Crystal and Molecular Structure of 17β-Hydroxy-17α-methyl-2-oxa-5α-androstan-3-one [1]

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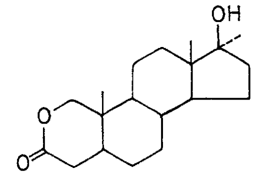
Crystals of the title compound (I) are monoclinic, $a = 9.146(3)$, $b = 9.591(3)$, $c = 9.512(4)$ Å, $\beta = 91.38(4)°$ space group $P2_1$, $Z = 2$. The structure was determined from diffractometer data by direct methods, and refined by full-matrix least-squares methods to R 0.035 for 1 429 observed reflexions. Ring A may be described as having either a slightly distorted half-chair conformation with a non-planar lactone group, or as having a flattened chair conformation. Rings B and C have regular chair, and ring D a C(13) envelope conformation. The molecules are linked by O–H ⋯ O hydrogen bonds (2.893 Å) and form infinite chains within layers perpendicular to the a axis. There are no short intermolecular contacts between layers.

17β-HYDROXY-17α-METHYL-2-OXA-5α-ANDROSTAN-3-ONE is an anabolic steroid (I) available commerically as Anavar or Oxandrolone. It was first prepared in 1962 and its potency as an anabolic steroid was found to be very high.[2] As part of a continuing investigation [3] into the structure–activity relationship in anabolic steroids we have undertaken an X-ray diffraction study of (I), one of the earliest therapeutically useful steroids with a heteroatom in the steroid nucleus.



(I)

EXPERIMENTAL

Crystals of (I) suitable for structural analysis were grown from acetone–water. Two crystal habits were seen, one orthorhombic and the other a monoclinic modification. The latter appeared to diffract Cu-K_α radiation to a greater extent than the former and was consequently used for all further experimental work.

Crystal Data.—$C_{19}H_{30}O_3$, $M = 306.4$. Monoclinic, $a = 9.146(3)$, $b = 9.591(3)$, $c = 9.512(4)$ Å, $\beta = 91.38(4)°$, $U = 834.1$ Å^3, $D_m = 1.21$, $Z = 2$, $D_c = 1.220$, $F(000) = 336$. Cu-K_α radiation, $\lambda = 1.5418$; μ(Cu-K_α) = 6.4 cm^{-1}. Space group $P2_1$ (C_2^2, No. 4).

Oscillation, Weissenberg, and precession photographs indicated monoclinic symmetry with the systematic absence $0k0$ when $k = 2n + 1$. This is consistent with space groups $P2_1$ (C_2^2, No. 4) and $P2_1/m$ (C_{2h}^2, No. 11). The former space group was assumed to be the correct choice in view of the fact that $Z = 2$, and the knowledge that the compound was optically active. A crystal of dimensions *ca.* $0.2 \times 0.6 \times 0.3$ mm^3 was used for intensity measurements and accurate values for unit-cell parameters were obtained by a least-squares fit of 24 $\sin^2\theta(hkl)$ values measured on a General Electric XRD 6 diffractometer.

Intensity data were measured on a Datex-automated General Electric XRD 6 diffractometer by the θ–2θ scan method at a rate of 2° min^{-1} in 2θ. A scintillation counter equipped with a nickel filter and pulse-height analyser ensured approximately monochromatic radiation. The crystal was mounted with b parallel to the goniostat axis. A total of 1 596 independent reflexions was measured with $2\theta \leqslant 135°$ (Cu-K_α radiation) of which 1 429, having $I \geqslant 3\sigma(I)$, where $\sigma^2(I) = S + B + (0.08S)^2$, and S is scan count and B background, were classified as observed. The intensity of a standard reflexion monitored periodically throughout data collection varied by up to 8%. Data were accordingly scaled, Lorentz and polarization corrections applied, and structure amplitudes derived. No absorption corrections were applied in view of the small absorption coefficient.

