

Fig. 1. Arrangement of chlorine and oxygen atoms around Eu. The bond lengths are given in Å.

The authors are indebted to Dr Littke for making available the facilities for obtaining the intensity data. Thanks are due to Professor Bärnighausen for drawing our attention to this problem. We are grateful to Miss B. Geiselmann for her assistance.

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BaCl₂·2H₂O

EuCl₂·2H₂O

Fig. 2. Comparison of the metal coordination arrangements of SrCl₂. 2H₂O or EuCl₂. 2H₂O with BaCl₂. 2H₂O.

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Acta Cryst. (1975). B31, 292

2,4-Dioxa-5α-androstan-17β-ol Acetate

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(Received 10 May 1974; accepted 26 August 1974)

Abstract. $C_{19}H_{30}O_4$, m.p. 120 °C, orthorhombic, space group $P2_12_12_1$, a=12.603 (2), b=23.44 (3), c=6.137 (1) Å, Z=4, M=322.45, $D_x=1.31$, $D_m=1.30$ g cm⁻³. The *A* ring has a symmetrical chair conformation with a mean ring torsional angle of 58.7°. The more perfect chair conformation is associated with the 2,4-dioxa

Introduction. Structural features of steroid A rings that are specifically related to activity are being explored through physical and pharmacological studies of a series of synthetic steroids having A rings of varying size and composition (Zanati & Wolff, 1971). The title

substitution which relieves the β -face diaxial interactions.

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compound has been observed to have approximately one third the activity of testosterone in androgenic myotrophic assays and its structure was undertaken as one of this series. A crystal, $0.2 \times 0.2 \times 0.4$ mm, was used to measure the lattice parameters and intensities. The data showed systematic absences h=2n+1 for h00, k=2n+1 for 0k0, and l=2n+1 for 00l, indicating space group $P2_12_12_1$, and the cell constants were determined by least-squares analysis of the angular settings of 30 reflections [at 20 °C; λ (Cu $K\alpha_1$) = 1.54051 Å]. The intensities of 1875 reflections (1193 reflections had $I > 2\sigma$) with $2\theta < 130^{\circ}$ were measured on a G. E. XRD-5 diffractometer using Cu Ka radiation monochromated by balanced nickel and cobalt filters. The linear absorption coefficient $\mu = 7.65$ cm⁻¹. After the usual Lorentz and polarization corrections had been applied normalized structure-factor amplitudes were computed, and the structure was solved by direct methods using MULTAN.

The positional and anisotropic thermal parameters of non-hydrogen atoms and positional and isotropic thermal parameters of 30 hydrogen atoms located by Fourier difference syntheses were refined by blockdiagonal least-squares calculations using all data for which $|F_c|/|F_o|$ was greater than 0.7. The weighting scheme used in the final refinement was $1/w = \{[(|F_o| - 7)/7]^2 + 1\}^{1/2}$ in which the constants were selected so that the quantity minimized, $\sum w(|F_o| - |F_c|)^2$, remained invariant with $|F_o|$. Refinement was terminated when all shifts were less than $\frac{1}{3}$ of their respective standard deviations. The *R* index, defined as $\sum (|F_c| - |F_o|)/\sum |F_o|$, had a final value of 11.1% for the 1634 reflections with $|F_c|/|F_o| > 0.7$, 10.4% for the 1193 reflections with $I > 2\sigma$, and 13.4% for all data. The final refined positional and thermal parameters are given in Table 1.*

