

Baert de leur avoir communiqué, avant publication, les résultats relatifs au composé bis(chloroéthynyl)-2 $\alpha$ ,17 $\alpha$  nor-A 5 $\alpha$ -estradiol-2 $\beta$ ,17 $\beta$ .

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## Structure of 3 $\beta$ -Acetoxy-5,6 $\alpha$ -dichloromethylene-5 $\beta$ -androstan-17-one\*†

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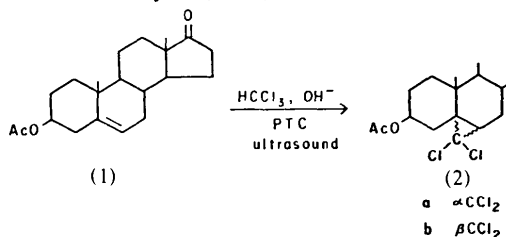
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**Abstract.** C<sub>22</sub>H<sub>30</sub>Cl<sub>2</sub>O<sub>3</sub>,  $M_r = 413.4$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 12.0931$  (6),  $b = 11.2148$  (5),  $c = 15.2104$  (6) Å,  $V = 2063$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.331$  Mg m<sup>-3</sup>.  $R_F = 0.052$  for 2640 observed reflections. The conformations of rings A and B approximate distorted chairs, both conformations attributable to the strain of the cyclopropyl ring. Ring C adopts a normal chair position while ring D exhibits a 14 $\alpha$ -envelope.

**Introduction.** The synthesis and isolation of the two dichloromethylene adducts (2a and 2b) of 3 $\beta$ -acetoxy-5-androsten-17-one (1) (Jennings, Boudreau, Braasch & Garganta, 1982) afforded the first-recorded pair of 5 $\alpha$ ,6 $\alpha$ - and 5 $\beta$ ,6 $\beta$ -dichloromethylene derivatives from the same  $\Delta^5$  steroid. Ultrasound instead of mechanical stirring (Jennings *et al.*, 1982) was used to generate dichlorocarbene from chloroform and base by phase transfer catalysis (PTC).



\* NRC Contribution No. 20400.

† Alternative nomenclature: 5,6 $\alpha$ -Dichloromethylene-17-oxo-5 $\beta$ -androstan-3 $\beta$ -yl Acetate.

A crystallographic study of the major product (2b) indicated a  $\beta$  isomer (Boudreau & Jennings, 1982), and the structure of the  $\alpha$  form (2a) is reported here as confirmation of its stereochemistry. Diffraction intensities were measured from a 0.4 × 0.4 × 0.3 mm ellipsoidal crystal enclosed in a quartz capillary to prevent sublimation. 5552 reflections were measured of which 65 were systematic absences, all of which gave net intensities below the 2.5 $\sigma(I)$  significance level. The remainder were averaged to give 2092 reflections with all indices positive and 1565 Friedel equivalents. Of these, 1540 and 1100 respectively were considered significant at the 2.5 $\sigma(I)$  level. The intensities were measured with graphite-monochromatized Mo  $K\alpha$  radiation using the  $\theta/2\theta$  scan technique with profile analysis (Grant & Gabe, 1978), to a maximum  $2\theta$  of 50°. The cell dimensions were determined by a least-squares process applied to the setting angles of 44 reflections with  $2\theta > 40^\circ$  ( $\lambda_{\text{Mo } K\alpha_1} = 0.70932$  Å). Normal Lorentz and polarization corrections were made but no absorption corrections ( $\mu = 3.33$  cm<sup>-1</sup>).

The structure was solved easily with *MULTAN* (Germain, Main & Woolfson, 1971) and, apart from minor difficulties with the H atoms, refined smoothly with block-diagonal least squares. The heavier atoms were refined anisotropically and the H atoms were included, but not refined, either at their calculated positions, or in the case of methyl H atoms, at positions found from a difference map. The H atoms on C(22) could not be found. The final residuals are  $R_F = 0.052$

