

C—C bond lengths in phenoxathiin are in direct conflict with certain of their conclusions concerning C—C bond lengths in the series of ten $C_{12}H_8XY$ structures for X, Y variously O, S, Se, Te. Specifically, while the range of differences in the present average C—C bond lengths (0.016 Å) is very similar to that given by Meyers *et al.* (0.019 Å), and is indeed less than the corresponding range for anthracene (0.071 Å) from the work of Lehmann & Pawley (1972), the pattern of lengths is quite different. Meyers *et al.* conclude that bonds C2—C3 and C7—C8 (our numbering; see Fig. 1) are of highest bond order and shortest at 1.374 (2) Å (weighted mean value for the ten structures), while C11—C12 and C13—C14 are of lowest bond order and longest at 1.393 (3) Å (weighted mean value); the present phenoxathiin data yield average values for these sets of 1.388 and 1.388 Å, respectively. For phenoxathiin, the minimum average bond length is for C3—C4 and C6—C7 at 1.380 Å while the maximum average bond length is for C11—C1 and C9—C14 at 1.396 Å. In view of the e.s.d.'s of the individual bond lengths, however, even this largest difference is of marginal significance.

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Structure of 6 α -Methylprogesteron-17 α -yl Pivalate

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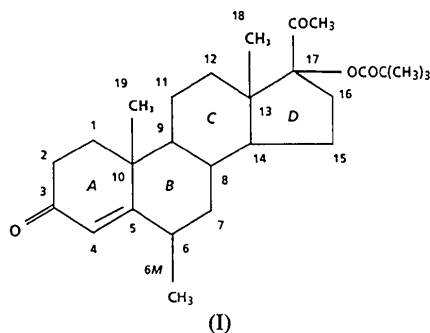
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Abstract. $C_{27}H_{40}O_4$, $M_r = 428.6$, orthorhombic, $P2_12_12_1$, $a = 9.821$ (3), $b = 25.766$ (6), $c = 9.802$ (3) Å, $V = 2480$ (2) Å³, $Z = 4$, $D_x = 1.15$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.70$ cm⁻¹, $F(000) = 936$, $T = 295$ K, final $R = 0.063$ for 2778 observed reflections. The A ring assumes a normal 1 α ,2 β -half-chair conformation. The progesterone

side chain has a conformation typical of 17 α -ester steroids; the C(16)—C(17)—C(20)—O(20) torsion angle is -17.9 (5)°.

Introduction. Previous reviews of crystallographic data have shown that 17 α -ester substitution has a very restricting influence on the conformation of the

progesterone side chain (Duax, Griffin & Rohrer, 1981). It has also been found that 17 α -hydroxy-6 α -methylprogesterone acetate (MPA) has the *A* ring in the inverted (1 β ,2 α -half-chair) conformation (Duax, Cody, Griffin, Hazel & Weeks, 1978). By comparison, related compounds such as 17 α -hydroxy-6 α -methylprogesterone (Duax & Strong, 1979), 17 α -hydroxyprogesterone acetate (Duax, Cody & Hazel, 1977) and 6 α -methyl-16-dehydroprogesterone (Duax, Strong & Weeks, 1979) have the *A* ring in the 'normal' (1 α ,2 β -half-chair) conformation. It was thus assumed that the combined presence of the 17 α -acetate and 6 α -methyl groups caused the inversion of the *A* ring in the solid state. Since MPA was shown to have a high affinity for the progesterone receptor in the rabbit uterus (Terenius, 1974) it was suggested that there is a correlation between *A*-ring inversion and biological activity (Duax, Cody, Griffin, Hazel & Weeks, 1978). The crystal structure of the title compound (I) has been determined in order to provide more information on the influence of 17 α -ester and 6 α -methyl substituents on the *A*-ring and progesterone side-chain conformation of steroids.