Discussion. The interatomic distances, valency angles and ring torsional angles among non-hydrogen atoms are given in Table 2 and Fig. 1 which also illustrates the structural formula. The standard deviations of the bond lengths range from 0.008 to 0.010 Å and from 0.4 to 0.6° for the bond angles. The average magnitude of the bond lengths and valency angles involving hydrogen atoms were 0.97 Å and 110° respectively. The C-H bond lengths range from 0.71 to 1.34 Å with the extremes observed in the geometry of the acetate side chain. The magnitude of the isotropic thermal parameters of the hydrogen atoms ranged from 0.44 to 5.5 Å^2 and no physical significance could be attributed to individual deviations from the average value of 3.37 Å. The conformation of the molecule is shown in Fig. 2 with 50% probability ellipsoids while Fig. 3 illustrates the deviations in Å from the least-squares plane through atoms C(5)–C(17). The A ring has a highly symmetrical chair conformation and the average of its intra-ring torsional angle magnitudes is 58.7°. This is significantly greater than the average of 55° observed from the structures of several androstanes with chair A-ring conformations. The effect of oxygen disubstitution is the removal of diaxial interactions at the 2- and 4-positions which permits the achievement of an ideal chair conformation. The B and C rings have

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30592 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

Table 1. Final fractional positional and thermal parameters for 2,4-dioxa-5 α -androstan-17 β -ol acetate

Thermal parameters are defined by exp $\{-2\pi^2(U_{11}h^2a^{*2}+2U_{12}hka^*b^*+...)\}$.

	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C (1)	0.5567 (5)	0.8885 (3)	0.9729 (14)	0.044 (3)	0.083 (5)	0.067 (4)	-0·017 (3)	-0.003(3)	0.010 (4)
O(2)	0.6596 (3)	0.8866(2)	0.8650 (10)	0.038(2)	0.111 (4)	0.075 (3)	-0.018(2)	0.007 (3)	0.006 (3)
C(3)	0.6795 (6)	0.8325(4)	0.7721 (16)	0.044 (4)	0·121 (6)	0.080 (5)	-0.002 (4)	0.006 (4)	0.001 (5)
O(4)	0.6025(3)	0.8166(2)	0.6180(10)	0.042(2)	0.097 (3)	0.075 (3)	-0.001 (2)	0.023 (2)	-0.004(3)
C(5)	0.4971 (5)	0.8155(3)	0.7192(12)	0.031(2)	0.078 (4)	0.057 (4)	0.004 (3)	0.011 (3)	0.001 (3)
C(6)	0.4206 (5)	0.7920(3)	0.5572 (14)	0.054 (4)	0.082 (5)	0.068 (5)	-0·004 (3)	0.014 (4)	-0.031(4)
C(7)	0.3099 (5)	0.7878(3)	0.6642(13)	0.046 (3)	0.079 (4)	0.053 (4)	-0·001 (3)	0.008 (3)	-0.019 (4)
C(8)	0.2755 (4)	0.8430(2)	0.7683 (10)	0.035 (2)	0.061 (3)	0.033 (3)	0.005 (2)	0.000 (2)	-0.000(3)
C(9)	0.3609 (5)	0.8685(2)	0.9221(10)	0.042 (3)	0.064 (3)	0.028 (3)	-0.001 (2)	0.005 (2)	0.008 (3)
C(10)	0.4693 (4)	0.8741(3)	0.8076 (11)	0.035 (3)	0.066 (3)	0.043 (3)	0.000 (2)	0.006 (3)	0.002 (3)
$\mathbf{C}(11)$	0.3225(5)	0.9229(3)	1.0362 (12)	0.051(3)	0.077 (4)	0.053 (4)	-0.011 (3)	0.000 (3)	-0.020(4)
C(12)	0.2136 (5)	0.9165(3)	1 1474 (12)	0.055 (3)	0.090 (5)	0.047 (4)	-0.001 (3)	0.005 (3)	-0.032 (4)
C(13)	0.1306(5)	0.8934(3)	0.9905 (11)	0.044(3)	0.067 (4)	0.036 (3)	0.002 (3)	0.005 (3)	-0.004(3)
C(14)	0.1719 (4)	0.8369(2)	0.8958 (10)	0.036(3)	0.028 (3)	0.037 (3)	0.000 (2)	-0.002(3)	0.005 (3)
C(15)	0.0746 (5)	0.8100(3)	0.7809(13)	0.040(3)	0.075 (4)	0.064 (4)	-0.011(3)	-0.010(3)	-0.013(4)
C(16)	-0.0187(5)	0.8304 (3)	0.9229(14)	0.042(3)	0.067 (4)	0.071 (5)	0.001 (3)	0.005 (3)	0.009 (4)
C(17)	0.0292 (5)	0.8697 (3)	1.0953 (11)	0.047(3)	0.067 (3)	0.040 (3)	0.009 (3)	0.009 (3)	0.002 (3)
C(18)	0.1026(5)	0.9372(3)	0.8151(12)	0.056 (3)	0.064 (4)	0.048 (3)	0.010 (3)	0.011 (3)	0.014 (3)
C(19)	0·4686 (5)	0.9190(3)	0.6254(13)	0.062(4)	0.078 (4)	0.052 (4)	-0.002(3)	0.008 (4)	0.028 (4)
C(20)	-0.1187(5)	0.9023(3)	1.3035 (13)	0.055 (4)	0.088 (5)	0.061 (4)	-0.005(3)	0.020 (4)	-0.001 (4)
C(21)	-0.1928(7)	0.9499 (4)	1.3400 (21)	0.070 (5)	0.106 (7)	0.122 (8)	0.021 (5)	0.029 (6)	-0.007(7)
O (17)	-0.0429(3)	0.9158(2)	1.1559 (9)	0.054(2)	0.069 (3)	0.064 (3)	0.009 (2)	0.021 (2)	0.002 (2)
O(20)	-0.1250(4)	0.8561(2)	1.3845(11)	0.073(3)	0.107 (4)	0.091 (4)	0.011 (3)	0.037 (3)	0.024 (3)

