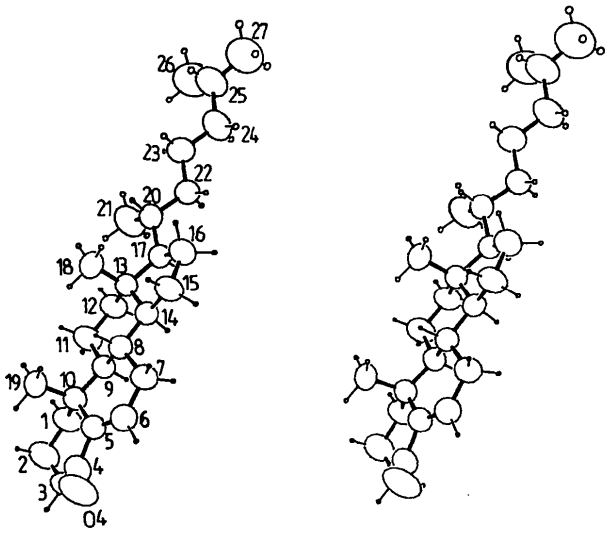

Fig. 1. *ORTEP* stereoview of the molecule with the atom-numbering scheme; ellipsoids are at the 65% probability level (Johnson, 1970).

has an intermediate sofa–half-chair conformation with asymmetry parameters $\Delta C_2^{5,6} = 9{\cdot}1$ and $\Delta C_s^6 = 14{\cdot}8$. The *C* ring has a chair conformation and the *D* ring has an envelope conformation with asymmetry parameters $\Delta C_s^{13} = 6{\cdot}1$ and $\Delta C_2^{16} = 16{\cdot}0$.

The side chain at C17 is fully extended (see Table 2) with a *−gauche,trans* conformation (Duax, Griffin, Rohrer & Weeks, 1980).

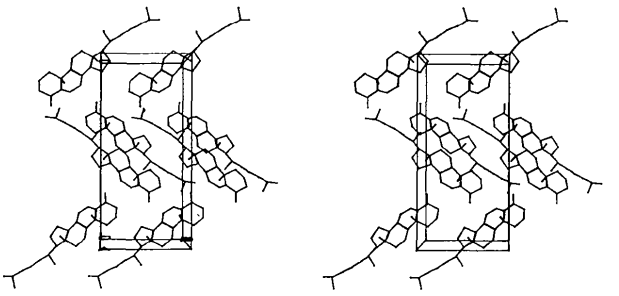

Fig. 2. Stereoview of the molecular packing in the unit cell, viewed down the *a* axis.

The authors express their appreciation to Dr Andrzej Szyczewski from the Adam Mickiewicz University for providing the crystals. This work was supported by project RP.II.10 from the Polish Ministry of National Education.

References

DUAX, W. L., GRIFFIN, J. F., ROHRER, D. C. & WEEKS, C. M. (1980). *Lipids*, **15**, 783–792.

DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*, Vol. 1, p. 18. New York: Plenum.

JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). *SHELX86*. In *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

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Structure of 6β,6′β-Bi(7α-allyl-3-oxo-4-estren-17β-yl acetate)

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Abstract. $C_{46}H_{62}O_6$, $M_r = 711{\cdot}0$, orthorhombic, $P2_12_12_1$, $a = 20{\cdot}187\ (3)$, $b = 22{\cdot}004\ (3)$, $c = 9{\cdot}180\ (1)$ Å, $V = 4078\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}16$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 1544$, $T = 295$ K, $R = 0{\cdot}096$ for 3894 unique observed reflections with $F_o > 2\sigma(F_o)$. The title compound is a dimer connected by a single bond between C6 and C6′ [bond length 1·560 (7) Å]. The two steroid moieties are oriented β-face to β-face, head to head and lie in almost parallel planes (7·6°), rotated by 45° to one another. The two conformations of the identical portions of the dimer differ chiefly in the orientation of the allyl and acetate groups. C23′ (acetate) and O3′ form the shortest intermolecular contact less than 3·5 Å; C···O = 3·35 (1) Å.

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Table 1. *Fractional positional parameters* ($\times 10^4$) *and equivalent isotropic atomic displacement parameters* ($Å^2 \times 10^2$) *for non-H atoms with e.s.d.'s in parentheses*

The second set of coordinates refers to the primed moiety.

