and about 90° in the analogous di-*exo* compounds. The calculated value of this torsion angle is 43·0 (5) (*A*), 43·8 (5)° (*B*) in (I) and −70·8 (8)° in (II). This confirms estimates from spectroscopic results of the values of these angles for di-*endo* (I) and di-*exo* (II) derivatives. The difference in torsion angles causes different molecular conformations in the di-*endo* and di-*exo* molecules, the latter isomer being more planar; this can substantially influence structurally specific action at receptor sites.

The molecules of the two compounds are connected through hydrogen bonds of N—H···S type to form dimers. The corresponding bond lengths and angles are H···S = 2·301 (2) (*A*), 2·466 (4) (*B*), N(1)···S = 3·322 (3) (*A*), 3·348 (5) Å (*B*), ∠N—H···S = 157·2 (2) (*A*), 159·5 (3)° (*B*) (I) and H···S = 2·474 (5), N(1)···S = 3·383 (6) Å, ∠N—H···S = 141·0 (4)° (II). These results are in agreement with the lengths of hydrogen bonds in similar molecules (Kapor *et al.*, 1987). Molecular packing in the crystal is shown in Fig. 2.

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Structure of 6α-Methyl-3,20-oxo-1,4,9(11)-pregnatrien-17α-yl Acetate

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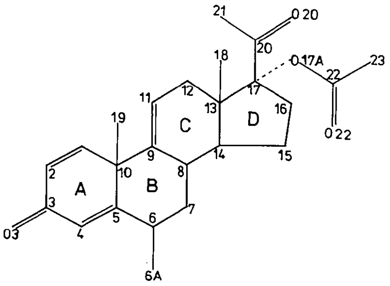
Abstract. $C_{24}H_{30}O_4$, $M_r = 382{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}091\,(2)$, $b = 19{\cdot}711\,(1)$, $c = 8{\cdot}242\,(1)$ Å, $V = 2126{\cdot}7\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}195$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54184$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 0{\cdot}56$ mm^{-1}, $F(000) = 824$, $T = 295$ K. Final $R = 0{\cdot}045$ for 2446 unique reflections. The planar *A* ring is bent relative to the rest of the steroid skeleton. The *B* ring has a typical chair conformation and the *C* and *D* rings assume 13β,14α-half-chair and 13β-envelope conformations, respectively. The conformation of the progesterone side chain is similar to the conformation observed in other 17α-ester pregnanes: C16—C17— C20—O20 torsion angle −27·4 (3)°.

Introduction. As is well known, a number of steroid hormones have a progesterone-like side chain at the C17 position. It is highly probable that the conformation of the side chain is responsible for control over the interaction of these hormones with their receptors (Duax, Cody, Griffin, Rohrer & Weeks, 1978). The 17α-ester substituents were found to have a restricting influence on the side-chain conformation (Duax, Griffin & Rohrer, 1981). The crystal structure of the title compound (I) has been determined as part of an effort to establish intramolecular features responsible for the progesterone side-chain conformation.



(I)

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Table 1. *Positional* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *with e.s.d.'s in parentheses, for the non-hydrogen atoms*

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

	x	y	z	U_{eq}
C1	11533 (2)	6526 (1)	728 (3)	61 (1)
C2	12528 (2)	6672 (1)	855 (3)	66 (1)
C3	13222 (2)	6554 (1)	−472 (4)	67 (1)
C4	12791 (2)	6273 (1)	−1967 (3)	59 (1)
C5	11796 (2)	6120 (1)	−2128 (3)	50 (1)
C6	11374 (2)	5797 (1)	−3645 (3)	53 (1)
C7	10873 (2)	5121 (1)	−3179 (3)	52 (1)
C8	10068 (1)	5180 (1)	−1839 (2)	45 (1)
C9	10476 (1)	5567 (1)	−374 (2)	44 (1)
C10	11037 (2)	6239 (1)	−760 (3)	50 (1)
C11	10333 (2)	5353 (1)	1134 (2)	48 (1)
C12	9724 (2)	4735 (1)	1636 (2)	47 (1)
C13	9066 (1)	4484 (1)	239 (2)	44 (1)
C14	9715 (1)	4476 (1)	−1315 (2)	43 (1)
C15	9086 (2)	4057 (1)	−2522 (3)	55 (1)
C16	8409 (2)	3590 (1)	−1489 (3)	60 (1)
C17	8716 (2)	3728 (1)	283 (3)	48 (1)
C18	8134 (2)	4952 (1)	61 (3)	59 (1)
C19	10224 (2)	6774 (1)	−1320 (4)	69 (1)
C20	7895 (2)	3597 (1)	1570 (3)	60 (1)
C21	8217 (2)	3494 (1)	3297 (4)	68 (1)
C22	9567 (2)	2669 (1)	802 (3)	60 (1)
C23	10574 (3)	2349 (1)	1056 (5)	82 (1)
C6*A*	12158 (2)	5689 (2)	−4997 (3)	69 (1)
O3	14144 (1)	6680 (1)	−371 (3)	95 (1)
O17*A*	9645 (1)	3346 (1)	669 (2)	51 (1)
O20	7000 (1)	3645 (1)	1204 (3)	87 (1)
O22	8758 (2)	2373 (1)	741 (3)	76 (1)

