

The Crystal and Molecular Structures of 5 α -Androstan-3 β -ol-17-one and 5 β -Androstane-3 α ,17 β -diol

BY CHARLES M. WEEKS, A. COOPER*, AND DORITA A. NORTON

The Medical Foundation of Buffalo, 73 High Street, Buffalo, N.Y. 14203, U.S.A.

AND HERBERT HAUPTMAN† AND JANET FISHER

U.S. Naval Research Laboratory, Washington, D.C. 20390, U.S.A.

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The crystal and molecular structures of 5 α -androstan-3 β -ol-17-one (epiandrosterone, C₁₉H₃₀O₂) and 5 β -androstan-3 α ,17 β -diol (C₁₉H₃₂O₂) have been determined from three-dimensional X-ray data. The initial phases for these structures were obtained by a least-squares analysis of the structure invariants $\cos(\varphi_1 + \varphi_2 + \varphi_3)$. Both substances crystallize in space group $P2_1$ with two molecules in the unit cell. The unit-cell dimensions are $a=6.596$, $b=21.521$, $c=6.313$ Å, and $\beta=109.36^\circ$ for epiandrosterone and $a=11.875$, $b=7.157$, $c=10.960$ Å, and $\beta=114.70^\circ$ for 5 β -androstan-3 α ,17 β -diol. In crystals of these two substances and of androsterone, the C(3) epimer of epiandrosterone, hydrogen bonds form spirals of molecules parallel to the symmetry axes and cause the packing and orientation of the epiandrosterone molecules within the unit cell to be different from the molecular stacking in androsterone and 5 β -androstan-3 α ,17 β -diol crystals. A detailed discussion of steroids having unsaturated side-chain linkage to the D ring at C(17) is presented.

Introduction

5 β -Androstane-3 α ,17 β -diol [Fig. 1(a)] and 5 α -androstan-3 β -ol-17-one [Fig. 1(b)] are androstane derivatives that possess little hormonal activity. The solution of their crystal structures is a continuation of our program in the search for relationships between the structure and biological function of steroid molecules; also, it represents further applications of the direct method of structure determination by least-squares analysis of structure invariants (Hauptman, Fisher, Hancock & Norton, 1969; Hauptman, 1970; Hauptman, Weeks & Fisher, 1971).

The skeleton of 5 β -androstan-3 α ,17 β -diol differs from its more common 5 α -epimer, in having a *cis* A/B ring junction. It occurs in human urine, and has been isolated from microbiological reactions of 5 β -androstan-3,17-dione, testosterone, and androst-4-ene-3,17-dione with putrefactive bacteria. As measured by the ability to produce comb growth in capons, the 5 α -epimer shows androgenic activity approaching that of testosterone, but the 5 β -epimer shows little such activity. On the other hand, in the Allen-Doisy test, the 5 β -epimer shows considerable estrogenic activity towards castrated female mice (Ercoli, 1938). 5 α -androstan-3 β -ol-17-one (epiandrosterone) is a quantitatively minor urinary metabolite of the primary male sex hormone, testosterone (White, Handler & Smith, 1964), and it possesses approximately $\frac{1}{10}$ of the androgenic

activity of testosterone in the capon comb test (Applezweig, 1962). The C(3) epimer, androsterone, is one of the major degradation products of testosterone and has a biological activity approximately ten times as great as that of epiandrosterone. Hydrogen bonds in crystals of 5 β -androstan-3 α ,17 β -diol, epiandrosterone, and androsterone (High & Kraut, 1966) create spirals of mol-

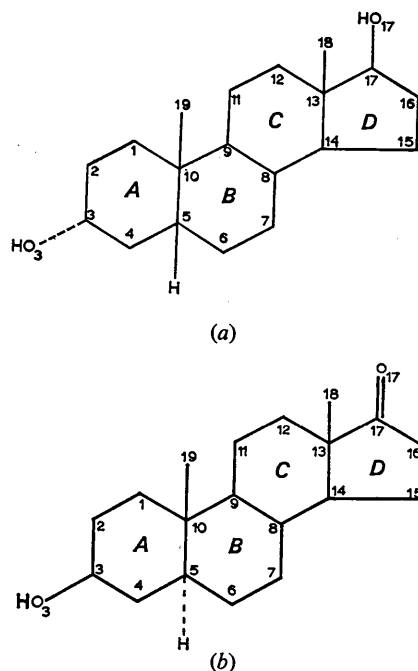


Fig. 1. Atomic numbering for (a) 5 β -androstan-3 α ,17 β -diol and (b) 5 α -androstan-3 β -ol-17-one (epiandrosterone).

* Present address: Hospital Data Sciences, Inc. 654 Madison Avenue, 20th floor, New York, New York 10021, U.S.A.

† Present address: The Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, U.S.A.

ecules parallel to the symmetry axes, but the long axes of the epiandrosterone molecules are approximately parallel to the symmetry axes whereas the long axes of the other molecules are nearly perpendicular to the symmetry axes. Consequently, the packing of epiandrosterone differs from the packing of the other two

androsteranes. Although the *intermolecular* geometry in the androsterone and epiandrosterone crystals is different, the *intramolecular* geometry is very similar, and it appears that the observed differences in the biological activities of these isomers arise from the differences in the way they interact with other hydrogen-bond forming substances as exemplified by their interactions with other molecules of the same kind in the crystalline state.

Experimental

The experimental measurements required for the X-ray analysis of 5β -androsterone- $3\alpha,17\beta$ -diol (I) and epiandrosterone (II) were performed on a General Electric single-crystal orienter using Cu $K\alpha$ radiation monochromatized by balanced nickel and cobalt filters. In both cases, the systematic absences ($0k0$ for k odd) in the diffraction pattern were consistent with the monoclinic space group $P2_1$ (C_2^2 , No. 4), and the unit-cell dimensions were determined by a least-squares analysis of 30 independent measurements of 2θ for high angle data (at 20°C ; λ Cu $K\alpha_1 = 1.54051 \text{ \AA}$). The densities of the crystals were determined by flotation in an aqueous solution of potassium iodide. The crystal data for the two compounds are summarized in Table 1.