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}	x	y	z	U_{eq}
C1	3992 (3)	8828 (3)	3034 (9)	7 (1)	7003 (3)	8437 (3)	−501 (9)	7 (1)
C2	4320 (4)	9353 (3)	2288 (11)	8 (1)	6602 (4)	8985 (3)	−874 (10)	8 (1)
C3	5014 (3)	9438 (3)	2819 (9)	7 (1)	5924 (3)	8826 (3)	−1372 (8)	7 (1)
C4	5378 (3)	8884 (2)	3055 (7)	5 (1)	5612 (3)	8330 (3)	−553 (6)	5 (1)
C5	5111 (2)	8328 (2)	2979 (5)	4 (1)	5933 (2)	7981 (2)	409 (5)	4 (1)
C6	5534 (2)	7764 (2)	2941 (6)	3 (1)	5563 (2)	7528 (2)	1340 (5)	4 (1)
C7	5283 (2)	7299 (2)	4063 (5)	3 (1)	5865 (2)	6892 (2)	1155 (5)	3 (1)
C8	4554 (2)	7146 (2)	3746 (6)	3 (1)	6613 (2)	6915 (2)	1472 (6)	3 (1)
C9	4116 (2)	7717 (2)	3801 (6)	4 (1)	6982 (2)	7376 (2)	513 (6)	4 (1)
C10	4366 (3)	8232 (2)	2834 (7)	4 (1)	6676 (2)	8016 (2)	604 (6)	4 (1)
C11	3394 (3)	7548 (3)	3447 (8)	5 (1)	7725 (3)	7392 (3)	909 (8)	6 (1)
C12	3117 (3)	7028 (2)	4346 (8)	5 (1)	8053 (3)	6758 (3)	855 (8)	6 (1)
C13	3561 (2)	6470 (2)	4239 (5)	4 (1)	7686 (2)	6320 (2)	1829 (6)	5 (1)
C14	4264 (2)	6659 (2)	4724 (6)	4 (1)	6953 (2)	6300 (2)	1341 (7)	4 (1)
C15	4636 (3)	6064 (2)	4941 (7)	5 (1)	6667 (3)	5748 (2)	2114 (9)	6 (1)
C16	4087 (4)	5623 (3)	5468 (10)	7 (1)	7249 (4)	5293 (3)	2130 (10)	8 (1)
C17	3441 (3)	5979 (2)	5406 (7)	5 (1)	7855 (3)	5645 (3)	1594 (9)	6 (1)
C18	3539 (3)	6183 (3)	2734 (7)	5 (1)	7761 (3)	6473 (3)	3437 (7)	6 (1)
C19	5424 (3)	7516 (3)	5608 (6)	5 (1)	5671 (3)	6632 (3)	−344 (7)	5 (1)
C20	6149 (3)	7528 (4)	5935 (7)	6 (1)	4964 (3)	6418 (3)	−332 (7)	6 (1)
C21	6508 (4)	7060 (5)	6217 (9)	8 (1)	4465 (4)	6648 (5)	−984 (8)	9 (1)
C22	2315 (3)	5632 (3)	5601 (10)	8 (1)	8790 (3)	5012 (3)	2008 (11)	8 (1)
C23	1843 (4)	5169 (4)	5038 (12)	9 (1)	9396 (4)	4929 (4)	2844 (15)	10 (1)
O3	5259 (2)	9942 (2)	2987 (7)	11 (1)	5646 (3)	9096 (2)	−2332 (6)	11 (1)
O17*B*	2906 (2)	5561 (2)	5024 (5)	6 (1)	8463 (2)	5501 (2)	2358 (6)	8 (1)
O22	2187 (3)	6052 (3)	6367 (9)	15 (1)	8581 (3)	4658 (3)	1090 (10)	14 (1)

Experimental. During an attempt to synthesize 7α- and 7β-substituted estradiols, the reaction between 17β-acetoxy-4,6-estradien-3-one and allyltrimethylsilane in the presence of $TiCl_4$ produced a 7α-allyl derivative identified by NMR and an isomeric compound with a strange NMR spectrum that could not be interpreted unambiguously (Kirk & Miller, 1988). A thin rectangular plate of the latter compound was grown from EtOAc/C_6H_{14}. Crystal size 0·28 × 0·30 × 0·60 mm. Nicolet *P*3 diffractometer, cell dimensions and Laue symmetry from 25 centered reflections ($20 < 2\theta < 27°$) checked with oscillation photographs, Mo $K\alpha$ radiation, Nb filtered, no monochromator, scan width variable, scan speed from 3 to 30° min^{-1} in 2θ, scan width [2·40 + 1·04 × $(2\theta_{K\alpha 2} - 2\theta_{K\alpha 1})$], $2\theta_{max} = 55°$, $0 \le h \le 25$, $-1 \le k \le 27$, $0 \le l \le 11$, 5245 independent reflections measured using a θ–2θ scan mode. Five standard reflections (10,1,1, 555, 763, 174, 3,11,2) were measured every 139 reflections and varied in intensity by ≤ 5% during the data collection.

Direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed positions of all non-H atoms. The positional and anisotropic displacement parameters of all non-H atoms were refined by full-matrix least squares on *F* using the 3894 reflections for which $F_o > 2\sigma(F_o)$. The H-atom positions were located in a difference map and refined with isotropic temperature parameters. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final $R = 0·096$, $wR = 0·068$, $S = 1·861$ for observed reflections and $R = 0·124$ for all data, $w = 1/\sigma^2$, $(\Delta/\sigma)_{max} = 0·40$. Weighting scheme based on estimates of experimental errors from counting statistics was used to calculate *w*. Final difference map showed maximum positive and negative peaks of +0·40 (−0·39) e $Å^{-3}$. No corrections for absorption or extinction were made.

Atomic parameters are listed in Table 1. Distances, angles and selected torsion angles are listed in Table 2.* A stereoscopic view of the molecule and molecular conformation is given in Fig. 1. Fig. 2 is a schematic drawing with atomic numbering. The enantiomer chosen for the values in Table 2 and the view in Fig. 1 is that of the naturally occurring hormone, the starting material being of known chirality.

Related literature. The production of a dimer was an unexpected by-product of the synthetic reaction. The structure determination provided the proof of structure of the product that could not be identified from the NMR spectra. The dimerization most probably proceeded through a free-radical reaction (Kirk & Miller, 1988).

This work was supported by the National Institute of Diabetes and Digestive and Kidney Diseases, Grant No. DK26546-22.

* Lists of anisotropic displacement parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53491 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths*, (Å) *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

The second column of distances and angles refers to the primed moiety.

C1—C2	1·497 (10)	1·492 (10)	C9—C11	1·539 (7)	1·543 (7)
C1—C10	1·523 (8)	1·524 (9)	C11—C12	1·517 (8)	1·545 (9)
C2—C3	1·495 (10)	1·485 (10)	C12—C13	1·524 (7)	1·510 (8)
C3—C4	1·442 (8)	1·467 (9)	C13—C14	1·544 (7)	1·548 (7)
C3—O3	1·223 (7)	1·202 (9)	C13—C17	1·541 (8)	1·538 (8)
C4—C5	1·338 (7)	1·338 (8)	C13—C18	1·519 (8)	1·522 (9)
C5—C10	1·524 (7)	1·512 (7)	C14—C15	1·522 (7)	1·522 (8)
C5—C6	1·509 (7)	1·511 (7)	C15—C16	1·550 (9)	1·543 (9)
C6—C7	1·538 (7)	1·535 (7)	C16—C17	1·521 (9)	1·529 (10)
C6—C6′	1·560 (7)		C17—O17*B*	1·461 (7)	1·448 (8)
C7—C8	1·537 (6)	1·540 (7)	C19—C20	1·495 (8)	1·502 (8)
C7—C19	1·523 (7)	1·540 (8)	C20—C21	1·285 (12)	1·276 (10)
C8—C9	1·536 (7)	1·535 (7)	C22—C23	1·488 (11)	1·456 (13)
C8—C14	1·515 (7)	1·521 (7)	C22—O17*B*	1·314 (8)	1·303 (9)
C9—C10	1·525 (7)	1·541 (7)	C22—O22	1·190 (11)	1·223 (11)