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

C1—C2	1·338 (4)	C11—C12	1·514 (3)
C1—C10	1·499 (3)	C12—C13	1·521 (3)
C2—C3	1·441 (4)	C13—C14	1·537 (2)
C3—C4	1·464 (4)	C13—C17	1·559 (3)
C3—O3	1·235 (3)	C13—C18	1·537 (3)
C4—C5	1·344 (4)	C14—C15	1·533 (3)
C5—C6	1·508 (3)	C15—C16	1·535 (3)
C5—C10	1·521 (4)	C16—C17	1·539 (4)
C6—C7	1·534 (3)	C17—C20	1·532 (4)
C6—C6*A*	1·530 (4)	C17—O17*A*	1·465 (3)
C7—C8	1·531 (3)	C20—C21	1·498 (4)
C8—C9	1·525 (2)	C20—O20	1·214 (3)
C8—C14	1·525 (3)	C22—C23	1·476 (4)
C9—C10	1·548 (3)	C22—O17*A*	1·343 (3)
C9—C11	1·326 (2)	C22—O22	1·210 (4)
C10—C19	1·568 (3)		

C2—C1—C10	124·5 (2)	C11—C12—C13	110·7 (2)
C1—C2—C3	121·3 (2)	C12—C13—C14	108·7 (1)
C2—C3—C4	117·2 (2)	C12—C13—C17	117·4 (2)
C2—C3—O3	122·2 (2)	C12—C13—C18	109·1 (2)
C4—C3—O3	120·6 (2)	C14—C13—C17	99·9 (1)
C3—C4—C5	122·8 (2)	C14—C13—C18	111·4 (2)
C4—C5—C6	122·1 (2)	C17—C13—C18	110·0 (2)
C4—C5—C10	121·7 (2)	C8—C14—C13	113·2 (1)
C6—C5—C10	116·1 (2)	C8—C14—C15	118·0 (2)
C5—C6—C7	108·4 (2)	C13—C14—C15	104·4 (1)
C5—C6—C6*A*	114·6 (2)	C14—C15—C16	105·9 (2)
C7—C6—C6*A*	110·4 (2)	C15—C16—C17	105·6 (2)
C6—C7—C8	114·1 (2)	C13—C17—C16	102·9 (2)
C7—C8—C9	111·6 (2)	C13—C17—C20	112·5 (2)
C7—C8—C14	110·1 (2)	C13—C17—O17*A*	104·6 (2)
C9—C8—C14	109·7 (1)	C16—C17—C20	116·4 (2)
C8—C9—C10	115·6 (2)	C16—C17—O17*A*	109·4 (2)
C8—C9—C11	122·3 (2)	C20—C17—O17*A*	110·2 (2)
C10—C9—C11	122·1 (2)	C17—C20—C21	118·9 (2)
C1—C10—C5	112·5 (2)	C17—C20—O20	119·5 (2)
C1—C10—C9	111·1 (2)	C21—C20—O20	121·2 (2)
C1—C10—C19	106·3 (2)	C23—C22—O17*A*	111·6 (2)
C5—C10—C9	109·3 (2)	C23—C22—O22	125·6 (3)
C5—C10—C19	109·2 (2)	O17*A*—C22—O22	122·8 (2)
C9—C10—C19	108·3 (2)	C17—O17*A*—C22	117·7 (2)
C9—C11—C12	125·9 (2)		

Experimental. Crystals were grown from acetone solution. Crystal data were measured on a crystal of dimensions $0·12 \times 0·60 \times 0·80$ mm. Weissenberg photographs indicated space group $P2_12_12_1$. The unit-cell dimensions were determined from the setting of 31 reflections with $60 < \theta < 70°$. The intensity data for 2528 independent reflections were collected on an Enraf–Nonius CAD-4 diffractometer using Ni-filtered Cu $K\alpha$ radiation, corrected for Lp, absorption ignored, scan width $(0·80 + 0·20\tan\theta)°$. Data collection with $3 < 2\theta < 154°$, $0 \leq h \leq 16$, $0 \leq k \leq 24$, $0 \leq l \leq 10$, θ–2θ scan mode. Four standard reflections (3,12,2; 753; 0,10,4; 265) were measured every 4 h and varied in intensity by $\leq 2\%$ during the data collection. Positions of all non-hydrogen atoms were found using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); these atoms were refined anisotropically. All hydrogen atoms were located in a difference Fourier map and refined as 'riding groups' except for hydrogens from the terminal C21 and C23 methyl groups which were not refined. Scattering factors and anomalous-dispersion parameters were taken from *International Tables for X-ray Crystallography* (1974). The final agreement factors were $R = 0·045$, $wR = 0·046$, $S = 2·321$ $[w = 1/\sigma^2(F_o)]$ for 277 variables and 2446 observed reflections for which $F_o > 4\sigma(F_o)$. The maximum Δ/σ in the last refinement cycle was 0·17. The final difference Fourier map showed no peaks higher than $|0·25|$ e Å^{-3}.