Structure Analysis and Refinement.—Data were placed on an absolute scale by Wilson's method,[4] and normalized structure amplitudes $|E_{hkl}|$ derived. The structure was solved by direct methods, 278 reflexions with normalized structure factor $|E| \geqslant 1.30$ being used in the symbolic addition procedure for non-centrosymmetric crystals.[5-7] Refinement was by least-squares methods, the function minimized being $\Sigma w(F_o - F_c)^2$ with weights w derived from counting statistics. Two cycles of full-matrix least-squares refinement on positional and isotropic thermal parameters reduced R to 0.18. In these and all subsequent refinement cycles the y co-ordinate of atom O(3) was held constant in order to fix the origin of the unit cell. The non-hydrogen atoms were refined with anisotropic temperature factors and a difference-Fourier synthesis at this stage revealed all 30 hydrogen atom positions, the peaks due to the nine methyl hydrogen atoms being amongst the largest in the electron-density map. Hydrogen atoms were included in the refinement with isotropic temperature factors and R was reduced to 0.040. An examination of the observed and calculated structure factors revealed a trend which could be interpreted as an extinction problem and so the function minimized in the refinement was modified to include an extinction parameter thus $\Sigma w\{F_o - [F_c/(1 + gI)]\}^2$ where g is the extinction coefficient and I the uncorrected intensity of a reflexion. One reflexion (200) still showed severe extinction effects and was given zero weight in the final cycle of refinement. Thus at convergence R was 0.035 and R' 0.046 $[R' = \Sigma w(F_o - F_c)^2/\Sigma wF_o^2)]$. The weighting scheme proved satisfactory and gave constant values of $w\Delta^2$ over all ranges of F_o. The error in an observation of unit weight was 0.89. The final value for the extinction coefficient was $5.9(5) \times 10^{-7}$, and the maximum fluctuations in a final difference-Fourier synthesis were ± 0.3 eÅ^{-3}. No final parameter shift-to-error ratio was >0.69, mean 0.11.

Scattering factors for oxygen and carbon were taken from ref. 8, and for hydrogen from ref. 9. Measured and calculated structure amplitudes, Tables of anisotropic thermal

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parameters, origin-fixing reflexions, the results of phasing attempts, and least-squares planes are listed in Supplementary Publication No. SUP 21359 (21 pp., 1 microfiche)*. Final positional parameters are given in Table 1.

