

Fig. 2. View of unit cell along *b* showing hydrogen bonding. Symmetry code (i) denotes the equivalent position $\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$.

Discussion. The atomic numbering is shown in the perspective drawing (Fig. 1). Atomic parameters and bond lengths are given in Tables 1* and 2.

The bond lengths and angles are in good agreement with those for TAA (Wilson, Tollin & Howie, 1986). The N-glycosidic torsion angle χ is $66(1)^\circ$, in the *syn* range. The sugar pucker is 2T_3 (C2'-*endo*-

*Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43846 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C3'-*exo*), with $P = 181(1)^\circ$, and $\psi_m = 19(1)^\circ$. The C4'-C5' conformation, with $\gamma = 40(1)^\circ$ and $\gamma' = -75(1)^\circ$, is *+sc* (*gauche-gauche*). The conformational parameters used follow the guidelines of the IUPAC-IUB Commission on Biochemical Nomenclature (1983). There are two hydrogen bonds present in the structure: N1...N6 3.01 (2) ($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$) and N6...N7 3.09 (2) Å ($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$). Thus each molecule is involved in four hydrogen bonds (Fig. 2), two with each of two translationally related bases, forming a chain of paired bases along *c*, similar to the situation in TAA. There is a propeller twist (Dickerson, 1983) of $29(2)^\circ$, between the planes of the two paired bases. This represents one of the largest propeller twists observed in nucleoside structures. Such twists are reviewed by Wilson & Tollin (1987).

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(±)-14β-Hydroxy-1β,4β-methano-5β,8α,9β-androstane-7,17-dione

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Abstract. $C_{20}H_{28}O_3$, $M_r = 316.4$, triclinic, $P\bar{1}$, $a = 7.408(2)$, $b = 10.758(2)$, $c = 11.687(2)$ Å, $\alpha = 66.02(1)$, $\beta = 86.72(2)$, $\gamma = 74.85(2)^\circ$, $U = 820$ Å³, $Z = 2$, $D_x = 1.28$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, μ

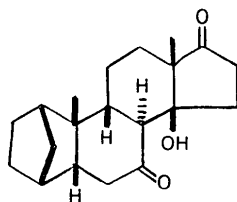
$= 0.079$ mm⁻¹, $F(000) = 344$, $T = 298$ K, $R = 0.0408$ ($wR = 0.0518$) for 2800 observed [$I > 3\sigma(I)$] reflections. In the title compound the 1β,4β-methano bridge forces rings *A* and *B* into boat conformations. Ring *C*,

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however, has a chair conformation. The *cis* *A/B* and *C/D* ring junctions result in the molecule's having a significantly folded overall conformation with mean planes through rings *A* and *D* making angles of *ca* 84 and 117°, respectively, with a mean plane through rings *B* and *C*. Ring *D* has a C(14) α -envelope conformation with puckering constants $\Delta = -22.3$ (7) and $\varphi_m = 41.1$ (2)°. The crystal packing is determined by hydrogen bonds involving the 14 β -hydroxy group.

Introduction. A modification of the Torgov steroid synthesis (Ananchenko & Torgov, 1959, 1963) has led to the total synthesis of the title compound (1), a steroid containing a 1,4 carbon-bridged *A* ring. A preliminary account of this synthesis and the characterization of (1) have been given (Douglas, Sawyer & Yates, 1985). In the present paper we report full details of the crystallographic characterization of (1).



(1)