Plots were made with *ORTEP* (Johnson, 1970) and *PLUTO* (Motherwell, 1976). All calculations except for *MULTAN* were performed using *SHELX76* (Sheldrick, 1976). Fractional positional and thermal parameters are presented in Table 1. Bond lengths and angles are presented in Table 2.*

Discussion. Molecular diagrams are shown in Fig. 1. The *A* ring is planar and significantly bent toward the α face of the steroid skeleton. The side of the skeleton on which the C18 and C19 angular methyls are placed is called the β face whereas the opposite

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* Lists of anisotropic thermal parameters, H-atom parameters, torsion angles, coded-structure references and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52766 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

side is called the α face. The *B* ring has typical chair conformation and the *C* ring is in 13β,14α-half-chair conformation with asymmetry parameters $\Delta C_2^{9,11} = 1{\cdot}5$ and $\Delta C_s^{9} = 22{\cdot}9$ (Duax & Norton, 1975). The *D* ring has 13β-envelope conformation with asymmetry parameters $\Delta C_s^{13} = 3{\cdot}5$ and $\Delta C_2^{15} = 18{\cdot}0$. The distance of O3 from the plane defined by atoms C5 through C17 can be used as a measure of a degree of bending of the *A* ring relative to the rest of the steroid skeleton. Among six pregnane structures (Griffin, Duax & Weeks, 1984) distances vary from 2·13 to 2·94 Å (PR50,52,55,82,91,96; see deposited material) with the average value 2·45 Å. The distance found in the present structure is 2·30 Å which indicates that in spite of the additional unsaturation between the C9 and C11 atoms the molecule retains its bow typical for pregnanes with the 1,4-dien-3-one system.

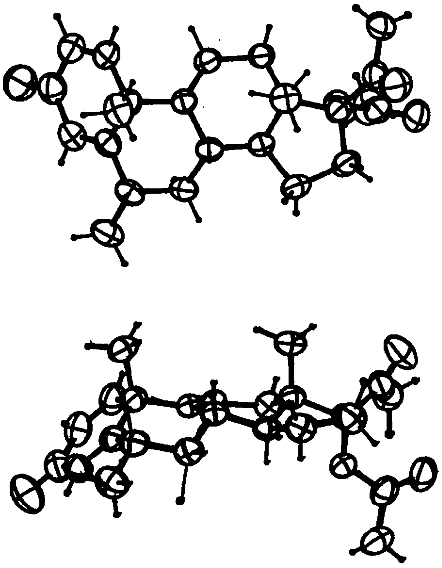

Fig. 1. *ORTEP* views of the steroid molecule, with thermal ellipsoids at 50% probability.

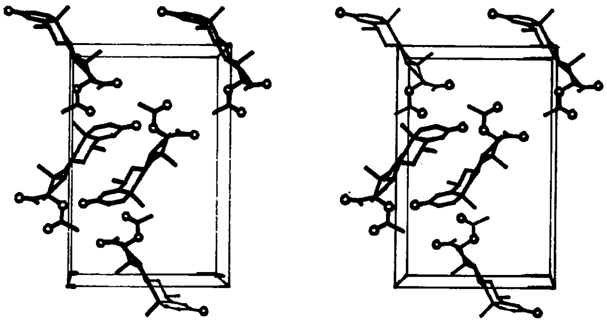

Fig. 2. Crystal packing diagram along the **c** direction.

It has been shown that in eight 17α-ester substituted steroid structures the C16—C17—C20—O20 torsion angle is between −24 and −18° with the average value −21 (2)° (Duax, Griffin & Rohrer, 1981). The C16—C17—C20—O20 torsion angle is −27·4 (3)° in the present study, slightly beyond the range observed before. In recently published structures of 11β,17α-dihydroxy-21-methyl-5α-pregn-4-ene-3,20-dione 17-butyrate (Barnes, Paton, Logan & Redpath, 1985), 17α-hydroxyprogesterone caproate (Krstanović, Cvetković, Oberti & Karanović, 1989), 17α-acetoxy-6-methylene-4-pregnene-3,20-dione (Petrow, Padilla, McPhail, Bruchovsky & Schneider, 1989) and 6α-methyl-17α-hydroxyprogesterone pivalate (Wawrzak, Grochulski, Gałdecki, Duax & Strong, 1990) the torsion angle was −22·2 (5), −24 (1), −22·8 (4) and −17·9 (5)°, respectively. The average value of the torsion angle for 13 structures, including the title molecule, is −21 (8)°.

The crystal packing diagram along the **c** direction is shown in Fig. 2.

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