

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

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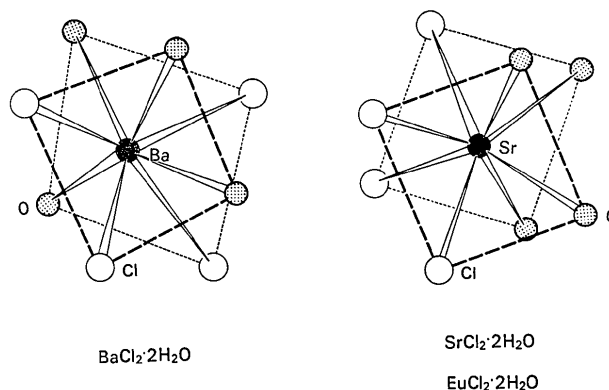


Fig. 2. Comparison of the metal coordination arrangements of  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{EuCl}_2 \cdot 2\text{H}_2\text{O}$  with  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

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## 2,4-Dioxa-5 $\alpha$ -androstan-17 $\beta$ -ol Acetate

BY VIVIAN CODY,\* WILLIAM L. DUAX AND CHARLES M. WEEKS

*Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, U.S.A.*

AND MANFRED E. WOLFF

*Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California 94143, U.S.A.*

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**Abstract.**  $\text{C}_{19}\text{H}_{30}\text{O}_4$ , m.p.  $120^\circ\text{C}$ , 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  $58.7^\circ$ . The more perfect chair conformation is associated with the 2,4-dioxa

substitution which relieves the  $\beta$ -face diaxial interactions.

**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

\* Author to whom correspondence should be addressed.

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  $20^\circ\text{C}$ ;  $\lambda(\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}$ ]. 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  $K\alpha$  radiation monochromated by balanced nickel and cobalt filters. The linear absorption coefficient  $\mu = 7.65 \text{ cm}^{-1}$ . 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 block-diagonal 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  $110^\circ$  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<sup>2</sup> and no physical significance could be attributed to individual deviations from the average value of 3.37 Å<sup>2</sup>. 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  $58.7^\circ$ . This is significantly greater than the average of  $55^\circ$  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 1NZ, England.

Table 1. Final fractional positional and thermal parameters for 2,4-dioxa-5 $\alpha$ -androstan-17 $\beta$ -ol acetate

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

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
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)
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)	0.058 (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)



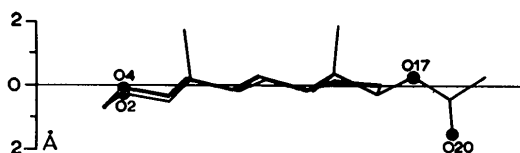


Fig. 3. Least-squares plane through atoms C(5)–C(17) of 2,4-dioxa-5 $\alpha$ -androstan-17 $\beta$ -ol acetate.

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

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## 2,7-Dimethyl-5-acetylamino-pyrazolo[1,5-*a*]pyrimidine

BY R. E. BALLARD AND E. K. NORRIS

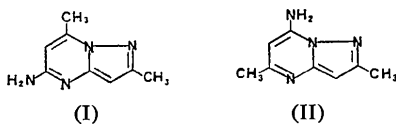
*School of Chemical Sciences, University of East Anglia, Norwich NOR 88 C, England*

AND G. M. SHELDRIK

*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England*

(Received 3 September 1974; accepted 16 September 1974)

**Abstract.** C<sub>10</sub>N<sub>4</sub>H<sub>12</sub>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<sup>-3</sup>. 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...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  $\beta$ -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 analyses as C<sub>8</sub>N<sub>4</sub>H<sub>10</sub>; 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 –NH<sub>2</sub> 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°. Intensities were estimated visually from equi-inclination Weissenberg photographs (layers  $hk0$  to  $hk5$  and  $h0l$  to  $h3l$ ) of a crystal of dimensions 0.43 × 0.11 × 0.16 mm taken with Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å). No correction was made for absorption.

Conventional symbolic-addition and multisolution  $\Sigma_2$  refinement (in space group *C2/c*) and multisolution 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 2<sup>16</sup>) of sign permutations were expanded by the  $\Sigma_2$  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  $\Sigma_2$  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-