Experimental. The sample was provided by Professor R. Weichert, Schering, Berlin. A crystal of dimensions 0.4 × 0.09 × 0.8 mm was grown from acetone/hexane solution. The space group was determined by the symmetry of oscillation photographs and absences on zero and first level Weissenberg photographs. After structure refinement, coordinates were tested for tetragonal symmetry using *MISSYM* (Gabe, Le Page, Chanrland, Lee & White, 1989). No higher symmetry was found. X-ray data were collected on a Nicolet P3 diffractometer using Mo $K\alpha$ (Nb filter) radiation from 4 to 60° in 2θ . Scan speed varied from 3 to 30° min⁻¹ in θ and scan width was 2.4° + 1.04(2 $\theta_{K\alpha_2}$ - 2 $\theta_{K\alpha_1}$)°. Cell dimensions calculated by least-squares refinement for 25 reflections, 20 < 2 θ < 29°. Intensities of four standard reflections (800, 015, 1, 016, 383) were measured every 96 reflections and varied by less than 2% throughout the data collection. Intensity data collected for 4089

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C(1)	8685 (4)	1730 (1)	10999 (3)	57 (1)
C(2)	7824 (4)	1973 (2)	12109 (4)	69 (1)
C(3)	6655 (4)	2268 (1)	11522 (5)	73 (1)
C(4)	6057 (4)	2044 (1)	10311 (4)	66 (1)
C(5)	6515 (3)	1620 (1)	9664 (3)	52 (1)
C(6)	5715 (3)	1359 (2)	8556 (4)	62 (1)
C(7)	6599 (4)	1284 (2)	7294 (4)	62 (1)
C(8)	7917 (3)	1003 (1)	7596 (3)	46 (1)
C(9)	8718 (3)	1292 (1)	8706 (3)	40 (1)
C(10)	7874 (3)	1376 (1)	10040 (4)	44 (1)
C(11)	10116 (3)	1045 (1)	8967 (3)	47 (1)
C(12)	10948 (3)	960 (1)	7674 (3)	48 (1)
C(13)	10148 (3)	651 (1)	6622 (3)	44 (1)
C(14)	8802 (3)	945 (1)	6344 (3)	46 (1)
C(15)	8222 (4)	677 (2)	5080 (3)	63 (1)
C(16)	9468 (4)	544 (2)	4238 (4)	70 (1)
C(17)	10734 (4)	611 (1)	5140 (3)	54 (1)
C(18)	9896 (5)	98 (1)	7135 (4)	62 (1)
C(19)	7584 (5)	861 (1)	10774 (4)	59 (1)
C(20)	11791 (5)	178 (1)	4997 (4)	75 (1)
C(21)	13170 (5)	260 (2)	5594 (5)	85 (2)
C(22)	12011 (4)	1173 (1)	3694 (3)	63 (1)
C(23)	12637 (4)	1716 (2)	3541 (3)	74 (1)
C(24)	12709 (7)	1852 (4)	2053 (7)	118 (3)
C(25)	14088 (9)	1672 (4)	4092 (10)	163 (4)
C(26)	11841 (12)	2109 (3)	4326 (10)	172 (6)
C(6M)	4368 (5)	1621 (3)	8186 (6)	97 (2)
O(3)	6202 (4)	2653 (1)	12060 (4)	115 (1)
O(17A)	11382 (2)	1112 (1)	4886 (2)	53 (1)
O(20)	11481 (4)	-230 (1)	4502 (3)	106 (1)
O(22)	12119 (4)	840 (1)	2857 (3)	98 (1)

reflections of which 2778 had $I > 2\sigma(I)$, range h, k, l , $0 \leq 14$, $0 \leq 37$, $0 \leq 14$. The structure was determined using *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least-squares methods. All H atoms were located by difference Fourier synthesis and were refined isotropically except for the thermal parameters on the C(21), C(24), C(25) and C(26) hydrogens. Those H-atom thermal parameters were assigned values $\Delta U = 0.013 \text{\AA}^2$ greater than the C atoms to which they were bonded. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final $R = 0.063$, $wR = 0.063$, $S = 2.331$, $w = 1/\sigma^2$, $(\Delta/\sigma)_{\max} = 0.76$. The final difference map showed maximum positive and negative peaks of +0.27, -0.27 e \AA^{-3} .

Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.* Fig. 1 shows a stereoview of the molecule with atomic numbering, drawn with *ORTEPII* (Johnson, 1976). Fig. 2 is a stereoview of the crystal packing along the *a* axis.

Discussion. The bond lengths, angles and torsion angles are given in Table 2.