TABLE 1

Final positional parameters (fractional × 10^4, H × 10^3), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	2 049(3)	−4 514(4)	−2 159(3)
O(2)	2 303(3)	−3 948(3)	52(2)
O(3)	3 137(2)	3 043	6 417(2)
C(1)	2 222(4)	−2 928(4)	1 194(3)
C(3)	2 159(3)	−3 591(4)	−1 295(3)
C(4)	2 189(3)	−2 079(4)	−1 707(3)
C(5)	1 938(3)	−1 045(4)	−521(2)
C(6)	2 276(4)	453(4)	−965(3)
C(7)	1 942(3)	1 471(4)	220(3)
C(8)	2 698(3)	1 083(3)	1 619(2)
C(9)	2 368(2)	−452(3)	2 021(2)
C(10)	2 787(2)	−1 486(3)	831(2)
C(11)	3 012(3)	−841(4)	3 485(2)
C(12)	2 552(3)	184(3)	4 636(2)
C(13)	2 908(2)	1 693(3)	4 252(2)
C(14)	2 184(3)	2 020(3)	2 808(2)
C(15)	2 338(4)	3 608(4)	2 663(3)
C(16)	2 291(4)	4 155(4)	4 188(3)
C(17)	2 240(3)	2 870(3)	5 170(2)
C(18)	4 586(3)	1 884(4)	4 254(3)
C(19)	4 449(3)	−1 554(4)	633(3)
C(20)	684(3)	2 574(4)	5 621(3)
H(1a)	276(4)	−331(4)	195(4)
H(1b)	116(4)	−285(3)	147(3)
H(4a)	310(4)	−193(4)	−218(4)
H(4b)	142(4)	−193(5)	−252(4)
H(5)	92(3)	−108(3)	−31(3)
H(6a)	330(4)	58(4)	−123(3)
H(6b)	170(4)	72(4)	−189(4)
H(7a)	230(4)	244(4)	−6(4)
H(7b)	93(3)	145(3)	39(3)
H(8)	377(3)	124(3)	147(3)
H(9)	132(3)	−53(3)	214(2)
H(11a)	410(3)	−85(3)	345(3)
H(11b)	265(3)	−186(4)	380(3)
H(12a)	306(3)	−7(3)	557(3)
H(12b)	153(3)	8(3)	472(3)
H(14)	106(3)	176(3)	288(3)
H(15a)	329(3)	387(4)	224(3)
H(15b)	152(4)	397(5)	210(4)
H(16a)	321(4)	474(4)	438(4)
H(16b)	144(5)	476(5)	432(4)
H(18a)	502(3)	131(3)	362(3)
H(18b)	499(4)	281(6)	403(4)
H(18c)	498(4)	171(4)	525(4)
H(19a)	495(4)	−68(5)	40(4)
H(19b)	496(4)	−187(5)	147(4)
H(19c)	472(4)	−211(5)	−9(5)
H(20a)	3(3)	244(4)	480(3)
H(20b)	62(3)	173(4)	621(3)
H(20c)	37(4)	331(5)	619(4)
H(O3)	272(4)	358(5)	692(4)

DISCUSSION

Figure 1 is a stereoscopic view of the steroid molecule showing the atomic numbering scheme. For the sake of clarity the hydrogen atoms are not labelled. The correct absolute configuration of the molecule is shown. Thermal ellipsoids are quite small, indicating very little thermal motion. Bond lengths and valency angles with their standard deviations are listed in Table 2. The $C(sp^3)$–$C(sp^3)$ bond distances range from 1.519 to 1.560 Å, mean 1.538 Å, which agrees well with that found in other steroid molecular structure determinations.[3,10,11] The C–H distances range from 0.92 to 1.09 Å mean 0.99 Å (for twenty-nine bonds). The predicted [12] mean valency angles in the six-membered rings (109.5, 110.5, and 111.5°) about quaternary-, tertiary-, and secondary-substituted carbon atoms agree reasonably well with the means found for rings B and C (109.4, 111.7, and 112.0°). The poorest agreement is for tertiary-substituted carbon atoms, but this same trend was noted in (II), a similar steroid 17β-hydroxy-17α-methyl-5α-androst-1-en-3-one.[3]

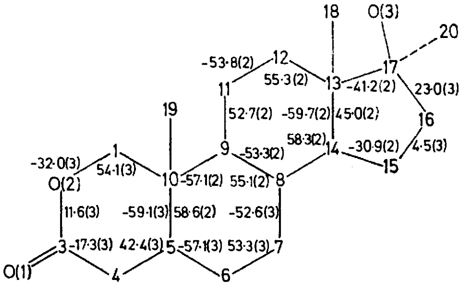
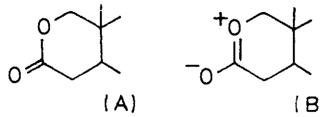


FIGURE 2 Dihedral angles in (I)

Figure 2 shows the dihedral angles within the molecule and their estimated standard deviations. Ring A, although containing no formal endocyclic double bonds, shows considerable departure from the usual chair conformation. The presence of the carbonyl group alone is sufficient to distort the conformation to that of a slightly flattened chair, but the presence of the δ-lactone group C(1)–O(2)–C(3)–O(1)–C(4) imposes a greater distortion on the ring due to the planarity of the canonical form (B) which is assumed to contribute to the structure.