The diffraction intensities were measured by the stationary-counter stationary-crystal technique, and, after the usual Lorentz and polarization corrections had been made, they were placed on an absolute scale by fitting a scaling equation of the type

$$I = I_0 A \exp(B \sin^n \theta / \lambda^n)$$

where the constants A , B , and n were obtained by a least-squares analysis of the data and were found to be 0.5940, 7.3737, and 2.5 for (I) and 0.1199, 8.5254, and 2.4 for (II), respectively. Normalized structure-factor amplitudes were derived from the scaled intensities, and phases were determined by a least-squares analysis of the structure invariants, $\cos(\varphi_1 + \varphi_2 + \varphi_3)$, as described in the preceding paper (Hauptman, Weeks & Fisher, 1971). The positional and anisotropic thermal parameters of the nonhydrogen atoms were refined by

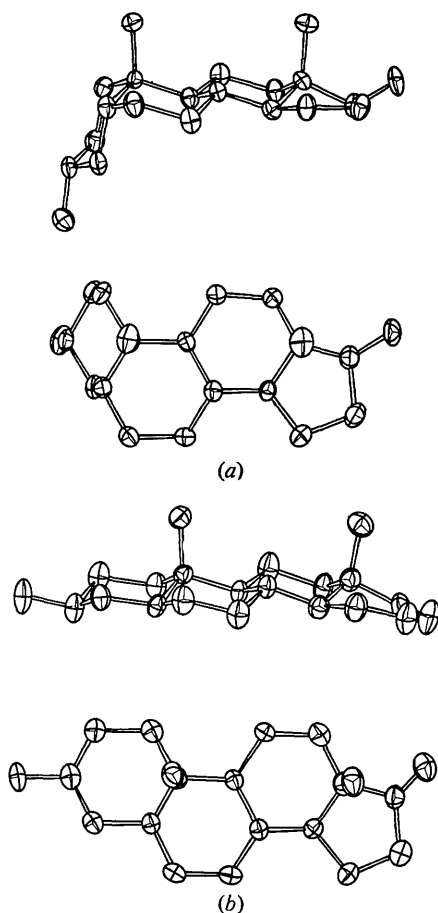


Fig. 2. Thermal vibration ellipsoids, scaled to 50% probability, of the nonhydrogen atoms. (a) 5β -androsterone- $3\alpha,17\beta$ -diol and (b) 5α -androstan- 3β -ol-17-one (epiandrosterone).

Table 1. Crystal data

	5α -Androstan- 3β -ol-17-one (epiandrosterone)	5β -Androstane- $3\alpha,17\beta$ -diol
Formula	$C_{19}H_{30}O_2$	$C_{19}H_{32}O_2$
Mol. wt.	290.4	292.3
Space group	$P2_1$	$P2_1$
Z	2	2
a	$6.596 \pm 0.001 \text{ \AA}$	$11.875 \pm 0.002 \text{ \AA}$
b	21.521 ± 0.001	7.157 ± 0.001
c	6.313 ± 0.001	10.960 ± 0.002
β	$109.39 \pm 0.01^\circ$	$114.70 \pm 0.02^\circ$
V	845.3 \AA^3	846.2 \AA^3
D_m (g.cm^{-3})	1.15	1.14
D_c (g.cm^{-3})	1.14	1.15
μ (cm^{-1})	5.61	5.61
$F(000)$	320	324

least-squares, using a block-diagonal approximation to the normal equations.*

A Fourier difference synthesis was computed for epandrosterone when the reliability index R, was

* Quantity minimized: $\sum w(|F_o| - |F_c|)^2$. Scattering factors: *International Tables for X-ray Crystallography* (1962), Table 3.3.1A.

7.4%, and this synthesis revealed the locations of the 30 hydrogen atoms. The positional and thermal parameters ($B_{180}=2.0$) of the hydrogen atoms were held constant, and the parameters of the nonhydrogen atoms were subjected to further refinement after which the final R index was 6.4% for all 1768 reflections. The weighting scheme used was of the Hughes type where $\sqrt{w}=1$ if $|F_o| < 12$, and $\sqrt{w}=12/|F_o|$ otherwise.

Table 2. Comparison of $|F_o|$ and $|F_c|$ for the refined atomic parameters

The structure amplitudes are given on ten-times absolute scale.

5 β -Androstane-3 α ,17 β -diol

Table with 64 columns (M, K, L, P, O, F, C) and 1768 rows of numerical data representing structure amplitudes.

Table 3. Atomic coordinates and thermal parameters of the atoms

The anisotropic thermal parameters of the nonhydrogen atoms are of the form $\exp[-2\pi^2(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl) + \dots]$. The standard deviations of the last two figures are given in parentheses.

5 β -Androstane-3 α ,17 β -diol nonhydrogen atoms

	X/A	Y/B	Z/C	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	0-16083 (57)	0-4170 (—)	0-21184 (64)	0-0308 (30)	0-0355 (35)	0-0309 (23)	-0 0105 (29)	0 0140 (22)	-0-0051 (25)
C(2)	0-14761 (58)	0-4934 (11)	0-33525 (62)	0-0296 (29)	0-0441 (38)	0-0254 (21)	-0-0070 (29)	0-0108 (20)	0-0043 (25)
C(3)	0-07558 (51)	0-6775 (09)	0-30099 (60)	0-0221 (25)	0-0353 (33)	0-0277 (23)	-0-0023 (26)	0-0117 (19)	-0-0027 (25)
C(4)	0-13708 (54)	0-8192 (10)	0-24623 (64)	0-0245 (27)	0-0386 (37)	0-0299 (21)	0-0006 (27)	0-0128 (21)	0-0002 (25)
C(5)	0-15058 (51)	0-7398 (10)	0-11989 (56)	0-0234 (25)	0-0384 (34)	0-0206 (18)	0-0013 (27)	0-0083 (18)	0-0055 (23)
C(6)	0-20648 (59)	0-8897 (11)	0-06192 (65)	0-0318 (31)	0-0454 (41)	0-0289 (22)	0-0041 (31)	0-0115 (22)	0-0101 (24)
C(7)	0-34672 (59)	0-9187 (09)	0-15298 (68)	0-0326 (30)	0-0291 (32)	0-0346 (24)	0-0026 (27)	0-0154 (22)	0-0090 (27)
C(8)	0-41937 (50)	0-7355 (09)	0-18044 (57)	0-0232 (24)	0-0308 (31)	0-0233 (19)	0-0013 (25)	0-0109 (18)	0-0018 (21)
C(9)	0-36284 (49)	0-5910 (09)	0-24360 (53)	0-0212 (23)	0-0291 (30)	0-0190 (17)	0-0024 (23)	0-0071 (17)	0-0035 (19)
C(10)	0-22430 (51)	0-5543 (10)	0-14971 (56)	0-0248 (26)	0-0367 (34)	0-0213 (19)	-0-0032 (28)	0-0096 (18)	-0-0022 (24)
C(11)	0-44192 (56)	0-4116 (09)	0-28979 (68)	0-0274 (30)	0-0235 (30)	0-0377 (26)	-0-0001 (26)	0-0102 (22)	0-0021 (22)
C(12)	0-58078 (54)	0-4527 (09)	0-37636 (60)	0-0265 (27)	0-0355 (34)	0-0259 (21)	0-0022 (27)	0-0106 (20)	0-0084 (23)
C(13)	0-63444 (50)	0-5863 (09)	0-30693 (56)	0-0249 (25)	0-0322 (32)	0-0235 (19)	0-0024 (25)	0-0125 (18)	-0-0011 (22)
C(14)	0-55481 (51)	0-7666 (09)	0-27470 (54)	0-0258 (26)	0-0326 (31)	0-0194 (18)	-0-0020 (26)	0-0111 (18)	-0-0004 (21)
C(15)	0-63021 (60)	0-9109 (10)	0-23517 (70)	0-0313 (31)	0-0394 (37)	0-0369 (26)	-0-0043 (30)	0-0149 (23)	0-0093 (28)
C(16)	0-76655 (60)	0-8512 (12)	0-31873 (68)	0-0301 (31)	0-0509 (42)	0-0321 (24)	-0-0120 (33)	0-0118 (23)	0-0047 (28)
C(17)	0-76139 (52)	0-6702 (10)	0-39400 (59)	0-0235 (26)	0-0431 (37)	0-0236 (20)	-0-0021 (28)	0-0076 (19)	0-0060 (24)
C(18)	0-63762 (66)	0-4964 (12)	0-17912 (67)	0-0443 (37)	0-0573 (48)	0-0272 (23)	0-0016 (36)	0-0184 (25)	-0-0102 (29)
C(19)	0-21023 (61)	0-4645 (12)	0-01497 (65)	0-0357 (33)	0-0600 (47)	0-0252 (22)	-0-0079 (35)	0-0128 (22)	-0-0132 (29)
O(3)	0-06977 (41)	0-7513 (09)	0-41806 (45)	0-0371 (23)	0-0633 (32)	0-0317 (17)	-0-0106 (26)	0-0213 (17)	-0-0127 (22)
O(17)	0-86724 (37)	0-5601 (09)	0-41541 (46)	0-0216 (18)	0-0636 (32)	0-0348 (17)	0-0052 (23)	0-0157 (15)	0-0144 (21)