Table 1 (cont.)

	X/a	Y/b	Z/c
H(1A)	0.563 (6)	0.860 (3)	1.095 (14)
H(1B)	0.561 (6)	0·920 (3)	1.011 (14)
H(3A)	0.758 (6)	0.824(3)	0.667 (16)
H(3 <i>B</i>)	0.669 (5)	0.798 (2)	0.935 (13)
H(5)	0.501 (5)	0.787 (2)	0.854 (13)
H(6A)	0.413 (6)	0.816 (3)	0.441 (14)
H(6B)	0.445 (7)	0.751 (4)	0.513 (19)
H(7 <i>A</i>)	0.256 (5)	0.775 (3)	0.572 (14)
H(7 <i>B</i>)	0.305 (6)	0.755 (2)	0.775 (14)
H(8)	0.272 (5)	0.869 (2)	0.658 (13)
H(9)	0.369 (5)	0.839 (2)	1.040 (12)
H(11A)	0.357 (6)	0.948 (2)	1.163 (14)
H(11 <i>B</i>)	0.317 (5)	0.952 (2)	0.913 (12)
H(12A)	0.230 (5)	0 ·881 (2)	1.251 (13)
H(12B)	0.191 (5)	0.943 (2)	1.205 (13)
H(14)	0.187 (4)	0.812 (2)	1.002 (11)
H(15A)	0.072 (6)	0.826 (3)	0.605 (14)
H(15B)	0.076 (6)	0.767 (3)	0.798 (15)
H(16A)	<i>−</i> 0·049 (6)	0.854 (3)	0.846 (14)
H(16B)	− 0·066 (6)	0•799 (3)	1.000 (15)
H(17)	0.049 (5)	0.844 (2)	1.209 (12)
H(18A)	0.056 (6)	0.922 (3)	0.698 (15)
H(18 <i>B</i>)	0.072 (6)	0.960 (3)	0.863 (14)
H(18C)	0.173 (6)	0.952 (3)	0.732 (14)
H(19A)	0.408 (5)	0.923 (3)	0.537 (13)
H(19 <i>B</i>)	0.467 (6)	0.951 (3)	0.700 (17)
H(19C)	0.532 (5)	0.936 (3)	0.539 (14)
H(21A)	-0.162(5)	0.979 (2)	1.376 (13)
H(21B)	-0.226 (7)	0.959 (3)	1.253 (16)
H(21C)	-0·270 (6)	0.928 (3)	1.461 (16)

normal chair conformations and the averages of their intra-ring torsional angle magnitudes (54.9 and 54.9°), are seen to be unexceptional. The *D* ring is a distorted 13 β -envelope conformation.