C2—C1—C10	113·0 (5)	114·1 (5)	C5—C10—C9	112·2 (4)	110·1 (4)
C1—C2—C3	111·2 (6)	112·4 (6)	C9—C11—C12	114·6 (4)	112·8 (5)
C2—C3—C4	114·9 (5)	114·4 (5)	C11—C12—C13	110·8 (4)	110·4 (5)
C2—C3—O3	122·3 (5)	122·7 (5)	C12—C13—C14	107·7 (4)	108·3 (4)
C4—C3—O3	122·7 (5)	122·9 (5)	C12—C13—C17	115·3 (4)	115·2 (4)
C3—C4—C5	124·0 (5)	123·9 (5)	C12—C13—C18	112·1 (4)	112·6 (4)
C4—C5—C10	122·0 (4)	121·9 (4)	C14—C13—C17	97·7 (4)	98·3 (4)
C4—C5—C6	121·6 (4)	120·8 (4)	C14—C13—C18	113·7 (4)	112·5 (4)
C10—C5—C6	116·3 (4)	117·3 (4)	C17—C13—C18	109·7 (4)	109·1 (4)
C5—C6—C7	110·2 (4)	110·0 (4)	C8—C14—C13	112·0 (4)	112·5 (4)
C5—C5—C6′	108·5 (4)	109·4 (4)	C8—C14—C15	119·7 (4)	120·2 (4)
C7—C6—C6′	115·0 (4)	115·0 (4)	C13—C14—C15	105·0 (4)	104·5 (4)
C8—C7—C19	115·0 (4)	115·5 (4)	C14—C15—C16	103·1 (4)	103·5 (5)
C8—C7—C6	109·5 (4)	109·8 (4)	C15—C16—C17	106·2 (5)	106·1 (5)
C19—C7—C6	110·7 (4)	109·7 (4)	C13—C17—C16	104·6 (4)	105·5 (5)
C7—C8—C9	111·5 (4)	112·9 (4)	C13—C17—O17*B*	113·0 (4)	109·3 (5)
C7—C8—C14	114·3 (4)	113·4 (4)	C16—C17—O17*B*	108·6 (4)	114·3 (5)
C9—C8—C14	109·6 (4)	108·9 (4)	C7—C19—C20	112·0 (4)	110·6 (4)
C8—C9—C10	113·5 (4)	112·3 (4)	C19—C20—C21	125·3 (5)	128·4 (5)
C8—C9—C11	109·9 (4)	110·6 (4)	C23—C22—O17*B*	111·2 (5)	113·6 (6)
C10—C9—C11	111·7 (4)	110·8 (4)	C23—C22—O22	126·7 (6)	125·0 (6)
C1—C10—C5	111·0 (4)	112·5 (4)	O17*B*—C22—O22	121·8 (5)	121·4 (6)
C1—C10—C9	114·0 (4)	110·3 (4)	C17—O17*B*—C22	120·0 (4)	119·4 (5)

C10—C1—C2—C3	−57·8 (8)	−54·2 (8)
C2—C1—C10—C5	41·6 (7)	36·2 (7)
C2—C1—C10—C9	169·5 (5)	159·6 (5)
C1—C2—C3—C4	39·9 (9)	40·2 (8)
C1—C2—C3—O3	−142·7 (7)	−142·3 (7)
C2—C3—C4—C5	−7·5 (9)	−10·0 (9)
O3—C3—C4—C5	175·1 (6)	172·6 (6)
C3—C4—C5—C10	−8·5 (9)	−7·8 (9)
C3—C4—C5—C6	167·8 (5)	172·8 (5)
C4—C5—C10—C1	−9·0 (7)	−5·6 (7)
C4—C5—C10—C9	−137·8 (5)	−129·0 (5)
C6—C5—C10—C1	174·6 (5)	173·8 (5)
C6—C5—C10—C9	45·8 (6)	50·4 (6)
C4—C5—C6—C7	131·0 (5)	125·3 (5)
C4—C5—C6—C6′	−102·3 (6)	−107·5 (5)
C10—C5—C6—C7	−52·5 (5)	−54·1 (6)
C10—C5—C6—C6′	74·2 (5)	73·1 (5)
C5—C6—C7—C8	57·6 (5)	54·3 (5)
C5—C6—C7—C19	−70·3 (5)	−73·6 (5)
C6′—C6—C7—C8	−65·3 (5)	−69·7 (5)
C6′—C6—C7—C19	166·8 (4)	162·4 (4)
C5—C6—C6′—C5′	66·7 (5)	
C5—C6—C6′—C7′	−169·0 (4)	−169·5 (4)
C7—C6—C6′—C7′	−45·2 (6)	
C19—C7—C8—C9	66·6 (5)	68·0 (6)
C19—C7—C8—C14	−58·4 (6)	−56·4 (6)
C6—C7—C8—C9	−58·8 (5)	−56·6 (5)
C6—C7—C8—C14	176·1 (4)	179·0 (4)
C8—C7—C19—C20	167·8 (5)	159·1 (5)
C6—C7—C19—C20	−67·4 (6)	−76·2 (6)
C7—C8—C9—C10	53·0 (5)	54·1 (5)
C7—C8—C9—C11	178·8 (4)	178·3 (4)
C14—C8—C9—C10	−179·4 (4)	−179·0 (4)
C14—C8—C9—C11	−53·5 (5)	−54·8 (5)
C7—C8—C14—C13	−173·1 (4)	−173·6 (4)
C7—C8—C14—C15	−49·6 (6)	−50·0 (6)
C9—C8—C14—C13	60·9 (5)	59·8 (5)
C9—C8—C14—C15	−175·6 (5)	−176·5 (5)
C8—C9—C10—C1	−172·1 (5)	−173·1 (5)
C8—C9—C10—C5	−44·9 (6)	−48·4 (5)
C11—C9—C10—C1	63·0 (6)	62·8 (6)
C11—C9—C10—C5	−169·8 (4)	−172·5 (4)