5 α -Androstan-3 β -ol-17-one (epiandrosterone) nonhydrogen atoms

	X/A	Y/B	Z/C	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	0-51742 (68)	0-77500 (—)	0-47294 (75)	0-0390 (21)	0-0315 (21)	0-0396 (18)	-0-0018 (17)	0-0083 (16)	-0-0028 (16)
C(2)	0-46564 (69)	0-84447 (19)	0-45170 (79)	0-0413 (23)	0-0311 (21)	0-0434 (21)	0-0031 (18)	0-0049 (17)	-0-0005 (17)
C(3)	0-58527 (74)	0-87887 (19)	0-66549 (82)	0-0505 (25)	0-0284 (22)	0-0436 (20)	0-0026 (18)	0-0118 (18)	-0-0032 (17)
C(4)	0-82312 (68)	0-86742 (19)	0-73248 (77)	0-0413 (21)	0-0298 (20)	0-0388 (18)	-0-0043 (17)	0-0092 (16)	-0-0077 (16)
C(5)	0-87434 (63)	0-79748 (17)	0-75105 (66)	0-0375 (20)	0-0287 (20)	0-0286 (15)	-0-0006 (16)	0-0066 (14)	-0-0006 (14)
C(6)	1-11561 (68)	0-78515 (21)	0-83587 (76)	0-0381 (22)	0-0368 (21)	0-0396 (18)	-0-0040 (18)	0-0005 (16)	-0-0079 (18)
C(7)	1-16309 (67)	0-71591 (21)	0-87598 (76)	0-0364 (21)	0-0376 (21)	0-0369 (18)	-0-0002 (18)	0-0017 (15)	-0-0054 (17)
C(8)	1-04721 (61)	0-67629 (18)	0-67236 (64)	0-0348 (19)	0-0270 (18)	0-0283 (14)	-0-0000 (15)	-0-0067 (13)	-0-0008 (14)
C(9)	0-80320 (58)	0-69105 (17)	0-58664 (65)	0-0310 (18)	0-0234 (16)	0-0304 (15)	0-0014 (14)	0-0086 (13)	-0-0005 (13)
C(10)	0-75877 (61)	0-76166 (17)	0-53200 (61)	0-0389 (19)	0-0238 (16)	0-0239 (14)	-0-0032 (15)	0-0072 (13)	0-0006 (12)
C(11)	0-67694 (70)	0-64754 (20)	0-39151 (79)	0-0409 (22)	0-0322 (21)	0-0398 (19)	-0-0003 (18)	-0-0047 (17)	-0-0050 (16)
C(12)	0-71627 (71)	0-57834 (20)	0-45098 (80)	0-0420 (22)	0-0303 (22)	0-0448 (20)	-0-0036 (18)	-0-0016 (17)	-0-0019 (17)
C(13)	0-95912 (65)	0-56500 (19)	0-52670 (67)	0-0429 (21)	0-0300 (19)	0-0297 (16)	-0-0006 (17)	0-0094 (15)	-0-0019 (15)
C(14)	1-07236 (61)	0-60712 (18)	0-72615 (66)	0-0358 (20)	0-0321 (19)	0-0258 (15)	0-0030 (16)	0-0056 (14)	0-0010 (13)
C(15)	1-29892 (72)	0-57846 (22)	0-82262 (80)	0-0407 (22)	0-0397 (24)	0-0431 (19)	0-0059 (19)	0-0037 (17)	0-0013 (18)
C(16)	1-25110 (80)	0-50774 (23)	0-79976 (86)	0-0511 (25)	0-0392 (24)	0-0481 (22)	0-0113 (21)	0-0076 (19)	0-0021 (20)
C(17)	1-02935 (69)	0-50181 (20)	0-63383 (73)	0-0462 (22)	0-0336 (20)	0-0377 (17)	0-0070 (18)	0-0153 (16)	-0-0014 (16)
C(18)	1-04913 (94)	0-56864 (25)	0-33142 (80)	0-0845 (36)	0-0473 (26)	0-0322 (19)	0-0051 (26)	0-0166 (21)	-0-0064 (19)
C(19)	0-83215 (79)	0-78128 (21)	0-33412 (69)	0-0649 (28)	0-0366 (21)	0-0290 (16)	0-0031 (21)	0-0138 (17)	0-0039 (16)
O(3)	0-54531 (57)	0-94419 (14)	0-63892 (67)	0-0616 (21)	0-0272 (17)	0-0663 (19)	0-0044 (15)	0-0121 (16)	-0-0073 (14)
O(17)	0-92097 (57)	0-45510 (16)	0-59648 (68)	0-0604 (21)	0-0309 (15)	0-0693 (20)	-0-0029 (16)	0-0135 (16)	0-0021 (15)