A similar structure, that of 6α-bromo-17β-hydroxy-17α-methyl-4-oxa-5α-androstan-3-one (III), has been described [13] with bond lengths of 1.21(3), 1.28(3), and 1.45 (2) Å corresponding to C(3)–O(1) 1.211(5), C(3)–O(2) 1.330(4), and C(1)–O(2) 1.466(4) Å in (I). The trend in the observed ratios of $C(sp^2)$–O single bonds to $C(sp^3)$–O bonds in δ- and γ-lactones [14,15] was first noted by Mathieson and Taylor.[16] They formulated the rule that these two bond lengths should differ by *ca.* 0.1 Å and also suggested that the five atoms comprising the lactone group should be coplanar. As more structural data for lactones became

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* For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

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available, Sim[17] noted that δ-lactones normally adopt the half-chair conformation if free to do so, but may adopt the half-chair conformation as a result of special circumstances, *e.g.* steric constraints imposed by fusion to a five-membered ring.

The five atoms comprising the lactone grouping in (I) are not rigorously planar with deviations from the mean plane through the five atoms ranging from −0.076(4) to 0.068(3) Å, and the C(4)–C(3)–O(2)–C(1) dihedral angle is 11.66(3)°. In (III) the deviations from the mean plane through the lactone grouping range from −0.13 to 0.09 Å and the corresponding dihedral angle is −23° which suggests that the lactone grouping is less planar than that in (I). The C(sp^2)–O distance in (I) (1.330 Å) is not as short as that in (III) but is certainly shorter than that (1.41 Å) in detigloylswietenine,[18] which contains a δ-lactone group. Corresponding distances in other δ-lactones are: 1.34 glaucarubin,[19] 1.32 limonin,[20] 1.40 isocolumbin,[21] and 1.36 Å mean for iridomyrmecin and isoiridomyrmecin.[14] The valency angle of 122.5(3)° for C(3)–O(2)–C(1) lends further support for the inclusion of (B) in the structure. The corresponding angle in (III) is 120(1)°. This would certainly suggest some sp^2 hybridization at O(2). The difference (0.136 Å) in the length of bonds C(1)–O(2) and C(3)–O(2) is in agreement with the prediction of Mathieson and Taylor.[16]

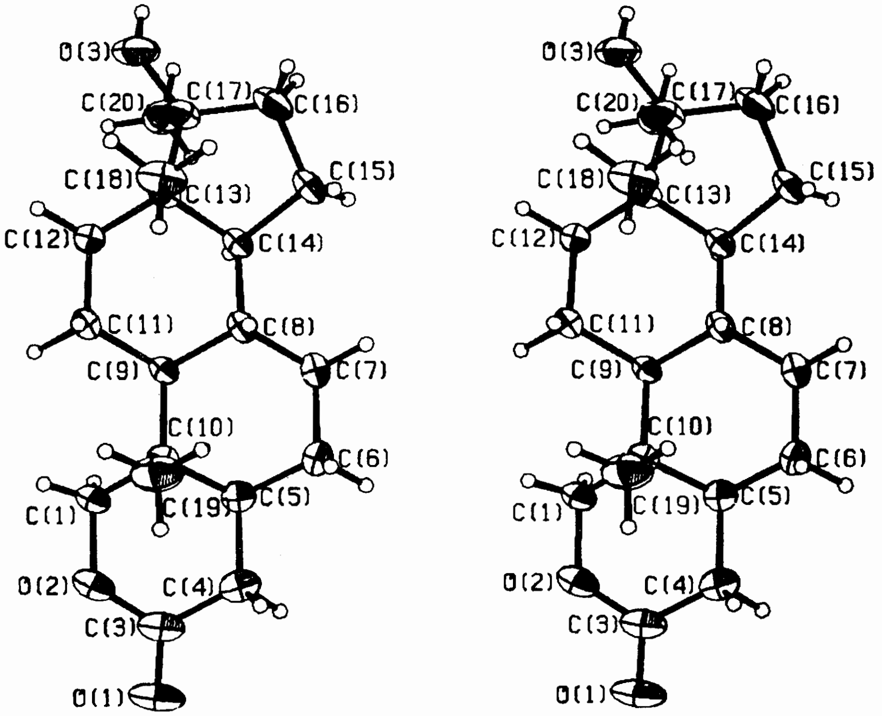

FIGURE 1 Stereoscopic view of (I)