* Lists of structure factors, anisotropic displacement parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53248 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The geometry of the steroid skeleton of the title compound, in terms of bond lengths and angles, is consistent with the average of 4-en-3-one compounds (Griffin, Duax & Weeks, 1984). The *B* and *C* rings have chair and the *D* ring $13\beta,14\alpha$ -half-chair conformations with asymmetry parameters $\Delta C_2(16) = 0.8$ (Duax & Norton, 1975). The *A* ring has an only slightly distorted normal $1\alpha,2\beta$ -half-chair conformation with asymmetry parameters $\Delta C_2(1,2) = 6.8$ and $\Delta C_s(1) = 18.2$. The *A*-ring orientation in the title compound relative to the rest of the steroid skeleton is very similar to the progesterone molecule (Campsteyn, Dupont & Dideberg, 1972). The distance of O(3) from the mean plane through C(5) to C(17) is 1.90 Å in both molecules. It would appear that the combined presence of a 6α -methyl group and 17α -ester does not cause *A*-ring inversion in every case. Whereas MPA has the inverted *A* ring, the propionate is a disordered structure with inverted and non-inverted populations varying with temperature. The calculated energy difference between the normal and inverted *A* rings in MPA has been calculated to be 1.67 kJ mol⁻¹.

It has been shown that in 81 out of 85 progesterone analogue structures, the C(16)—C(17)—C(20)—O(20) torsion angle is between -46 and 0°. In eight 17α -ester-substituted steroid structures, for which X-ray data were compiled, this torsion angle varied from -24 to -18° with the average value -21 (2)° (Duax, Griffin & Rohrer, 1981). The

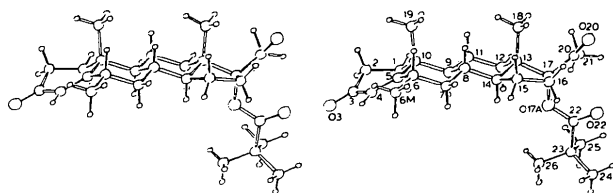


Fig. 1. ORTEP (Johnson, 1976) stereoview of the molecule with atomic numbering.

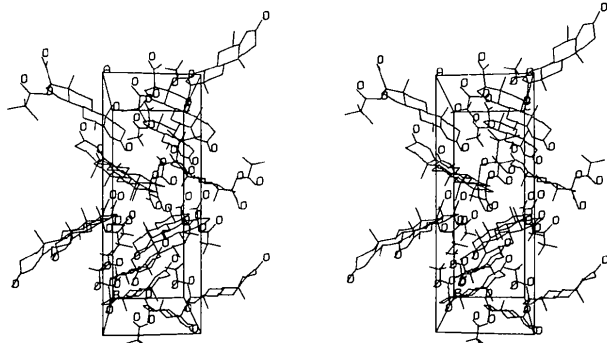


Fig. 2. Stereoview of the molecular packing in the unit cell viewed down the *a* axis.