Table 3 (*cont.*)*5β*-Androstane-3 α ,17 β -diol hydrogen atoms

	<i>X/A</i>	<i>Y/B</i>	<i>Z/C</i>
H(1A)	0.2036	0.3100	0.2342
H(1B)	0.0785	0.3996	0.1458
H(2A)	0.2327	0.5149	0.4116
H(2B)	0.0923	0.4034	0.3705
H(3)	-0.0082	0.6488	0.2290
H(4A)	0.2151	0.8445	0.3098
H(4B)	0.0919	0.9328	0.2182
H(5)	0.0665	0.7163	0.0462
H(6A)	0.1620	1.0169	0.0501
H(6B)	0.1954	0.8371	-0.0154
H(7A)	0.3822	1.0069	0.1014
H(7B)	0.3641	0.9708	0.2391
H(8)	0.4208	0.6887	0.1031
H(9)	0.3662	0.6423	0.3321
H(11A)	0.4131	0.3373	0.3465
H(11B)	0.4352	0.3601	0.2120
H(12A)	0.5985	0.4998	0.4552
H(12B)	0.6167	0.3343	0.3843
H(14)	0.5434	0.8198	0.3623
H(15A)	0.6170	1.0276	0.2522
H(15B)	0.6071	0.9127	0.1416
H(16A)	0.7977	0.8373	0.2585
H(16B)	0.8091	0.9546	0.3779
H(17)	0.7541	0.6907	0.4741
H(18A)	0.6370	0.5844	0.1256
HC(18B)	0.6858	0.3898	0.2048
H(18C)	0.5601	0.4521	0.1258
H(19A)	0.2445	0.5354	-0.0196
H(19B)	0.2478	0.3497	0.0392
H(19C)	0.1289	0.4626	-0.0407
H(O3)	0.0232	0.6820	0.4439
H(O17)	0.8818	0.4781	0.4777

5α-Androstan-3 β -ol-17-one (epiandrosterone) hydrogen atoms

	<i>X/A</i>	<i>Y/B</i>	<i>Z/C</i>
H(1A)	0.4537	0.7598	0.6122
H(1B)	0.4390	0.7560	0.3256
H(2A)	0.5100	0.8634	0.3260
H(2B)	0.3046	0.8469	0.4306
H(3)	0.5236	0.8649	0.8024
H(4A)	0.8837	0.8822	0.6139
H(4B)	0.8885	0.8893	0.8943
H(5)	0.8172	0.7769	0.8681
H(6A)	1.1914	0.8018	0.7035
H(6B)	1.1818	0.8062	0.9901
H(7A)	1.3229	0.7113	0.9102
H(7B)	1.1080	0.7008	0.9968
H(8)	1.0933	0.6890	0.5425
H(9)	0.7494	0.6838	0.7264
H(11A)	0.5065	0.6588	0.3557
H(11B)	0.7220	0.6628	0.2610
H(12A)	0.6660	0.5667	0.5868
H(12B)	0.6529	0.5571	0.3086
H(14)	1.0062	0.5969	0.8448
H(15A)	1.3870	0.6032	0.7112
H(15B)	1.3681	0.5961	0.9720
H(16A)	1.3385	0.4897	0.7179
H(16B)	1.2682	0.4887	0.9513
H(18A)	1.0530	0.6130	0.2600
H(18B)	1.2250	0.5612	0.3931
H(18C)	0.9412	0.5460	0.2186
H(19A)	0.8126	0.8316	0.2934
H(19B)	0.9782	0.7678	0.3676
H(19C)	0.7568	0.7667	0.1922
HO(3)	0.3862	0.9508	0.5778

value obtained using the geometrically expected positions of the hydrogen atoms.

Refinement was terminated for both structures when the calculated shifts in the atomic parameters were less than $\frac{1}{3}$ the corresponding standard deviations. The observed and calculated structure-factor amplitudes for these structures are presented in Table 2.

Discussion

The refined positional and thermal parameters of the atoms in *5β*-androstane-3 α ,17 β -diol and epiandrosterone are listed in Table 3, and the thermal parameters are also shown graphically in the form of their 50% probability ellipsoids in Fig. 2 which illustrates the configurations of the atoms and the stereochemistry of the molecules. The intramolecular geometries of *5β*-androstane-3 α ,17 β -diol, epiandrosterone, and androsterone are expressed in terms of the interatomic distances, valency angles, and torsional angles in Table 4. The estimated standard deviations of the interatomic distances and angles for *5β*-androstane-3 α ,17 β -diol lie in the ranges 0.006–0.009 Å and 0.3–0.5° respectively, and the corresponding ranges for epiandrosterone are 0.005–0.007 Å and 0.2–0.5°.

Table 4. *Intramolecular geometry of (I) 5β-androstane-3α,17β-diol (II) epiandrosterone, and (III) androsterone*

The numbers in parentheses are standard deviations of the last two figures.

(a) Interatomic distances

	(I)	(II)	(III)
C(1)—C(2)	1.530 (7) Å	1.530 (6) Å	1.532 (5) Å
C(1)—C(10)	1.541 (7)	1.537 (6)	1.544 (5)
C(2)—C(3)	1.526 (8)	1.512 (7)	1.512 (6)
C(3)—C(4)	1.516 (7)	1.504 (6)	1.491 (6)
C(3)—O(3)	1.424 (6)	1.430 (5)	1.444 (6)
C(4)—C(5)	1.551 (7)	1.539 (6)	1.534 (5)
C(5)—C(6)	1.525 (7)	1.525 (6)	1.529 (5)
C(5)—C(10)	1.561 (7)	1.545 (5)	1.550 (6)
C(6)—C(7)	1.535 (7)	1.526 (6)	1.500 (6)
C(7)—C(8)	1.534 (7)	1.521 (6)	1.532 (6)
C(8)—C(9)	1.550 (7)	1.551 (5)	1.547 (5)
C(8)—C(14)	1.524 (6)	1.524 (6)	1.519 (5)
C(9)—C(10)	1.566 (6)	1.564 (5)	1.551 (5)
C(9)—C(11)	1.543 (7)	1.552 (6)	1.543 (6)
C(10)—C(19)	1.536 (7)	1.541 (6)	1.541 (5)
C(11)—C(12)	1.538 (6)	1.537 (6)	1.546 (5)
C(12)—C(13)	1.521 (7)	1.539 (6)	1.507 (6)
C(13)—C(14)	1.546 (7)	1.530 (6)	1.540 (6)
C(13)—C(17)	1.533 (6)	1.521 (6)	1.517 (5)
C(13)—C(18)	1.547 (7)	1.537 (7)	1.548 (5)
C(14)—C(15)	1.546 (7)	1.543 (6)	1.531 (5)
C(15)—C(16)	1.545 (7)	1.551 (7)	1.537 (6)
C(16)—C(17)	1.545 (8)	1.496 (7)	1.520 (8)
C(17)—O(17)	1.427 (6)	1.211 (6)	1.891 (6)

(b) Valency angles

	(I)	(II)	(III)
C(2)—C(1)—C(10)	114.7 (4)°	112.8 (3)°	113.5 (3)°
C(1)—C(2)—C(3)	110.6 (4)	111.4 (3)	112.4 (3)
C(2)—C(3)—C(4)	110.7 (3)	111.0 (3)	111.5 (3)
C(2)—C(3)—O(3)	110.5 (4)	110.8 (4)	107.1 (4)
C(4)—C(3)—O(3)	109.0 (3)	109.2 (3)	111.0 (3)

Table 4 (cont.)