Atoms C(5) and C(10) are displaced from the lactone mean plane by 0.278(2) and 0.438(2) Å, which would tend to indicate a slightly distorted half-chair conformation for ring A, with a non-planar lactone group. Alternatively, ring A could be described as a flattened chair, as the disdisplacements of atoms C(10) and C(3) from the mean plane through atoms O(2), C(1), C(4), and C(5) are −0.721(2) and 0.151(3) Å. In fact this description is probably just as valid as the distorted half-chair in view of the distribution of dihedral angles (Figure 2) which is almost antisymmetric about the C(3) ··· C(10) vector.

Rings B and C appear to be largely unaffected by the distortions in ring A and have normal chair conformations, as indicated by their dihedral angles (Figure 2), which agree closely with expected values for ' standard ' B and C rings.[12] When compared with those angles in the B and C rings of (II)[3] the agreement is good for the B ring but less so for the C ring. Ring D has a C(13) envelope conformation as determined by inspection of least-squares plane calculations through sets of four atoms. Atoms C(14)—(17) form the best plane with C(13) −0.684(2) Å from it. The maximum angle of torsion[22] (ϕ_m) is 46.0°, and the phase angle of pseudorotation (Δ) is 23.5°, compared to 43.9 and 11.4° in (II). The dihedral angles in ring D compare favourably with those predicted[23] for one of a number of conformational energy

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minima (Table 3). The minimum energy conformation for ring D in (I) is not the same one as in (II).

Figure 3 is a view of the steroid skeleton parallel to the bestplane through atoms C(5)—(17). The skeleton is convex towards the β-side; the C(18) ··· C(19) intramolecular non-bonded distances of 4.65 in (II) and 4.77 Å in (I) show that the degree of bending is slightly greater in (I). The marked similarity between Figure 3 and the corresponding view of (II) is to be expected since the only chemical difference between these two steroids is in ring A.

Figure 4 is a stereoscopic view of the contents of the unit cell. Hydrogen atoms with the exception of H(O3) have been omitted for clarity. The molecules are well separated in the unit cell, the only close intermolecular contact being the O–H ··· O hydrogen bond between the 17β-hydroxy group of one molecule and the carbonyl oxygen atom of a molecule related to the former by a translation operation. O(1) ··· O(3) is 2.893(3) Å, the angle O(3)–H(O3) ··· O(1) is 160(4)°, and the angle C(3)–O(1) ··· H(O3) is 153(1)° compared with 2.76 Å, 169.7, and 118.1° in (II). The O(3)–H(O3) distance in (I) is 0.80(4) Å and C(17)–O(3)–H(O3) is 107(3)°. Thus the hydrogen bond would appear to be weaker in (I). There is only one other intermolecular contact <3.5 Å and that involves atom O(2). Atoms C(15) and O(2) in molecules related by the translation *x*, *y* — 1, *z* are separated by 3.414(4) Å. The presence of a C–H ··· O hydrogen bond does not appear likely, however, in view of the contact dis-

TABLE 2

Bond lengths (Å), and valency angles (°), with estimated standard deviations in parentheses