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

C(1)—C(2)	1.513 (5)	C(12)—C(13)	1.522 (4)		
C(1)—C(10)	1.532 (4)	C(13)—C(14)	1.548 (4)		
C(2)—C(3)	1.492 (6)	C(13)—C(17)	1.566 (4)		
C(3)—C(4)	1.445 (6)	C(13)—C(18)	1.530 (4)		
C(3)—O(3)	1.208 (5)	C(14)—C(15)	1.529 (5)		
C(4)—C(5)	1.341 (5)	C(15)—C(16)	1.516 (6)		
C(5)—C(6)	1.500 (5)	C(16)—C(17)	1.535 (5)		
C(5)—C(10)	1.520 (4)	C(17)—C(20)	1.532 (5)		
C(6)—C(7)	1.523 (5)	C(17)—O(17A)	1.460 (4)		
C(6)—C(6M)	1.528 (7)	C(20)—C(21)	1.491 (7)		
C(7)—C(8)	1.512 (5)	C(20)—O(20)	1.196 (5)		
C(8)—C(9)	1.535 (4)	C(22)—C(23)	1.535 (6)		
C(8)—C(14)	1.511 (4)	C(22)—O(17A)	1.331 (4)		
C(9)—C(10)	1.564 (4)	C(22)—O(22)	1.193 (4)		
C(9)—C(11)	1.534 (4)	C(23)—C(24)	1.501 (8)		
C(10)—C(19)	1.536 (4)	C(23)—C(25)	1.529 (10)		
C(11)—C(12)	1.523 (4)	C(23)—C(26)	1.493 (10)		
C(2)—C(1)—C(10)	113.4 (3)	C(12)—C(13)—C(18)	110.3 (3)		
C(1)—C(2)—C(3)	111.3 (3)	C(14)—C(13)—C(17)	100.5 (2)		
C(2)—C(3)—C(4)	115.2 (3)	C(14)—C(13)—C(18)	112.1 (3)		
C(2)—C(3)—O(3)	122.2 (3)	C(17)—C(13)—C(18)	107.7 (3)		
C(4)—C(3)—O(3)	122.5 (3)	C(8)—C(14)—C(13)	113.4 (2)		
C(3)—C(4)—C(5)	125.3 (3)	C(8)—C(14)—C(15)	119.2 (3)		
C(4)—C(5)—C(6)	122.1 (3)	C(13)—C(14)—C(15)	103.8 (2)		
C(4)—C(5)—C(10)	121.1 (3)	C(14)—C(15)—C(16)	104.0 (3)		
C(6)—C(5)—C(10)	116.7 (3)	C(15)—C(16)—C(17)	108.3 (3)		
C(5)—C(6)—C(7)	110.3 (3)	C(13)—C(17)—C(16)	104.1 (3)		
C(5)—C(6)—C(6M)	115.3 (3)	C(13)—C(17)—C(20)	112.4 (3)		
C(7)—C(6)—C(6M)	110.9 (3)	C(13)—C(17)—O(17A)	105.1 (2)		
C(6)—C(7)—C(8)	112.9 (3)	C(16)—C(17)—C(20)	114.4 (3)		
C(7)—C(8)—C(9)	110.2 (3)	C(16)—C(17)—O(17A)	110.8 (3)		
C(7)—C(8)—C(14)	112.4 (3)	C(20)—C(17)—O(17A)	109.5 (3)		
C(9)—C(8)—C(14)	109.2 (2)	C(17)—C(20)—C(21)	118.4 (3)		
C(8)—C(9)—C(10)	112.9 (2)	C(17)—C(20)—O(20)	120.3 (3)		
C(8)—C(9)—C(11)	112.1 (2)	C(21)—C(20)—O(20)	121.1 (3)		
C(10)—C(9)—C(11)	113.1 (2)	C(23)—C(22)—O(17A)	112.3 (3)		
C(1)—C(10)—C(5)	111.1 (2)	C(23)—C(22)—O(22)	123.6 (6)		
C(1)—C(10)—C(9)	108.7 (2)	O(17A)—C(22)—O(22)	124.0 (3)		
C(1)—C(10)—C(19)	108.8 (3)	C(22)—C(23)—C(24)	109.0 (4)		
C(5)—C(10)—C(9)	108.7 (2)	C(22)—C(23)—C(25)	105.7 (4)		
C(5)—C(10)—C(19)	107.9 (3)	C(22)—C(23)—C(26)	111.0 (4)		
C(9)—C(10)—C(19)	111.7 (3)	C(24)—C(23)—C(25)	108.4 (5)		
C(9)—C(10)—C(12)	113.6 (3)	C(24)—C(23)—C(26)	111.5 (5)		
C(11)—C(12)—C(13)	111.2 (3)	C(25)—C(23)—C(26)	110.9 (5)		
C(12)—C(13)—C(14)	107.7 (2)	C(17)—O(17A)—C(22)	117.2 (2)		
C(12)—C(13)—C(17)	118.2 (2)				
Ring A					
C(10)—C(1)—C(2)—C(3)	-56.0 (4)	Ring C			
C(1)—C(2)—C(3)—C(4)	35.8 (5)	C(14)—C(8)—C(9)—C(11)	-51.6 (3)		
C(2)—C(3)—C(4)—C(5)	-3.8 (6)	C(8)—C(9)—C(11)—C(12)	51.0 (3)		
C(3)—C(4)—C(5)—C(10)	-9.5 (5)	C(9)—C(11)—C(12)—C(13)	-53.9 (3)		
C(4)—C(5)—C(10)—C(1)	-10.5 (4)	C(11)—C(12)—C(13)—C(14)	56.4 (3)		
C(5)—C(10)—C(1)—C(2)	42.7 (4)	C(12)—C(13)—C(14)—C(8)	-60.9 (3)		
Ring B				C(13)—C(14)—C(8)—C(9)	58.3 (3)
C(10)—C(5)—C(6)—C(7)	-52.3 (4)	Ring D			
C(5)—C(6)—C(7)—C(8)	53.7 (4)	C(17)—C(13)—C(14)—C(15)	43.9 (3)		
C(6)—C(7)—C(8)—C(9)	-56.3 (4)	C(13)—C(14)—C(15)—C(16)	-35.9 (3)		
C(7)—C(8)—C(9)—C(10)	55.4 (3)	C(14)—C(15)—C(16)—C(17)	13.3 (4)		
C(8)—C(9)—C(10)—C(5)	-51.3 (3)	C(15)—C(16)—C(17)—C(13)	14.0 (4)		
C(9)—C(10)—C(5)—C(6)	50.8 (3)	C(16)—C(17)—C(13)—C(14)	-35.0 (3)		
C(16)—C(17)—C(20)—O(20) torsion angle					