	(I)	(II)	(III)
C(3)—C(4)—C(5)	111.5 (4)°	111.3 (4)°	112.7 (3)°
C(4)—C(5)—C(6)	110.2 (4)	112.0 (3)	113.1 (3)
C(4)—C(5)—C(10)	112.6 (4)	112.9 (2)	113.2 (3)
C(6)—C(5)—C(10)	112.6 (4)	112.0 (4)	112.1 (3)
C(5)—C(6)—C(7)	111.5 (3)	111.2 (3)	111.5 (3)
C(6)—C(7)—C(8)	112.1 (4)	112.9 (2)	113.2 (3)
C(7)—C(8)—C(9)	110.0 (4)	110.6 (3)	110.8 (3)
C(7)—C(8)—C(14)	111.3 (3)	111.9 (3)	112.0 (3)
C(9)—C(8)—C(14)	108.7 (3)	107.5 (3)	109.0 (3)
C(8)—C(9)—C(10)	110.3 (3)	111.9 (2)	112.7 (2)
C(8)—C(9)—C(11)	112.1 (3)	112.0 (4)	111.5 (3)
C(10)—C(9)—C(11)	113.4 (3)	113.5 (3)	113.6 (2)
C(1)—C(10)—C(5)	107.6 (4)	106.7 (3)	106.2 (3)
C(1)—C(10)—C(9)	112.6 (3)	109.8 (3)	109.9 (3)
C(1)—C(10)—C(19)	106.2 (4)	109.3 (3)	109.7 (3)
C(5)—C(10)—C(9)	108.6 (3)	106.7 (3)	107.4 (2)
C(5)—C(10)—C(19)	109.5 (4)	113.2 (3)	112.4 (3)
C(9)—C(10)—C(19)	112.2 (3)	111.0 (4)	111.1 (2)
C(9)—C(11)—C(12)	113.5 (3)	112.8 (3)	113.4 (3)
C(11)—C(12)—C(13)	111.7 (3)	109.3 (3)	109.7 (3)
C(12)—C(13)—C(14)	107.4 (3)	108.6 (3)	110.5 (3)
C(12)—C(13)—C(17)	116.5 (3)	115.9 (3)	116.4 (3)
C(12)—C(13)—C(18)	110.9 (5)	112.4 (3)	112.5 (3)
C(14)—C(13)—C(17)	98.9 (4)	99.8 (3)	99.2 (3)
C(14)—C(13)—C(18)	113.0 (4)	114.6 (3)	111.9 (3)
C(17)—C(13)—C(18)	109.7 (3)	105.1 (3)	105.5 (2)
C(8)—C(14)—C(13)	113.7 (3)	114.1 (3)	113.4 (3)
C(8)—C(14)—C(15)	118.2 (3)	119.9 (3)	120.8 (3)
C(13)—C(14)—C(15)	104.7 (2)	103.5 (3)	104.3 (3)
C(14)—C(15)—C(16)	103.1 (3)	102.4 (3)	102.6 (4)
C(15)—C(16)—C(17)	106.5 (4)	105.7 (3)	106.0 (3)
C(13)—C(17)—C(16)	104.4 (3)	108.5 (3)	107.8 (3)
C(13)—C(17)—O(17)	116.7 (3)	125.6 (5)	127.1 (4)
C(16)—C(17)—O(17)	110.0 (3)	125.8 (3)	125.1 (4)

(c) Torsional angles in the rings

ϕ_{A-B} is the torsional angle about the $A-B$ bond, in which the other two atoms required to define the angle are those attached to either end of the bond, and are in the ring in question. The sign convention for the direction of the torsional angle is that of Klyne & Prelog (1960).

Ring	Bond	(I) ϕ_{A-B}	(II) ϕ_{A-B}	(III) ϕ_{A-B}
A	C(1)—C(2)	56.6	-57.7	-56.8
	C(2)—C(3)	-55.8	55.1	51.9
	C(3)—C(4)	56.4	-54.5	-52.3
	C(4)—C(5)	-56.3	56.7	57.5
	C(5)—C(10)	52.7	-55.7	-57.1
	C(1)—C(10)	-53.8	56.2	57.0
B	C(5)—C(6)	-54.1	-57.8	-58.5
	C(6)—C(7)	54.1	53.3	53.5
	C(7)—C(8)	-56.7	-52.3	-51.7
	C(8)—C(9)	59.2	56.0	55.4
	C(9)—C(10)	-58.1	-58.6	-58.4
	C(5)—C(10)	55.9	59.4	59.5
C	C(8)—C(9)	-51.1	-52.7	-52.9
	C(9)—C(11)	50.0	54.1	53.8
	C(11)—C(12)	-53.4	-55.6	-54.8
	C(12)—C(13)	56.6	57.4	55.4
	C(13)—C(14)	-61.8	-62.0	-59.0
	C(8)—C(14)	58.9	58.4	56.3
D	C(13)—C(14)	46.3	44.4	44.8
	C(14)—C(15)	-31.8	-39.2	-38.6
	C(15)—C(16)	4.6	17.9	16.6
	C(16)—C(17)	24.4	9.9	11.5
	C(13)—C(17)	-42.7	-33.6	-34.3

The intramolecular geometries of these structures are essentially normal. The A , B , and C rings all have chair conformations, and are slightly flattened in that the torsional angles are less than 60° . The $C(2)-C(3)$ distance of $1.512 \pm 0.007 \text{ \AA}$ and the $C(3)-C(4)$ distance of $1.504 \pm 0.006 \text{ \AA}$ observed in epiandrosterone differ from the expected value of 1.533 \AA (Bartell, 1959) by more than two standard deviations; therefore, the differences are considered significant. Similar short distances were observed in androsterone, and the $C(3)-C(4)$ distance in 5β -androsterone- $3\alpha,17\beta$ -diol is also significantly shortened using the same criterion. Indeed, of the 10 steroid crystal structures having a free hydroxyl group at $C(3)$, 5 possess a $C(2)-C(3)$ distance and 5 possess a $C(3)-C(4)$ distance, significantly less than 1.533 \AA . Because no steroid structures having a totally saturated, unsubstituted A ring have been determined by X-ray analysis, it is uncertain that the observed shortening of the distances involving $C(3)$ result from the presence of the hydroxyl group bonded to this carbon atom. There are few differences between the intermolecular distances and valency angles of epiandrosterone and androsterone. Of the 21 interatomic distances between bonded nonhydrogen atoms, only 4 differ by more than 0.02 \AA , and only 2 of the 39 valency angles involving bonded nonhydrogen atoms differ by more than 2° . The three-dimensional configuration of the molecules, as reflected by the torsional angles is also very similar, and it would seem that the observed differences in the biological activities of the epimers must result from the different orientations of the hydroxyl oxygen $O(3)$ and not from any subtle differences in the molecular geometry.