(*a*) Bond distances

O(1)–C(3)	1.211(5)	C(9)–C(10)	1.560(4)
O(2)–C(1)	1.466(4)	C(9)–C(11)	1.544(3)
O(2)–C(3)	1.330(4)	C(10)–C(19)	1.537(4)
O(3)–C(17)	1.436(3)	C(11)–C(12)	1.539(4)
C(1)–C(10)	1.519(5)	C(12)–C(13)	1.529(5)
C(3)–C(4)	1.503(6)	C(13)–C(14)	1.543(3)
C(4)–C(5)	1.524(4)	C(13)–C(17)	1.560(4)
C(5)–C(6)	1.532(5)	C(13)–C(18)	1.545(3)
C(5)–C(10)	1.546(3)	C(14)–C(15)	1.536(5)
C(6)–C(7)	1.528(4)	C(15)–C(16)	1.543(4)
C(7)–C(8)	1.531(4)	C(16)–C(17)	1.548(4)
C(8)–C(9)	1.553(5)	C(17)–C(20)	1.523(4)
C(8)–C(14)	1.528(4)		

(*b*) Valency angles

C(1)–O(2)–C(3)	122.5(3)	C(14)–C(13)–C(17)	100.7(2)
O(2)–C(1)–C(10)	114.5(2)	C(14)–C(13)–C(18)	112.4(2)
O(1)–C(3)–O(2)	118.1(4)	C(17)–C(13)–C(18)	108.4(2)
O(1)–C(3)–C(4)	122.0(3)	C(8)–C(14)–C(13)	114.0(2)
O(2)–C(3)–C(4)	119.8(3)	C(8)–C(14)–C(15)	119.1(2)
C(3)–C(4)–C(5)	115.5(2)	C(13)–C(14)–C(15)	104.1(2)
C(4)–C(5)–C(6)	111.8(2)	C(14)–C(15)–C(16)	104.3(2)
C(4)–C(5)–C(10)	110.8(3)	C(15)–C(16)–C(17)	107.4(3)
C(6)–C(5)–C(10)	112.7(2)	O(3)–C(17)–C(13)	108.8(2)
C(5)–C(6)–C(7)	110.5(2)	O(3)–C(17)–C(16)	112.4(2)
C(6)–C(7)–C(8)	113.1(3)	O(3)–C(17)–C(20)	107.9(2)
C(7)–C(8)–C(9)	111.0(2)	C(13)–C(17)–C(16)	102.7(2)
C(7)–C(8)–C(14)	111.1(2)	C(13)–C(17)–C(20)	113.8(2)
C(9)–C(8)–C(14)	108.1(2)	C(16)–C(17)–C(20)	111.1(2)
C(8)–C(9)–C(10)	111.8(2)	C(5)–C(10)–C(19)	112.9(2)
C(8)–C(9)–C(11)	112.3(2)	C(9)–C(10)–C(19)	112.1(2)
C(10)–C(9)–C(11)	113.9(2)	C(9)–C(11)–C(12)	112 4(2)
C(1)–C(10)–C(5)	105.7(2)	C(11)–C(12)–C(13)	111.9(2)
C(1)–C(10)–C(9)	108.8(2)	C(12)–C(13)–C(14)	108.4(2)
C(1)–C(10)–C(19)	109.4(3)	C(12)–C(13)–C(17)	117.5(2)
C(5)–C(10)–C(9)	107.6(2)	C(12)–C(13)–C(18)	109.2(2)

(*c*) Distances involving hydrogen atoms

C(1)–H(1a)	0.94(3)	C(7)–H(7a)	1.02(4)
C(1)–H(1b)	1.01(3)	C(7)–H(7b)	0.94(3)
C(4)–H(4a)	0.97(4)	C(8)–H(8)	1.00(3)
C(4)–H(4b)	1.05(4)	C(9)–H(9)	0.98(3)
C(5)–H(5)	0.96(3)	C(11)–H(11a)	1.00(3)
C(6)–H(6a)	0.99(3)	C(11)–H(11b)	1.09(4)
C(6)–H(6b)	1.05(4)	C(12)–H(12a)	1.03(3)
C(12)–H(12b)	0.95(3)	C(18)–H(18c)	1.02(4)
C(14)–H(14)	1.06(3)	C(19)–H(19a)	0.98(5)
C(15)–H(15a)	1.00(3)	C(19)–H(19b)	0.97(4)
C(15)–H(15b)	0.97(4)	C(19)–H(19c)	0.92(5)
C(16)–H(16a)	1.02(4)	C(20)–H(20a)	0.98(3)
C(16)–H(16b)	0.99(4)	C(20)–H(20b)	0.99(4)
C(18)–H(18a)	0.91(3)	C(20)–H(20c)	0.94(4)
C(18)–H(18b)	0.99(5)	O(3)–H(O3)	0.80(4)