Experimental. Colorless crystals obtained from methanol, m.p. 483–485 K. Precession photographs to check crystal quality. D_m not determined. Further work on Enraf–Nonius CAD-4 diffractometer (graphite monochromator). Crystal bound by faces {010}, (111), ($\bar{1}\bar{1}\bar{1}$), (001) and (10 $\bar{1}$), 0.069, 0.131, 0.131, 0.100 and 0.110 mm, respectively, from an origin within crystal used throughout. Accurate unit-cell dimensions by least-squares refinement of setting angles for 25 reflections ($8.3 < \theta < 15.3^\circ$). Data collected using $\omega:2\theta$ scans over (ω) scan ranges ($0.70 + 0.35 \tan \theta$)°. Scan rates conditional on information collected in prescans (at $10^\circ \text{ min}^{-1}$) selected to give $I \geq 25\sigma(I)$ within a max. scan time of 75 s. 3 standard reflections monitored every 8500 s of exposure time showed no significant losses in intensity over data-collection period. Backgrounds by extending scan by 25% on either side of peak measured for half the time taken to collect the peak. 4158 reflections (inc. standards) in quadrants $h, \pm k, \pm l$ ($h_{\text{max}} = 9, k_{\text{max}} = 13, l_{\text{max}} = 15$) with $2\theta \leq 55^\circ$ measured. Lorentz and polarization corrections applied to all reflections. 293 symmetry-equivalent reflections averaged [$R_{\text{merge}}(I) = 0.016$] and 236 reflections with $F_{\text{obs}} = 0.0$ rejected to give final data set of 3520 reflections. Structure solution: direct methods (MULTAN11/82; Main *et al.*, 1982), least-squares, Fourier and ΔF Fourier syntheses. H atoms located in ΔF maps were allowed to refine in final

cycles. Full-matrix least-squares refinement [C and O anisotropic, all parameters refined (320 variables)] minimizing $\sum w\Delta F^2$ converged (max. $\Delta/\sigma = 0.04$) to final agreement indices $R = 0.0408$ ($wR = 0.0518$) for 2800 observed [$I \geq 3\sigma(I)$] reflections. Weights given by $w = 4F^2/[\sigma^2(I) + (0.03F^2)^2]^{-1}$ and, at convergence, S was 1.90. Remaining peaks in a final difference Fourier map were $< 0.29 \text{ e } \text{\AA}^{-3}$ in height and were clearly associated with the mid-points of several of the bonds in the molecule. Programs: Enraf–Nonius (1979) *SDP* package on a PDP 11/23 computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic positional and thermal parameters are given in Table 1.*

Discussion. A view of the molecule is given in Fig. 1 and bond lengths, bond angles and endocyclic torsion angles are given in Figs. 2–4. The structure found shows that rings *A* and *B* have boat conformations, ring *C* has a chair conformation and ring *D* is in a C(14) α -envelope conformation with C(14) 0.626 (1) Å out of the least-squares mean plane through C(13), C(15), C(16) and C(17) (deviations of these atoms are $< \pm 0.032$ Å). Equivalently, ring *D* may be described by the puckering constants (Altona, Geise & Romers, 1968) $\Delta = -22.3$ (7) and $\varphi_m = 41.1$ (2)°, using the torsion angles shown in Fig. 4. The conformation of ring *D* is very similar to that of ring *D* in androst-4-ene-3,17-dione, but is significantly different from the half-chair conformations observed in several other androstane derivations (Coiro, Giglio, Lucano & Puliti, 1973).

Owing to the methano bridge, ring *A* is much more distorted in its boat conformation than is ring *B*. Thus, C(1) and C(4) deviate by 0.774 (2) and 0.783 (2) Å, respectively from a mean plane through C(2), C(3), C(5) and C(10) [planar to ± 0.042 (2) Å] while C(6) and C(9) deviate by 0.520 (1) and 0.484 (1) Å from the C(5), C(7), C(8), C(10) plane, and the internal angles in ring *A* [av. 102.9 (1)°] are significantly smaller than those in ring *B* [av. 114.2 (1)°].