The geometry of the D ring of steroids is always a point of interest, and this is particularly true when one of the carbons in this ring has sp^2 hybridization, because the location of such an atom in a cyclopentane ring causes considerable deviation from normal sp^2 geometry. The 7 steroids having an sp^2 hybridized carbon at $C(17)$, for which the X-ray analysis has been completed, are listed in Table 5, and several geometrical features of the D rings in these structures are presented in Table 6. The distances $C(13)-C(17)$ and $C(16)-C(17)$ have lengths intermediate between the 1.533 \AA predicted for sp^3-sp^3 carbon-carbon bonds and the 1.505 \AA (Bartell & Bonham, 1960) predicted for sp^2-sp^3 carbon-carbon bonds. The angle $C(13)-C(17)-C(16)$ is always significantly less than the expected value of about 116° (Cooper & Norton, 1968) while at least one of the external angles $C(13)-C(17)-X$ or $C(16)-C(17)-X$ (where X is the atom joined to $C(17)$ by a double bond) is always significantly greater than about 120° . The best plane through the four atoms $C(13)$, $C(16)$, $C(17)$, and X was calculated for each of these molecules, and the maximum deviation from this plane is 0.03 \AA for $C(17)$ in 4-bromoestrone and $3\beta,6\beta$ -dimethoxy- $5\beta,19$ -cycloandrostan-17-one N -acetyl- p -bromobenzenesulphonylhydrazone. Since the atoms bonded to $C(17)$ do lie

nearly in a plane, the sum of the valency angles about C(17) must be nearly 360°, and the decrease in the angle C(13)–C(17)–C(16) below 116° must be compensated for by an increase in at least one of the other angles. The other valency angles in the *D* rings of these steroids are all less than the tetrahedral angle of 109°, and this observation confirms the theoretical predictions of Hendrickson (1961) which were reached by calculating the minimum energy configuration of a free cyclopentane ring. The valency angles in the *D* rings of steroids lacking *sp*² hybridization at C(17) are similar to those in steroids having this type of hybridization.

The three-dimensional conformation of a cyclopentane ring may be described most concisely by the parameters Δ and φ_m (Altona, Geise & Romers, 1968). The overall configuration of the ring is quantitatively defined by the parameter Δ ($\Delta = +36^\circ$, β -envelope; $\Delta = 0^\circ$, halfchair; $\Delta = -36^\circ$, α -envelope) while φ_m is the maximum torsional angle attainable in this conformation. Thus, the *D* ring of 5 β -androstane-3 α ,17 β -diol has a slightly distorted β -envelope conformation, defined by the parameters $\Delta = 24.3$ and $\varphi_m = 47.4$. It has been suggested, based on a consideration of bond-bending and torsional energies, that 17 β -substituted steroids adopt a β -envelope conformation while 17-keto-steroids normally prefer the α -envelope conformation (Brutcher & Bauer, 1962), and, in the small sample of 14 steroids studied by Altona, Geise &

Romers (1968), only the 2 molecules with *sp*² hybridization at C(17) possessed negative phase angles (Δ). The Δ and φ_m parameters for the C(17) *sp*² hybridized steroids are presented in Table 6, and the *D* ring conformation is seen to vary from the nearly perfect α -envelope in the case of 4-bromoestrone to the approximate half-chair seen in androsterone. Of the more than 60 steroids for which X-ray coordinates are available, only 5 others have negative phase angles. One of these, batrachotoxinin A *O*-*p*-bromobenzoate (Karle & Karle, 1969), has a double bond between C(16) and C(17) with the result that C(13), C(15), C(16), C(17) are forced to lie nearly in a plane, and coplanarity of these 4 atoms is the earmark of the α -envelope conformation. There is no outstanding feature common to the other four molecules, but it is apparent that features other than *sp*² hybridization can cause the *D* ring to assume a conformation approaching an α -envelope. However, while a cursory examination of the *D* ring torsional angles for the C(17) *sp*² steroids gives the impression that the conformation of all these rings is about the same, the Δ and φ_m parameters show that considerable variation does exist although it is true that the range of conformations assumed by the cyclopentane ring in these steroids is, for the most part, different from the conformations seen in 17- β -substituted steroids.

All available hydroxyl oxygen atoms in 5 β -androstane-3 α ,17 β -diol, epiandrosterone, and androsterone

Table 5. Steroid molecules having *sp*² hybridization at C(17) for which the X-ray analysis has been performed

Number	Structure	Reference
I	Epiandrosterone	Present paper
II	Androsterone	High & Kraut, 1966
III	Androsterone 3-bromoacetate	Kartha, Lu & Norton, unpublished
IV	4-Bromoestrone	Norton, Kartha & Lu, 1963
V	8-Azaestrone hydrobromide	Majeste & Trefonas, 1969
VI	3 β ,6 β -Dimethoxy-5 β ,19-cycloandrostan-17-one <i>N</i> -acetyl- <i>p</i> -bromobenzenesulphonyl-hydrazine	Tamura & Sim, 1968
VII	Fusidic acid methyl ester 3- <i>p</i> -bromobenzoate	Cooper & Hodgkin, 1968

Table 6. Some geometrical features of the *D* rings of steroids having *sp*² hybridization at C(17)

X is the atom joined to C(17) by the *sp*²–*sp*² bond. The torsional angles are the same as the *D* ring torsional angles listed in Table 4(c).

		I	II	III	IV	V	VI	VII
Interatomic distances	C(13)–C(17)	1.521	1.517	1.54	1.53	1.52	1.54	1.47
	C(16)–C(17)	1.496	1.520	1.51	1.57	1.55	1.56	1.53
Valency angles	C(13)–C(17)–C(16)	108.5	107.8	107	108	107	111	105
	C(13)–C(17)–X	125.6	127.1	127	127	128	118	136
	C(16)–C(17)–X	125.8	125.1	125	124	125	131	119
Torsional angles	C(13)–C(14)	44.4	44.8	42.4	39.8	46.9	46.1	–41.7
	C(14)–C(15)	–39.2	–38.6	–39.2	–41.1	–43.8	–45.7	34.9
	C(15)–C(16)	17.9	16.6	19.2	25.1	22.5	22.8	–16.3
	C(16)–C(17)	9.9	11.5	6.4	–1.9	5.2	6.8	–9.8
	C(13)–C(17)	–33.6	–34.3	–29.6	–23.5	–31.1	–34.1	31.8
Δ		–11.4	–7.8	–19.5	–39.9	–23.4	–22.0	–8.6
φ_m		44.6	45.0	43.0	42.4	47.9	46.9	–41.8