Table 2 (*cont.*)

C8—C9—C11—C12	51·8 (6)	54·1 (6)
C10—C9—C11—C12	178·7 (5)	179·2 (5)
C9—C11—C12—C13	−54·2 (6)	−55·8 (7)
C11—C12—C13—C14	56·3 (6)	56·9 (6)
C11—C12—C13—C17	164·1 (5)	165·9 (5)
C11—C12—C13—C18	−69·4 (6)	−68·1 (6)
C12—C13—C14—C8	−61·7 (5)	−61·2 (6)
C12—C13—C14—C15	166·9 (4)	166·8 (5)
C17—C13—C14—C8	178·6 (4)	178·6 (4)
C17—C13—C14—C15	47·1 (5)	46·6 (5)
C18—C13—C14—C8	63·1 (5)	63·9 (6)
C18—C13—C14—C15	−68·3 (5)	−68·1 (6)
C12—C13—C17—C16	−157·6 (5)	−155·4 (5)
C12—C13—C17—O17*B*	84·5 (6)	81·3 (6)
C14—C13—C17—C16	−43·8 (5)	−40·6 (6)
C14—C13—C17—O17*B*	−161·7 (4)	−163·8 (5)
C18—C13—C17—C16	74·8 (6)	76·8 (6)
C18—C13—C17—O17*B*	−43·1 (6)	−46·5 (6)
C8—C14—C15—C16	−159·2 (5)	−162·4 (5)
C13—C14—C15—C16	−32·4 (6)	−35·0 (6)
C14—C15—C16—C17	4·1 (6)	8·8 (7)
C15—C16—C17—C13	25·6 (6)	20·6 (7)
C15—C16—C17—O17*B*	146·4 (5)	140·7 (6)
C13—C17—O17*B*—C22	−100·5 (6)	−161·8 (6)
C16—C17—O17*B*—C22	144·0 (6)	80·2 (8)
C7—C19—C20—C21	−76·6 (9)	110·3 (8)
C23—C22—O17*B*—C17	178·6 (6)	179·1 (7)
O22—C22—O17*B*—C17	4·7 (11)	−3·1 (11)

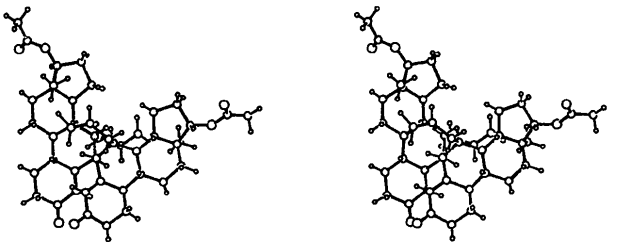

Fig. 1. *ORTEP*II (Johnson, 1976) stereoview of the molecule.

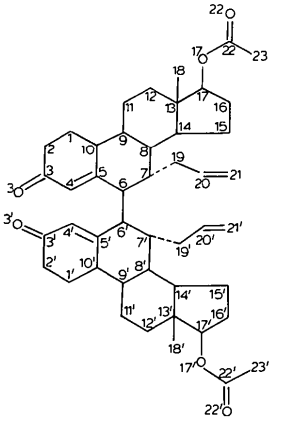

Fig. 2. A schematic drawing with atomic numbering.

References

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KIRK, D. N. & MILLER, B. W. (1988). *J. Chem. Res.* (*S*), pp. 278–279; *J. Chem. Res.* (*M*), pp. 2127–2156.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.