Asymmetry parameters for all four rings are given in Table 2. Ring *C* is slightly distorted from a regular chair conformation owing to the *cis* *C/D* ring junction as atoms C(9) and C(13) are pushed away from [0.732 (1) Å] and towards [−0.541 (1) Å] the mean plane through the other atoms [planar to ± 0.009 (2) Å]. This results in an increase in the internal angles at C(12), C(14) and particularly C(13) [115.7 (1)°]. However, angle C(8)–C(14)–C(15) [111.8 (1)°] is significantly smaller than the average

* Lists of structure factors, anisotropic temperature factors and least-squares mean planes and a view of the crystal packing have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43765 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

value of this angle [119.3 (19)°] found in 91 other steroids that have the *C/D* ring fusion *trans* (Duax, Weeks & Rohrer, 1976); the corresponding C(14)–C(13)–C(17) angle, 101.4 (1)°, is comparable to the

average [99.2 (22)°]. These angular changes increase the torsion angle $\tau[\text{O}(3)\text{--C}(14)\text{--C}(13)\text{--C}(18)]$ to +48.6 (2)° and decrease $\tau[\text{C}(12)\text{--C}(13)\text{--C}(14)\text{--C}(8)]$ to 44.1 (2)°.

Table 1. *Positional parameters and equivalent isotropic thermal parameters with their e.s.d.'s in parentheses*

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:

$$\frac{1}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
O(1)	1.0699 (1)	0.4738 (1)	0.3833 (1)	3.91 (3)
O(2)	0.5179 (2)	0.8462 (1)	−0.01185 (9)	4.22 (3)
O(3)	0.6371 (1)	0.6194 (1)	0.42940 (8)	3.06 (2)
C(1)	0.7490 (2)	0.2669 (1)	0.1697 (1)	3.27 (3)
C(2)	0.8775 (2)	0.3584 (1)	0.0935 (1)	3.46 (3)
C(3)	1.0629 (2)	0.2907 (2)	0.1758 (1)	3.69 (3)
C(4)	1.0244 (2)	0.1610 (1)	0.2825 (1)	3.72 (3)
C(5)	0.8895 (2)	0.1993 (1)	0.3756 (1)	2.98 (3)
C(6)	0.9515 (2)	0.2743 (1)	0.4469 (1)	3.11 (3)
C(7)	0.9440 (2)	0.4256 (1)	0.3716 (1)	2.41 (3)
C(8)	0.7729 (2)	0.5159 (1)	0.2824 (1)	2.09 (2)
C(9)	0.6262 (2)	0.4334 (1)	0.2909 (1)	2.35 (3)
C(10)	0.6996 (2)	0.2815 (1)	0.2960 (1)	2.62 (3)
C(11)	0.4715 (2)	0.5258 (1)	0.1885 (1)	3.02 (3)
C(12)	0.3724 (2)	0.6582 (1)	0.2075 (1)	3.23 (3)
C(13)	0.5049 (2)	0.7415 (1)	0.2152 (1)	2.46 (3)
C(14)	0.6843 (2)	0.6541 (1)	0.3027 (1)	2.20 (2)
C(15)	0.8113 (2)	0.7563 (1)	0.2588 (1)	2.90 (3)
C(16)	0.7755 (2)	0.8299 (1)	0.1167 (1)	3.35 (3)
C(17)	0.5886 (2)	0.8117 (1)	0.0907 (1)	2.78 (3)
C(18)	0.3946 (2)	0.8631 (2)	0.2505 (1)	3.55 (3)
C(19)	0.5482 (2)	0.2039 (2)	0.3566 (2)	4.04 (4)
C(20)	0.8920 (3)	0.1210 (2)	0.2151 (2)	4.33 (4)
H(1)	0.739 (2)	0.601 (2)	0.475 (2)	5.4 (4)*
H(11)	0.640 (2)	0.274 (1)	0.126 (1)	3.1 (3)*
H(21)	0.823 (2)	0.459 (1)	0.073 (1)	3.0 (3)*
H(22)	0.896 (2)	0.348 (2)	0.010 (1)	4.5 (4)*
H(31)	1.098 (2)	0.354 (1)	0.206 (1)	3.7 (3)*
H(32)	1.169 (2)	0.261 (2)	0.131 (1)	4.8 (4)*
H(41)	1.134 (2)	0.088 (1)	0.324 (1)	4.0 (4)*
H(51)	0.870 (2)	0.109 (1)	0.442 (1)	3.1 (3)*
H(61)	1.075 (2)	0.230 (1)	0.485 (1)	3.6 (3)*
H(62)	0.861 (2)	0.278 (1)	0.513 (1)	4.2 (4)*
H(81)	0.822 (2)	0.544 (1)	0.199 (1)	2.5 (3)*
H(91)	0.569 (2)	0.421 (1)	0.372 (1)	2.6 (3)*
H(111)	0.377 (2)	0.475 (1)	0.191 (1)	3.8 (4)*
H(112)	0.527 (2)	0.552 (1)	0.105 (1)	3.6 (3)*
H(121)	0.274 (2)	0.718 (1)	0.138 (1)	3.5 (3)*
H(122)	0.305 (2)	0.635 (2)	0.285 (1)	4.3 (4)*
H(151)	0.940 (2)	0.711 (1)	0.284 (1)	3.5 (3)*
H(152)	0.766 (2)	0.825 (1)	0.297 (1)	3.7 (3)*
H(161)	0.869 (2)	0.783 (2)	0.072 (2)	5.3 (4)*
H(162)	0.767 (2)	0.932 (2)	0.082 (1)	4.5 (4)*
H(181)	0.356 (3)	0.819 (2)	0.338 (2)	6.0 (5)*
H(182)	0.279 (2)	0.915 (2)	0.196 (2)	6.0 (5)*
H(183)	0.464 (2)	0.936 (2)	0.245 (2)	5.0 (4)*
H(191)	0.536 (3)	0.197 (2)	0.443 (2)	6.3 (5)*
H(192)	0.429 (2)	0.255 (2)	0.311 (2)	5.2 (4)*
H(193)	0.586 (2)	0.106 (2)	0.358 (2)	5.9 (5)*
H(201)	0.836 (2)	0.045 (2)	0.271 (1)	4.3 (4)*
H(202)	0.949 (2)	0.098 (2)	0.144 (2)	5.4 (4)*