are proton donors and form hydrogen bonds. The hydrogen bonds, as well as the other intermolecular contacts between nonhydrogen atoms in these structures that are less than 4 Å are listed in Table 7. The shortest hydrogen bonds (2.736 and 2.767 Å) exist in the 5 β -androstane-3 α ,17 β -diol crystals, and those in epiandrosterone (2.948 Å) and androsterone (3.037 Å) are quite weak although some interaction undoubtedly exists since the angles O-H...O are 168 and 164° respectively. In all three crystals, spirals of hydrogen-bonded molecules exist about the screw axes in the center of the unit cells (at $\frac{1}{2}, y, \frac{1}{2}$). In 5 β -androstane-3 α ,17 β -diol the second set of hydrogen bonds forms chains of molecules parallel to *a*. Of the 17 nonhydrogen–nonhydrogen intermolecular distances less than 4 Å (Table 7), 12 are between atoms in the proximity of the hydrogen bonds, and 4 are with the methyl groups between molecules related by the screw axes at $(\frac{1}{2}, y, 0)$. Five out of 14 and 7 out of 16 close contacts are between hydrogen-bonded molecules in epiandrosterone and androsterone crystals respectively.

Note that, although the *A* ring of 5 β -androstane-3 α ,17 β -diol is almost perpendicular to the remainder of the molecule, the packing in the crystal appears to be most efficient as shown by the unit-cell dimensions

which are almost identical with the linear 5 α -epimer (Table 8). Hydrogen-bonding in these two examples and in epiandrosterone and androsterone does not appear to assist in reducing the amount of 'empty space' in the crystals, since the corresponding 3,17-diones, in which there are no possibilities for intermolecular hydrogen bonding, occupy the same, or smaller, molecular volumes. Nevertheless, it seems that the hydrogen bonds are important in determining the way in which molecules pack in these crystals. The three-dimensional stacking of the molecules in these three substances is seen in projection along the crystallographic axes (Fig. 3). Despite the great similarity in the intramolecular structure of epiandrosterone and androsterone, the intermolecular geometry within the crystals is different as a result of the different orientations of the C(3) hydroxyl group. In epiandrosterone the β -oriented O(3) occupies an equatorial position with respect to the steroid nucleus, and as a result, the hydrogen bonds between the hydroxyl group and the ketone in the symmetry-related molecule give rise to spirals of molecules in which the long axis of the steroid [a line parallel to the vector joining C(10) and C(13)] is approximately parallel to the screw axis. Because of the axial orientation of O(3) in androsterone, the mol-

Table 7. Intermolecular distances less than 4.0 Å between nonhydrogen atoms in (I) 5 β -androstane-3 α ,17 β -diol, (II) epiandrosterone, and (III) androsterone

Contact	(I)		(II)		(III)	
	Position*	Distance	Position*	Distance	Position*	Distance
C(1)–C(7)			1/10 $\bar{1}$	3.929		
C(2)–C(3)					2/0 $\bar{1}$ 1	3.852
C(2)–C(4)					2/0 $\bar{1}$ 1	3.932
C(2)–C(16)	2/0 $\bar{1}$ 0	3.637				
C(2)–C(17)	2/0 $\bar{1}$ 0	3.564				
C(2)–O(17)	1/ $\bar{1}$ 00	3.815	2/000	3.428	1/001	3.712
C(3)–C(16)	1/ $\bar{1}$ 00	3.966				
C(3)–O(17)	1/ $\bar{1}$ 00	3.322	2/000	3.594	2/000	3.874
C(3)–O(17)	2/000	3.968				
C(4)–O(17)			2/100	3.612	2/000	3.864
C(5)–C(19)			1/001	3.798		
C(6)–C(18)	2/00 $\bar{1}$	3.888				
C(7)–C(11)	1/010	3.826				
C(7)–C(18)	2/00 $\bar{1}$	3.770				
C(11)–C(15)			1/ $\bar{1}$ 0 $\bar{1}$	3.922		
C(11)–C(19)					2/ $\bar{1}$ 00	3.970
C(12)–O(3)			2/0 $\bar{1}$ 0	3.314	2/0 $\bar{1}$ 0	3.842
C(14)–C(18)			1/001	3.961		
C(15)–C(19)	2/00 $\bar{1}$	3.953				
C(15)–O(3)					2/000	3.388
C(15)–O(17)					2/ $\bar{1}$ 0 $\bar{1}$	3.678
C(16)–C(17)					2/ $\bar{1}$ 0 $\bar{1}$	3.943
C(16)–C(18)					2/ $\bar{1}$ 0 $\bar{1}$	3.854
C(16)–C(19)	2/00 $\bar{1}$	3.883				
C(16)–O(3)	1/100	3.370	2/ $\bar{1}$ 00	3.716	2/000	3.499
C(16)–O(3)	2/000	3.960	2/ $\bar{1}$ 0 $\bar{1}$	3.616		
C(16)–O(17)					2/ $\bar{1}$ 0 $\bar{1}$	3.516
C(17)–O(3)	1/100	3.599	2/0 $\bar{1}$ 0	3.813	2/0 $\bar{1}$ 0	3.986
C(17)–O(3)	2/0 $\bar{1}$ 0	3.711	2/ $\bar{1}$ 00	3.947		
C(18)–O(3)			2/ $\bar{1}$ 00	3.746	1/ $\bar{1}$ 0 $\bar{1}$	3.861
O(3)–O(17)	1/ $\bar{1}$ 00	2.767	2/000	2.948	2/000	3.037
O(3)–O(17)	2/000	2.736				

* Equivalent position nomenclature: C(2)–C(16) 2/0 $\bar{1}$ 0 means that the second atom, C(16), is at equivalent position 2, translated 0, -1, and 0 unit cells in the *a*, *b*, and *c* directions respectively. The equivalent positions are 1 = *x*, *y*, *z*; 2 = 1 - *x*, $\frac{1}{2}$ + *y*, 1 - *z*.

ecules are not joined end-to-end, and the long axis of the molecule is approximately perpendicular to the symmetry axis. The resulting molecular packing is very similar to the packing of the configurationally dissimilar 5β -androstane- $3\alpha,17\beta$ -diol molecules in which the orientation of O(3) is also axial with respect to the plane of rings *B*, *C*, and *D* although it is equatorial to the *A* ring. The differences in the crystal packing of these steroids illustrate how a small configurational

change in a molecule [e.g. the change in the orientation of O(3)] can radically change the interaction of a molecule with other molecules and result in behavior resembling that of a seemingly dissimilar substance.