Although there are no hydrogen bonds, the closest intermolecular approaches involve the carbonyl oxygen O(20). The distances from O(20) to H(32), C(3) and C(7) are 2.4, 3.47 and 3.47 Å respectively.

A comparison of 2,4-dioxa-androstan- 17β -ol and dehydrotestosterone (the active steroidal androgen) reveals good agreement in overall conformation and space-filling characteristics. The A ring of the former is less bulky, lacking the O(3) atom and four hydrogens of the C(2) and C(4) positions. If a hydrophilic character is required for androgenicity then the difference in the relative position of the heterosubstituted oxygens of the synthetic steroid from the position of O(3) in



Fig. 1. Bond lengths, angles and torsional angles for 2,4dioxa-5 α -androstan-17 β -ol acetate.



Fig. 2. 50% probability thermal ellipsoids for 2,4-dioxa-5 α androstan-17 β -ol acetate. The steroid orientation in the unit cell can be defined by the relationships between a molecular axis system [length = C(10)-C(13), width = C(12)-C(14)] and the cell sides. In this crystal the length is nearly parallel to the *a* axis [C(10)-C(13) vector 16° to *a*] and the width is oriented parallel to a *bc* face diagonal [C(12)-C(14) vector 41° to *b*].

Table 2. Torsional angles for 2,4-dioxa- 5α -androstan- 17β -ol acetate

1	t	k	٤	¢	í	t	k	٤	¢	i	t	k	٤	¢	ĩ	t	k	٤	¢
C10	C1	02	C3	-58.4	C6	C 5	C10	C19	-62.6	C11	C9	C10	Cl	61.5	C12	C13	C17	C16	-159.2
02	C1	C10	C5	57.7	C5	C6	C7	C8	51.9	C11	C9	C10	C5	176.1	C12	C13	C17	017B	79.6
02	C1	C10	C9	173.0	C6	C7	C8	C9	-50.3	C11	C9	C10	C19	-61.6	C14	C13	C17	C16	-44.8
02	C1	C10	C19	-62.1	C6	C7	C8	C14	-173.6	C8	C9	C11	C12	50.5	C14	C13	C17	017B	-166.0
C1	02	C3	04	58.8	C7	C8	C9	C10	52.7	C10	C9	C11	C12	180.0	C18	C13	C17	C16	73.0
02	C3	04	C5	-58.6	C7	C8	C9	C11	-176.9	C9	C11	C12	C13	-52.7	C18	C13	C17	017B	-48.2
C3	04	C5	C6	-173.6	C14	C8	C9	C10	178.0	C11	C12	C13	C14	55.5	C8	C14	C15	C16	-160.6
C3	04	C5	C10	60.0	C14	C8	C9	C11	-51.5	C11	C12	C13	C17	163.5	C13	C14	C15	C16	-32.4
04	C5	C6	C7	177.3	C7	C8	C14	C13	-175.9	C11	C12	C13	C18	-69.3	C14	C15	C16	C17	3.6
C10	C5	C6	C7	-59.2	C7	C8	C14	C15	-52.0	C12	C13	C14	C8	-60.9	C15	C16	C17	C13	26.4
04	C5	C10	C1	-58.9	C9	C8	C14	C13	58.4	C12	C13	C14	C15	167.8	C15	C16	C17	017B	146.8
04	C5	C10	C9	-176.8	C9	C8	C14	C15	-177.7	C17	C13	C14	C8	178.7	C13	C17	017B	C20	-161.4
04	C5	C10	C19	58.8	C8	C9	C10	C1	-169.3	C17	C13	C14	C15	47.5	C16	C17	017B	C20	81.7
C6	C5	C10	C1	178.7	C8	C9	C10	C5	-54.7	C18	C13	C14	C8	63.0	C21	C20	017B	C17	-175.1
C6	C5	C10	C9	60.8	C8	C9	C10	C19	67.7	C18	C13	C14	C15	-68 2	020	C20	0178	C17	2 1



-ig. 3. Least-squares plane through atoms C(5)-C(17)2,4-dioxa-5α-androstan-17β-ol acetate.

the natural androgen suggests considerable flexibility in the target site requiring the hydrophilic contact.