Table 1. Atomic positional parameters and  $B_{eq}$ 

E.s.d.'s refer to the last digit printed.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
Cl (1)	0.16642 (9)	0.17201 (10)	0.52256 (7)	4.51 (6)
Cl (2)	0.34960 (10)	0.09500 (10)	0.62440 (7)	4.78 (6)
O(1)	0.52632 (20)	-0.15215 (21)	0.45786 (16)	3.85 (14)
O(2)	0.40659 (24)	-0.29886 (22)	0.48498 (19)	5.68 (17)
O(3)	0.0081 (3)	0.5601 (3)	0.18554 (20)	6.76 (19)
C(1)	0.3037 (3)	0.0139 (3)	0.33022 (24)	3.54 (22)
C(2)	0.3877 (3)	-0.0833 (3)	0.3535 (3)	4.24 (24)
C(3)	0.4336 (3)	-0.0702 (3)	0.44552 (24)	3.20 (21)
C(4)	0.4793 (3)	0.0552 (3)	0.45948 (23)	3.10 (21)
C(5)	0.3884 (3)	0.1447 (3)	0.44349 (23)	2.85 (19)
C(6)	0.3838 (3)	0.2628 (3)	0.4924 (3)	2.69 (19)
C(7)	0.3295 (3)	0.3722 (3)	0.45176 (23)	3.17 (20)
C(8)	0.2979 (3)	0.3615 (3)	0.35370 (22)	2.55 (19)
C(9)	0.2576 (3)	0.2358 (3)	0.32852 (22)	2.43 (19)
C(10)	0.3478 (3)	0.1419 (3)	0.34692 (22)	2.81 (19)
C(11)	0.2134 (3)	0.2320 (3)	0.23272 (24)	3.67 (23)
C(12)	0.1226 (3)	0.3258 (4)	0.21491 (24)	3.52 (21)
C(13)	0.1686 (3)	0.4491 (3)	0.23593 (22)	2.79 (19)
C(14)	0.2057 (3)	0.4511 (3)	0.33341 (23)	2.89 (21)
C(15)	0.2202 (3)	0.5833 (3)	0.3537 (3)	4.21 (23)
C(16)	0.1195 (3)	0.6391 (3)	0.3069 (3)	5.2 (3)
C(17)	0.0863 (3)	0.5510 (4)	0.2353 (3)	4.19 (23)
C(18)	0.2592 (4)	0.4869 (4)	0.1717 (3)	5.0 (3)
C(19)	0.4484 (3)	0.1666 (4)	0.2891 (3)	4.21 (24)
C(20)	0.3132 (3)	0.1634 (3)	0.52247 (23)	3.22 (20)
C(21)	0.5043 (4)	-0.2660 (4)	0.47867 (24)	4.82 (25)
C(22)	0.6057 (3)	-0.3418 (3)	0.4940 (3)	5.3 (3)

\*  $B_{eq}$  is the arithmetic mean of the principal axes of the thermal ellipsoid.

and  $R_w = 0.034$  for the observed data and 0.081 and 0.034 respectively for all data with counting statistics weights. Attempts to determine the absolute configuration led to inconclusive results and the residuals quoted do not include anomalous dispersion. Final positional and equivalent isotropic thermal parameters for the heavier atoms are given in Table 1.\* All calculations were performed with the NRC system of programs for the PDP-8e (Larson & Gabe, 1978), and scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The atomic-numbering scheme together with the bond lengths between the heavier atoms, and the bond angles between the same atoms is depicted in Fig. 1. A stereoview of the molecule is shown in Fig. 2. Analysis of these data clearly establishes the *trans* A/B junction of (2a).

Bond lengths and angles are in agreement with those observed for other  $\Delta^5$  steroid skeletons. The bond lengths between the Cl atoms, Cl(1) and Cl(2), and the cyclopropyl C atom, C(20), are 1.777 (6) and

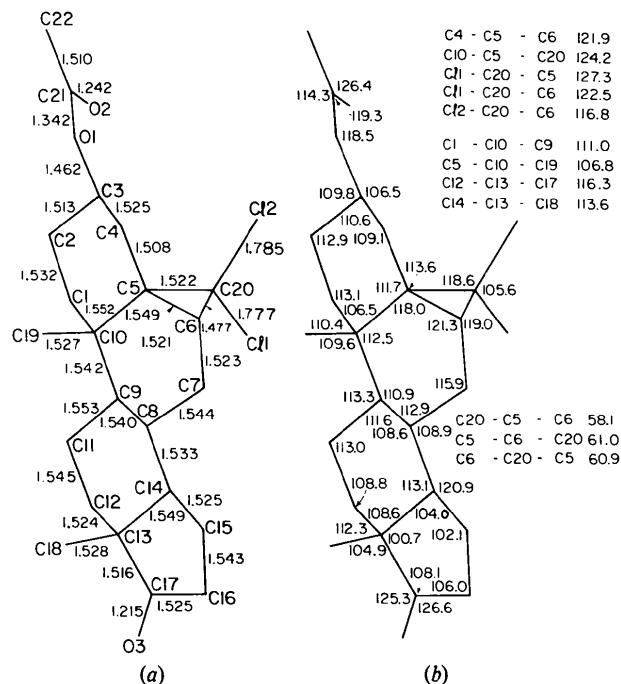


Fig. 1. (a) Bond lengths (Å) between non-H atoms in the molecule. E.s.d.'s are approximately 0.004 Å for C—Cl bonds, 0.005 Å for C—O bonds and 0.006 Å for C—C bonds. (b) Bond angles (°) for the same atoms. E.s.d.'s are Cl—C—Cl 0.2° and for all other angles 0.3°.