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Table 8. *Unit-cell dimensions*

	Space group	<i>Z</i>	<i>a</i>	<i>b</i>	<i>c</i>	β	Molecular volume	Density
5β -Androstane- $3\alpha,17\beta$ -diol	$P2_1$	2	11.875	7.157	10.960	114.7°	423.1	1.148
5α -Androstane- $3\alpha,17\beta$ -diol*	$P2_1$	2	12.352	7.189	10.364	114.1	420.0	1.156
5β -Androstane-3,17-dione*	$P2_12_12_1$	4	25.106	7.927	8.374	—	414.6	1.149
5α -Androstane-3,17-dione†	$A2$	4	21.337	6.186	12.704	91.3	419.1	1.143
5α -Androstan- 3β -o1-17-one (epiandrosterone)	$P2_1$	2	6.596	21.521	6.313	109.36	422.7	1.143
5α -Androstan- 3α -o1-17-one (androsterone)	$P2_1$	2	9.550	7.912	11.779	111.34	414.5	1.163

* Norton, Lu & Campbell, 1962.

† Ohrt, Haner & Norton, 1965.

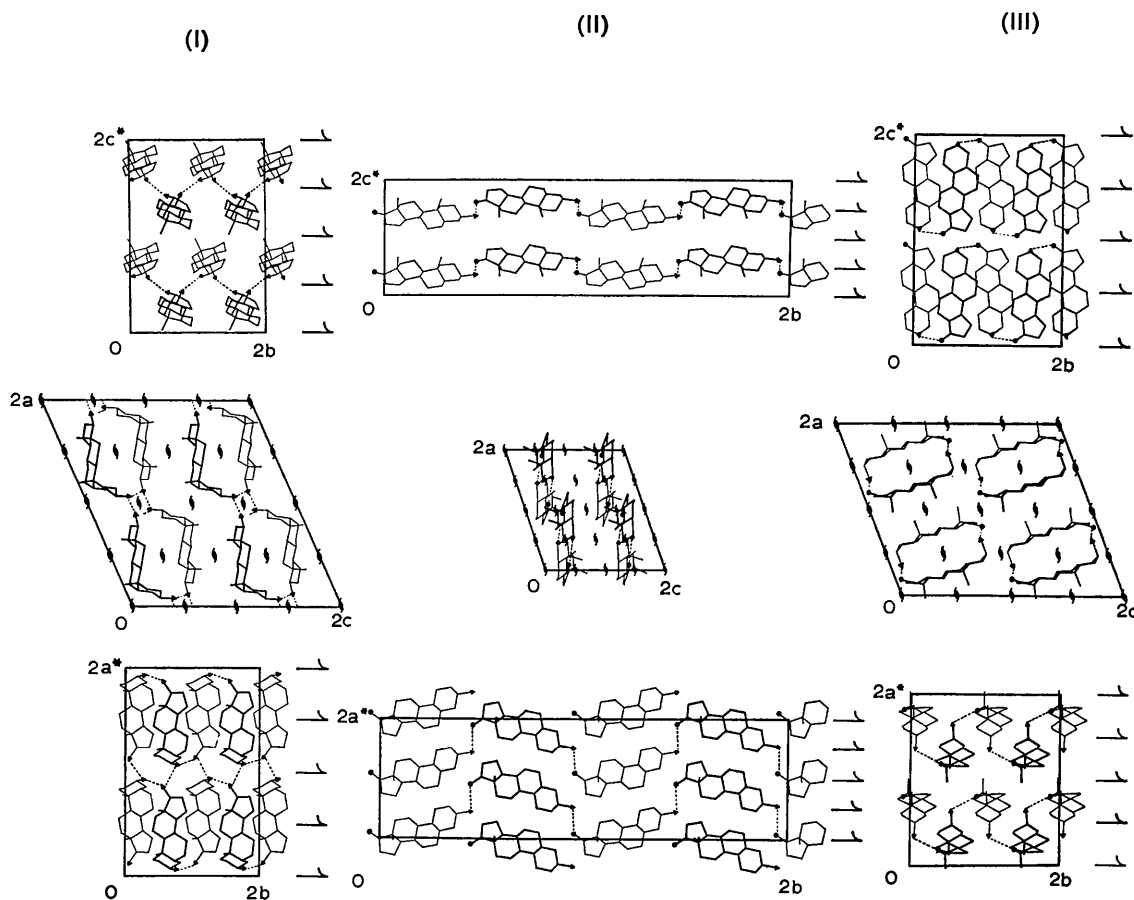


Fig. 3. Molecular stacking in (I) 5β -androstane- $3\alpha,17\beta$ -diol, (II) epiandrosterone, and (III) androsterone. Hydrogen bonds are indicated by broken lines. ● = keto oxygen, ▲ = hydroxyl oxygen. The contents of four unit cells are projected onto (*a*) the (100) plane, (*b*) the (010) plane, and (*c*) the (001) plane.

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Structure des Complexes Peroxydiques des Métaux de Transition.

I. Structure Cristalline du Diperoxodioxalatonibate d'Ammonium à une Molécule d'Eau, $(\text{NH}_4)_3\text{Nb}(\text{O}_2)_2(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}$

PAR G. MATHERN ET R. WEISS

Laboratoire de Cristallographie associé au C.N.R.S., Institut de Chimie de Strasbourg,
BP 296/R8, 67-Strasbourg, France

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The crystal structure of ammonium diperoxodioxalatonibate $(\text{NH}_4)_3\text{Nb}(\text{O}_2)_2(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}$ has been determined by X-ray diffraction. The crystals are monoclinic with $a = 12.09 \pm 0.02$, $b = 7.85 \pm 0.01$, $c = 14.30 \pm 0.02$ Å; $\beta = 94.7 \pm 0.1^\circ$; $Z = 4$; space group $P2/c$. The coordination polyhedron of niobium is a dodecahedron. The two peroxide groups are in *cis* positions. The $\text{Nb}(\text{O}_2)_2(\text{C}_2\text{O}_4)_2^{3-}$ anion has C_2 symmetry. The O-O mean distance in the peroxide groups is 1.48 Å.

Introduction

Les structures cristallines de plusieurs composés diperoxydiques sont connues (Stomberg, 1964, 1965, 1968; Mitschler, Le Carpentier & Weiss, 1968; Einstein & Penfold, 1964). Dans tous ces composés, le métal est un élément de transition de la colonne VI A. Sa coordination est de 6 ou 7. Le polyèdre de coordination est une pyramide pentagonale lorsque la coordination du métal est de 6 et une bipyramide pentagonale lorsqu'elle est de 7. Les deux groupements peroxydiques forment toujours deux des côtés du pentagone équatorial.

Nous avons entrepris l'étude de la structure du diperoxodioxalatonibate d'ammonium en vue de déterminer la stéréochimie du niobium dans ce composé.

Ce travail a déjà fait l'objet d'une publication préliminaire (Mathern, Weiss & Rohmer, 1969).

1. Préparation

Nous avons utilisé la méthode de Guerschais & Spinner (1965) qui consiste à dissoudre l'oxotrioxalatonibate d'ammonium dans une solution d'eau oxygénée à 30%. Les cristaux de diperoxodioxalatonibate d'ammonium se déposent sous forme de plaquettes, par évaporation lente à l'air de la solution. Il faut veiller à