TABLE 2 (*Continued*)

(*d*) Angles involving hydrogen atoms

C(17)–O(3)–H(O3)	107(3)	C(3)–C(4)–H(4a)	106(2)
O(2)–C(1)–H(1a)	105(2)	C(3)–C(4)–H(4b)	107(2)
O(2)–C(1)–H(1b)	108(2)	C(5)–C(4)–H(4a)	114(2)
C(10)–C(1)–H(1a)	111(2)	C(5)–C(4)–H(4b)	111(2)
C(10)–C(1)–H(1b)	109(2)	H(4a)–C(4)–H(4b)	102(3)
H(1a)–C(1)–H(1b)	108(3)	C(4)–C(5)–H(5)	106(2)
C(6)–C(5)–H(5)	108(2)	C(8)–C(9)–H(9)	108(2)
C(10)–C(5)–H(5)	107(2)	C(10)–C(9)–H(9)	107(1)
C(5)–C(6)–H(6a)	113(2)	C(11)–C(9)–H(9)	103(1)
C(5)–C(6)–H(6b)	111(2)	C(9)–C(11)–H(11a)	110(1)
C(7)–C(6)–H(6a)	109(2)	C(9)–C(11)–H(11b)	111(2)
C(7)–C(6)–H(6b)	111(2)	C(12)–C(11)–H(11a)	109(2)
H(6a)–C(6)–H(6b)	102(3)	C(12)–C(11)–H(11b)	107(2)
C(6)–C(7)–H(7a)	108(2)	H(11a)–C(11)–H(11b)	108(2)
C(6)–C(7)–H(7b)	109(2)	C(11)–C(12)–H(12a)	109(2)
C(8)–C(7)–H(7a)	108(2)	C(11)–C(12)–H(12b)	106(2)
C(8)–C(7)–H(7b)	106(2)	C(13)–C(12)–H(12a)	111(2)
H(7a)–C(7)–H(7b)	113(3)	C(13)–C(12)–H(12b)	110(2)
C(7)–C(8)–H(8)	105(2)	H(12a)–C(12)–H(12b)	109(2)
C(9)–C(8)–H(8)	112(2)	C(8)–C(14)–H(14)	103(1)
C(14)–C(8)–H(8)	110(2)	C(13)–C(14)–H(14)	107(1)
C(15)–C(14)–H(14)	109(2)	H(18a)–C(18)–H(18c)	111(3)
C(14)–C(15)–H(15a)	112(2)	H(18b)–C(18)–H(18c)	103(3)
C(14)–C(15)–H(15b)	109(3)	C(10)–C(19)–H(19a)	117(2)
C(16)–C(15)–H(15a)	110(2)	C(10)–C(19)–H(19b)	112(2)
C(16)–C(15)–H(15b)	111(2)	C(10)–C(19)–H(19c)	114(2)
H(15a)–C(15)–H(15b)	111(3)	H(19a)–C(19)–H(19b)	104(3)
C(15)–C(16)–H(16a)	108(2)	H(19a)–C(19)–H(19c)	101(4)
C(15)–C(16)–H(16b)	111(2)	H(19b)–C(19)–H(19c)	108(4)
C(17)–C(16)–H(16a)	112(2)	C(17)–C(20)–H(20a)	111(2)
C(17)–C(16)–H(16b)	111(3)	C(17)–C(20)–H(20b)	113(2)
H(16a)–C(16)–H(16b)	107(3)	C(17)–C(20)–H(20c)	109(2)
C(13)–C(18)–H(18a)	112(2)	H(20a)–C(20)–H(20b)	107(3)
C(13)–C(18)–H(18b)	119(2)	H(20a)–C(20)–H(20c)	112(3)
C(13)–C(18)–H(18c)	108(2)	H(20b)–C(20)–H(20c)	105(3)
H(18a)–C(18)–H(18b)	103(3)		