C(16)—C(17)—C(20)—O(20) torsion angle is -17.9 (5)° in the present study. This value is on the edge of the range observed before. In recently published structures of $11\beta,17\alpha$ -dihydroxy-21-methyl- 5α -pregn-4-ene-3,20-dione 17-butyrate (Barnes, Paton, Logan & Redpath, 1985), 17α -hydroxyprogesterone caproate (Krstanovic, Cvetkovic, Oberti & Karanovic, 1989) and 17α -acetoxy-6-methylene-4-pregnene-3,20-dione (Petrow, Padilla, McPhail, Bruhovskiy & Schneider, 1989), the torsion angles were -22.2 (5), -24 (1) and -22.9 (4)°, respectively.

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1,2,4-Trioxan-5-ones, a New Class of Endoperoxides: Structures of Three Representative Derivatives

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Abstract. (I): 7,8,15-Trioxadispiro[5.2.5.2]hexadecan-16-one, C₁₃H₂₀O₄, m.p. 366–367 K, $M_r = 240.3$, monoclinic, $P2_1/c$, $a = 11.160$ (2), $b = 11.588$ (1), $c = 11.169$ (3) Å, $\beta = 118.72$ (2)°, $V = 1266.7$ (5) Å³, $Z = 4$, $D_x = 1.26$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.086$ mm⁻¹, $F(000) = 520$, room temperature, $R (= wR) = 0.089$ for 582 observed reflections [$|F_o| > 3\sigma(F_o)$ and $|F_o| > 7.0$]. (II): (6*RS*,3*RS*)-6-(Adamant-1-yl)-3-cyclohexyl-1,2,4-trioxan-5-one, C₁₉H₂₈O₄, m.p. 395 K, $M_r = 320.4$, monoclinic, $P2_1/n$, $a = 12.150$ (4), $b = 10.693$ (2), $c = 12.909$ (2) Å, $\beta = 90.78$ (1)°, $V = 1677.0$ (7) Å³, $Z = 4$, $D_x = 1.27$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.082$ mm⁻¹, $F(000) = 696$, room temperature, $R (= wR) = 0.066$ for 1804 observed reflections [$|F_o| > 4\sigma(F_o)$ and $|F_o| > 8.0$]. (III): (6*RS*,3*SR*)-6-(Adamant-1-yl)-3-phenyl-1,2,4-trioxan-5-one, C₁₉H₂₂O₄, m.p. 372–375 K, $M_r = 314.4$, orthorhombic, $P2_12_12_1$, $a = 6.5317$ (16), $b = 11.316$ (3), $c = 21.216$ (3) Å, $V = 1568.1$ (6) Å³, $Z = 4$,

$D_x = 1.33$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.086$ mm⁻¹, $F(000) = 672$, room temperature, $R (= wR) = 0.052$ for 1039 observed reflections [$|F_o| > 4\sigma(F_o)$ and $|F_o| > 8.0$]. 1,2,4-Trioxan-5-ones are potentially fragile entities with respect to concomitant decarboxylation and scission of the endoperoxide bond. However, they are thermally stable at ambient temperatures. Some are suitably crystalline, thereby permitting their structures to be determined. The trioxane rings in (I) and (II) adopt a flattened half-chair conformation and an envelope in (III). In all three compounds the greatest puckering amplitude is associated with the peroxide bond. None displayed significant antimalarial activity.

Introduction. Our search for new therapeutic compounds related to the antimalarial arteannuin or *Qinghaosu* (Qinghaosu Antimalarial Coordinating Research Group, 1979) has led us to devise methods for the synthesis of simpler analogues of its crucial