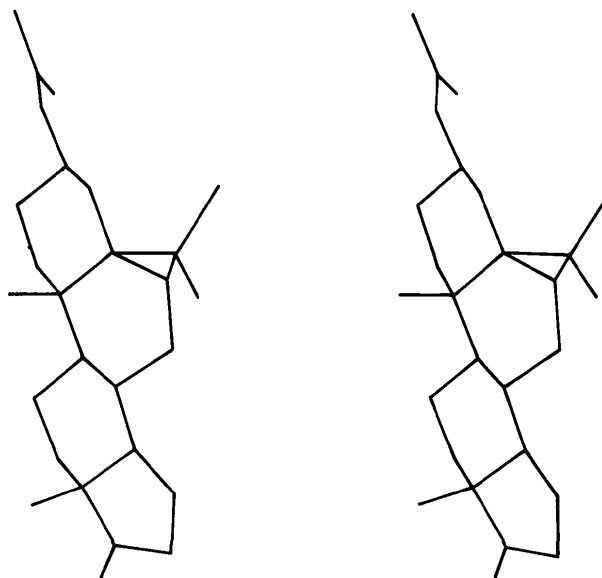


Fig. 2. A stereoview of the molecule.

1.785 (4) Å respectively. Ring A has the more common slightly distorted chair conformation, in comparison to the unusual boat conformation exhibited in compound (2b). Ring B is a severely distorted chair with the sum of the ring torsion angles equal to 196° in contrast to the 335° summation for a 'normal' cyclohexane ring. This ring puckering is attributed to the strain from the

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36984 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Ring B torsion angles ( $^{\circ}$ ) for the  $\alpha$ - and  $\beta$ -isomers

$\tau$	$\alpha$	$\beta$
C(5)–C(6)–C(7)–C(8)	–9.9 (5)	5.1
C(6)–C(7)–C(8)–C(9)	36.0 (4)	–37.9
C(7)–C(8)–C(9)–C(10)	–59.6 (4)	65.7
C(8)–C(9)–C(10)–C(5)	55.3 (4)	–55.3
C(9)–C(10)–C(5)–C(6)	–29.2 (4)	21.1
C(10)–C(5)–C(6)–C(7)	6.6 (5)	3.1
$\sum  \tau_i $	196.6	188.2

substituted cyclopropyl ring, C(5)–C(6)–C(20). The ring B torsion angles for the  $\alpha$ - and  $\beta$ -isomers shown in Table 2 clearly indicate opposite configurations. An almost 'normal' chair conformation is adopted by the C ring (torsion angle summation of  $342^{\circ}$ ), but deviation is caused by the fusion of a five-membered and six-membered ring system.

The geometry of the D ring is of special interest due to C(17)  $sp^2$  hybridization. The distances C(13)–C(17) and C(16)–C(17), 1.516 (4) and 1.525 (3) Å, are

intermediate between 1.505 Å, predicted for  $sp^2$ – $sp^3$  bonds, and 1.533 Å, predicted for  $sp^3$ – $sp^3$  bonds (Bartell & Bonham, 1960). The overall configuration of the D ring with a maximum torsion angle of  $42.6^{\circ}$ , is a slightly distorted 14 $\alpha$ -envelope.

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## Structures of 7-Chloro-5-phenyl-1-[(S)-1-phenylethyl]-1,3-dihydro-2H-1,4-benzodiazepin-2-one and its 3-Methyl Derivative

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**Abstract.** C<sub>23</sub>H<sub>19</sub>ClN<sub>2</sub>O (I),  $M_r = 374.86$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 17.500$  (3),  $b = 12.036$  (2),  $c = 9.212$  (2) Å,  $Z = 4$ ,  $U = 1940.32$  Å<sup>3</sup>,  $D_x = 1.283$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.216$  mm<sup>-1</sup>; C<sub>24</sub>H<sub>21</sub>ClN<sub>2</sub>O (II),  $M_r = 388.91$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 15.912$  (7),  $b = 14.403$  (7),  $c = 8.835$  (4) Å,  $Z = 4$ ,  $U = 2024.81$  Å<sup>3</sup>,  $D_x = 1.275$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.209$  mm<sup>-1</sup>. Final  $R = 0.047$  for 1778 observed reflexions [ $I > 2\sigma(I)$ ] (compound I) and  $R = 0.029$  for 1482 observed reflexions [ $I > 3\sigma(I)$ ] (compound II). The interatomic distances and angles are in agreement with the given atom type, hybridization and conjugation. The benzodiazepine ring exhibits a boat form with a *P* absolute conformation in both compounds. The absolute configuration at C(1) is

*S* (compounds I and II) whereas at the induced chiral centre C(3) (compound II) it is *R*.

**Introduction.** Over 2000 benzodiazepines have been synthesized and more than 100 have been tested for pharmacological activities. In man and mammals, the effects are sedation, hypnosis, decreased anxiety, muscle relaxation, and anticonvulsant activity (Goodman, Gilman, Goodman & Gilman, 1980).

Moreover, chiral 1,4-benzodiazepin-2-ones can be used for enantioselective synthesis of  $\alpha$ -amino acids (Decorte, Toso, Sega, Šunjić, Ružić-Toroš, Kojić-Prodić, Bresciani-Pahor, Nardin & Randaccio, 1981). In the course of that work it was crucial to determine the absolute conformation of the seven-membered ring