TABLE 3

Dihedral angles (deg.) in ring D compared with predicted values for a conformational energy minimum

Bond	Found	Calc.*
C(13)–C(14)	45.0(2)	43.0
C(14)–C(15)	−30.9(2)	−29.8
C(15)–C(16)	4.5(3)	5.0
C(16)–C(17)	23.0(3)	21.8
C(17)–C(13)	−41.2(2)	−40.0

* According to ref. 23.

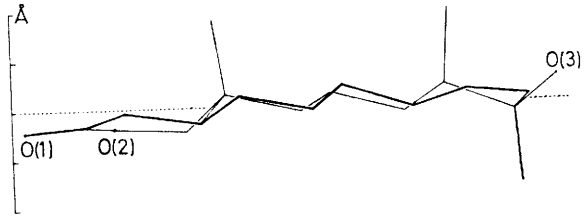

FIGURE 3 Steroid skeleton viewed parallel to the best plane through atoms C(5)—(17)

tances and bond angles: O(2) ··· H(15a) 3.07(3), O(2) ··· H(15b) 2.89(4) Å, C(15)–H(15b) ··· O(2) 101(2)°, and C(15)–H(15b) ··· O(2) 114(3)°. The sum of the van der Waals radii for oxygen and hydrogen is usually taken as 2.6 Å.[24] A hydrogen bond of this type would also be unlikely in view of the contribution to the structure of canonical form (B). A residual positive charge on atom O(2) would certainly hinder its role as an acceptor atom. The packing of the molecules in the solid state thus consists of alternate layers of hydrogen-bonded chains of steroid molecules with no interlayer hydrogen bonds.

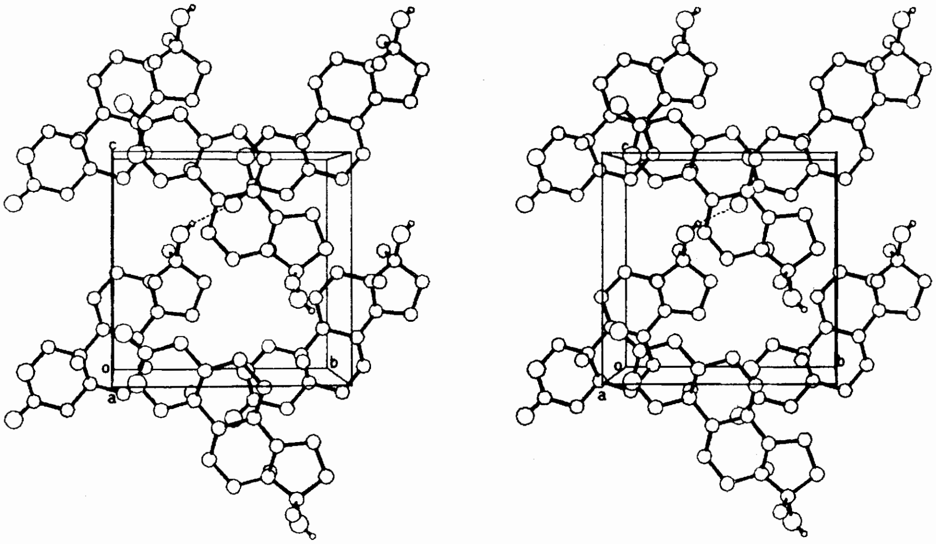

FIGURE 4 Stereoscopic view of the unit cell with a^* pointing toward the viewer

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[24] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.