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Acta Cryst. (1975). B31, 295

2,7-Dimethyl-5-acetylaminopyrazolo[1,5-a]pyrimidine

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Abstract. $C_{10}N_4H_{12}O$, monoclinic, space group C2/c, a=14.24 (5), b=16.70 (5), c=9.43 (2) Å, $\beta=110.5$ (5)°, Z=8, $D_m=1.29$ (1), $D_x=1.29$ g cm⁻³. The structure of the acetyl derivative of the isomer which melts at 185–186 °C is found to be that of the acetyl derivative of 2,7-dimethyl-5-aminopyrazolo[1,5-a]pyrimidine (I) rather than (II). The molecules are arranged in planes separated by a/4; within the layers the amide groups are linked into $O \cdots H-N$ hydrogen-bonded chains.



Introduction. Compounds containing the pyrazolo-[1,5-a]pyrimidine ring with structures (I) and (II) have important pharmacological properties (Takamizawa & Sawashima, 1966: Takamizawa & Hamajima, 1966: Takamizawa, Hayashi & Hamajima, 1969). The structure of the product, m.p. 201-202°, formed by the reaction of β -aminocrotonitrile and hydrazine at 100° or less has been variously assigned as (I) (von Meyer, 1915) and (II) (Takamizawa & Sawashimo, 1966). It has been suggested by Kobylecki (1973) that both (I) and (II) can in fact be made from the same reactants, the isomer m.p. 201-202° probably having structure (II) and the isomer m.p. 185-186° structure (I). Both analyse as $C_8N_4H_{10}$; the low m.p. isomer is formed by mixing cold aqueous solutions of the reactants and heating the precipitate to about 250 °C, whereas the high m.p. isomer is formed by refluxing the aqueous solutions. Since the usual spectroscopic techniques are unable to distinguish between the isomers, it was decided to acetylate the -NH₂ group and to determine the crystal structure of the low m.p. isomer. The result confirms the assignment suggested by Kobylecki.

The low m.p. isomer was prepared by Kobylecki's (1973) method. It was refluxed with acetic anhydride and the product precipitated by the addition of water. Crystallization from ethanol followed by slow crystallization (two weeks) from a dilute solution in chloroform gave transparent needles, m.p. $238-239^{\circ}$. Intensities were estimated visually from equi-inclination Weissenberg photographs (layers hk0 to hk5 and h0l to h3l) of a crystal of dimensions $0.43 \times 0.11 \times 0.16$ mm taken with Cu K α radiation ($\lambda = 1.5418$ Å). No correction was made for absorption.

Conventional symbolic-addition and multisolution $\sum_{n \in \mathbb{N}} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{$ tangent refinement (in Cc) failed to solve the structure, possibly because the arrangement of molecules into planes perpendicular to x^* invalidated the statistical assumptions. Eventually the structure was solved (in C2/c) by a multisolution technique (Sheldrick, 1975). A large number (here 2¹⁶) of sign permutations were expanded by the \sum_{i} formula. If the internal consistency of a permutation fell below a preset value at any stage during the expansion, the permutation was rejected. Finally a 'similarity test' was applied to avoid having to calculate too many virtually identical E maps. 21 E maps were computed, of which the eighth (in terms of \sum_{2} consistency) revealed the complete structure except for C(15). We subsequently found that if a quartet test (Giacovazzo, 1974; Schenk, 1974) was included in the index of merit, the second E map in the ranking order was essentially correct. The structure was refined by full-matrix least-squares calculations with anisotropic temperature factors for all atoms; no attempt was made to locate the hydrogen atoms. Neutral-atom scattering factors were employed (Cromer & Mann, 1968; Cromer & Liberman, 1970). The final weighted residual $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o|$ was 0.126, with a corresponding unweighted R of 0.113. The weighting scheme em-