* Atoms refined isotropically.

Table 2. *Asymmetry parameters (Duax et al., 1976)*

Ring	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
	<i>C</i> ₁ (1)	<i>C</i> ₁ (6)	<i>C</i> ₁ (8)	<i>C</i> ₁ (9)
	7.9	8.1	12.7	2.9
	<i>C</i> ₂ (2–3)	<i>C</i> ₂ (5–10)	<i>C</i> ₂ (8–9)	<i>C</i> ₂ (8–14)
	6.7	7.6	10.9 < ϕ > 53.3	16.0
	<i>C</i> ₃ (11)	<i>C</i> ₃ (9–11)	<i>C</i> ₃ (13–14)	
	9.9	5.1	12.5	
	<i>C</i> ₄ (13)	<i>C</i> ₄ (14)		
	24.5	6.0		

E.s.d.'s are ≤ 0.37°.



Fig. 1. Stereoscopic view of the molecule. Thermal ellipsoids are drawn at the 50% probability level. All H atoms are drawn with uniform thermal parameters.

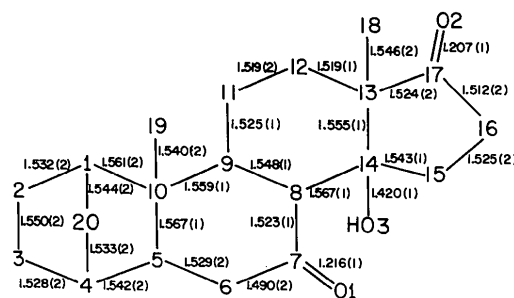


Fig. 2. Bond lengths (Å) between the non-H atoms.

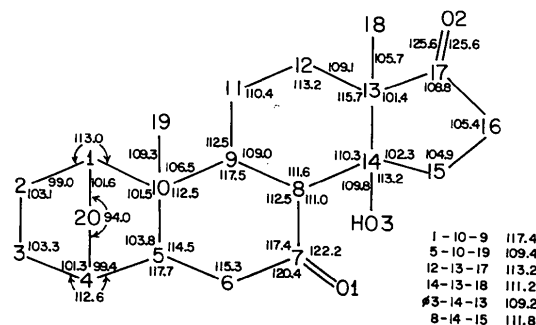


Fig. 3. Bond angles (°) involving the non-H atoms (e.s.d.'s are ≤ 0.1°).

