-membered ring in a sofa conformation, while the central rings are in chair conformations. The five-membered ring adopts a slightly distorted 13 β ,14 α -half-chair conformation. The cyanobenzylidene moiety has an *E* configuration with respect to the carbonyl group at position 17.

Comment

The structure determination of the title compound, (I), was undertaken to investigate the conformation of the fused-ring system and the configuration of the 16-(4-cyanobenzylidene) functionality with respect to the carbonyl group at position 17. Compound (I), an androgen derivative, is a steroid with the normal 8 β ,9 α ,10 β ,13 β ,14 α configuration. The absolute configuration of (I) is based on the known configuration of the starting material, namely androstenedione (Busetta *et al.*, 1972).



Ring *A* adopts a sofa conformation with C1 in the α -position, as is evident from the deviation of C1 by -0.600 (5) Å from the mean C2/C3/O30/C4/C5/C10 plane. The puckering amplitudes (Cremer & Pople, 1975) are $Q = 0.435$ (3) Å, $\theta = 54.5$ (4)° and $\varphi = 11.2$ (6)°. The C2–C3 bond distance of 1.489 (5) Å is comparable with the reported value of 1.492 Å in a related structure (Cowe *et al.*, 1982), in which ring *A* also has the 1 α -sofa conformation.

Rings *B* and *C* adopt normal chair conformations. The C4–C5 distance of 1.335 (4) Å confirms the localization of a double bond at this position. In a few typical related steroid structures (Cowe *et al.*, 1982; Bhadbhade & Venkatesan, 1984; Galdecki *et al.*, 1990), the C4–C5 bond distance is in the range 1.309 (8)–1.363 (3) Å.

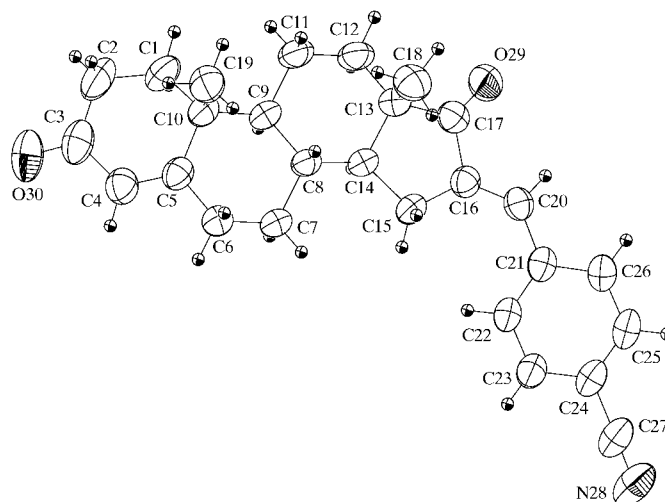


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The conformation of ring *D* can be expressed by two parameters, a pseudo-rotation angle, Δ , and a maximum torsion angle, φ_m (Altona *et al.*, 1968). For a perfect envelope (*C_s* symmetry), Δ is 36°, whereas it is 0° for a half chair. In (I), ring *D* exhibits a slightly distorted 13 β ,14 α -half-chair conformation ($\Delta = 11.4^\circ$ and $\varphi_m = 38.1^\circ$).

The C17–C16–C20–C21 torsion angle of -177.5 (3)° indicates that the 4-cyanobenzylidene ring has an *E* configuration with respect to the carbonyl group at position 17. Atom H20 is *Z* with respect to this carbonyl group. The exocyclic C15–C16–C20 angle [132.5 (2)°] is found to be significantly greater than the normal value and this may be due to the steric repulsion between atoms H15*B* and H22 [$H \cdots H$ 2.0531 (2) Å].

The pseudo-torsion angle C19–C10 \cdots C13–C18 is observed to be 7.4 (2)°. The C27–N28 bond length [1.134 (4) Å] and the C24–C27–N28 angle [177.1 (3)°] confirm the C–N triple bond. Atoms O29 and O30 are both equatorially substituted, at C17 and C3, respectively. The dihedral angle between the cyanobenzylidene ring and the androstenedione moiety is 11.86 (8)°. The geometry of the rings is *trans* at the *B/C* and *C/D* ring junctions. The molecules are found to pack in antiparallel arrangements.

Experimental

The title compound was prepared by dissolving 16-(4-cyanobenzylidene)-17-oxo-5-androsten-3 β -ol (1 g, 2.49 mmol) in dry toluene

Table 1
Selected geometric parameters (Å, °).

| | | | |
|--------------|-------------|--------------|-------------|
| C1–C2 | 1.516 (4) | C17–O29 | 1.212 (3) |
| C3–O30 | 1.214 (4) | | |
| C2–C1–C10 | 114.2 (3) | O30–C3–C4 | 122.2 (3) |
| C10–C1–C2–C3 | -54.1 (4) | C3–C4–C5–C10 | -4.3 (5) |
| C1–C2–C3–C4 | 30.5 (5) | C4–C5–C10–C1 | -17.7 (4) |
| C2–C3–C4–C5 | -2.2 (5) | C2–C1–C10–C5 | 46.1 (4) |

(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 0.6 g, 60.3%; m.p 528–531 K).

Crystal data

$C_{27}H_{29}NO_2$
 $M_r = 399.51$
 Orthorhombic, $P2_12_1$
 $a = 7.7638$ (10) Å
 $b = 8.4584$ (10) Å
 $c = 33.220$ (5) Å
 $V = 2181.5$ (5) Å³
 $Z = 4$
 $D_x = 1.216$ Mg m⁻³

Cu $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 20$ – 30°
 $\mu = 0.59$ mm⁻¹
 $T = 293$ (2) K
 Plate, colourless
 $0.30 \times 0.25 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.842$, $T_{\max} = 0.943$
 2365 measured reflections
 2320 independent reflections (plus 43 Friedel-related reflections)

1957 reflections with $I > 2 \sigma(I)$
 $R_{\text{int}} = 0.014$
 $\theta_{\max} = 67.9^\circ$
 $h = 0 \rightarrow 9$
 $k = -10 \rightarrow 5$
 $l = 0 \rightarrow 39$
 2 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.105$
 $S = 1.11$
 2363 reflections
 272 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.2836P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.005$
 $\Delta\rho_{\max} = 0.14$ e Å⁻³
 $\Delta\rho_{\min} = -0.12$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0029 (3)

All H atoms were treated as riding, with C–H = 0.93–0.98 Å, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H and $1.2U_{\text{eq}}(\text{C})$ for all others.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *DIRDIF98* (Beurskens *et al.*, 1998); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL97*.

DPJ thanks CSIR, India, for financial assistance and Cipla Ltd., Mumbai, for providing the steroid. GV thanks the UGC, India, for the award of an FIP fellowship (1999–2001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1179). Services for accessing these data are described at the back of the journal.

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