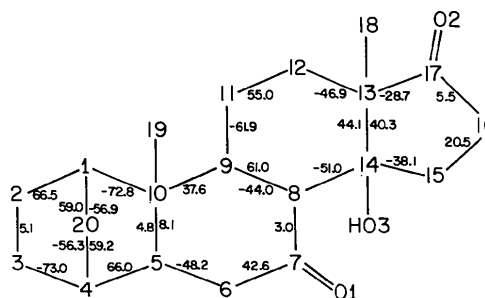


Fig. 4. Endocyclic torsion angles (°) (e.s.d.'s are 0.1–0.2°).

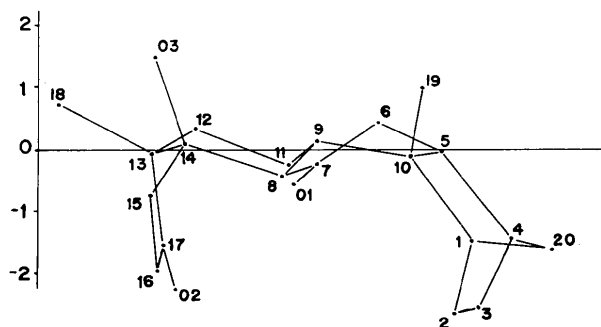


Fig. 5. A view of the overall conformation of the steroid. The molecule is viewed parallel to the least-squares mean plane through rings *B* and *C* and perpendicular to the C(8)–C(14) bond. The scale is in Ångström units.

It is usual to define a least-squares mean plane through the atoms C(5)–C(7) as a reference element for the gross analysis of steroid conformations (Duax *et al.*, 1976). However, owing to the *cis* junctions of rings *A/B* and *C/D*, rings *A* and *D* are significantly folded towards each other on the α face to give a compact molecule. In fact, mean planes through rings *A* and *D* make angles of *ca* 84 and 117°, respectively, with the mean plane through rings *B* and *C* (Fig. 5). Likewise the twist about the length of the molecule is defined using the torsion angle C(19)–C(10)···C(13)–C(18), which has a value of 36.9 (2)° in the present molecule. This value is considerably smaller than those obtained when ring *B* has 8 β sofa or 7 α ,8 β half-chair conformations (Duax *et al.*, 1976).

The longer bonds in the molecule (Fig. 2) involve atoms with attached H atoms and/or substituents approximately eclipsed. The crystal packing is determined by hydrogen bonds involving the 14 β -hydroxy group [O(1)···H(1) ($-x$, $1-y$, $1-z$) = 2.00 (2) Å, O(1)···H(1)–O(3) = 164 (1)°, C(7)–O(1)···H(1) = 97.3 (4)°]. Other short intramolecular O···H contacts are O(1)···H(61) = 2.39 (1) and O(3)···H(181) = 2.48 (2) Å.

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Structure of Sperminium Tetranitrate*†

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Abstract. 1,5,10,14-Tetraazoniatetradecane tetranitrate, $C_{10}H_{30}N_4^{4+}.4NO_3^-$, $M_r = 454.4$, monoclinic, $P2_1/c$, $a = 9.593$ (1), $b = 8.4623$ (7), $c = 13.314$ (2) Å, $\beta = 91.38$ (1)°, $V = 1080.5$ (2) Å³, $Z = 2$, $D_x =$

1.396 Mg m^{−3}, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, $\mu = 1.00$ mm^{−1}, $F(000) = 484$, $T = 290$ K, $R = 0.057$ for 1241 observed reflexions. The centrosymmetric sperminium tetracation adopts a generally stretched form with all bonds *trans* except for the terminal N–C–C–C torsion angles which are *gauche*. One nitrate anion forms H bonds only with secondary $-\text{NH}_2^+$ ammonium groups while the other accepts H bonds exclusively from primary $-\text{NH}_3^+$ groups. Each

* Studies of Biogenic Polyamines. II.

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