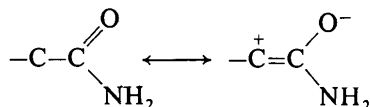


Table 3. Bond distances (Å) with e.s.d.'s in parentheses and bond angles (°) (e.s.d.'s 0.1–0.2° for non-hydrogen and 1.0–2.3° for H atoms)

C(1)–O	1.254 (9)	O–C(1)–N	121.7
C(1)–N	1.326 (10)	O–C(1)–C(2)	121.1
C(1)–C(2)	1.476 (18)	N–C(1)–C(2)	117.2
C(2)–C(3)	1.502 (6)	C(1)–C(2)–C(3)	115.6
N–H(1)	1.07 (10)	H(1)–N–H(2)	127
N–H(2)	0.92 (8)	C(1)–N–H(1)	118
C(2)–H(3)	0.95 (12)	C(1)–N–H(2)	113
C(3)–H(5)	1.07 (10)	C(1)–C(2)–H(3)	104
C(3)–H(6)	0.91 (10)	C(3)–C(2)–H(3)	109
C(3)–H(7)	1.17 (11)	C(2)–C(3)–H(5)	111
		C(2)–C(3)–H(6)	119
		C(2)–C(3)–H(7)	77

The presence of this resonance in amides, imides, amino acids, peptides and proteins (Robertson, 1953) affects their chemical behaviour.

The C(1)–C(2) (1.476 Å) and C(2)–C(3) lengths (1.502 Å) are shorter than usual (1.54 Å), indicating that the following type of resonance also occurs:



The fact that the C(1)–C(2)–C(3) bond angle (115.6°) is larger than tetrahedral also suggests the above resonance.

The unusually large standard deviations in positional and thermal parameters of the H atoms are the expected results of radiation damage. From ESR results, it is possible to identify the free-radical type, but it is not possible to decide which H atoms are lost upon irradiation (Adler & Petropoulos, 1965). However, the structure analysis shows clearly that H(4) and H(7) are responsible for the free-radical formation. This result is very important for the understanding of the solid-state behaviour of this type of compound. The H atoms which contribute to hydrogen bonding are not affected by radiation, and thus have good parameters and e.s.d.'s.

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Structure of 7 α -Methyl-4-androstene-3,17-dione

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Abstract. C₂₀H₂₈O₂, $M_r = 300.2$, $D_m = 1.21$, $D_c = 1.21$ Mg m⁻³, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 6.424$ (2), $b = 9.466$ (2), $c = 27.008$ (6) Å, $U = 1642.4$ Å³, $\mu(\text{Mo } K\alpha) = 0.041$ mm⁻¹. Final $R = 3.8\%$ for 1452 reflexions. Ring A adopts a 1 α -sofa conformation and rings B and C are observed as chair conformations. Ring D adopts an envelope conformation with C(14) at the flap.

Introduction. In an attempt to explain the antifertility activity of RMI 12,936 (Cox, Mkandawire & Mallinson, 1981), various possible metabolites have been examined. 7 α -Methyl-4-androstene-3,17-dione was prepared from 7 α -methyltestosterone (Cox & Sim, 1982) by oxidation with sodium dichromate/acetic acid. Crystallographic data were obtained from an Enraf-Nonius CAD-4 automated diffractometer using mono-

Table 1. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

For non-hydrogen atoms $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U/U_{eq}</i>
O(1)	5205 (4)	10324 (3)	7228 (1)	77 (2)
O(2)	12449 (3)	2921 (2)	4796 (1)	58 (2)
C(1)	8025 (5)	9013 (3)	6166 (1)	45 (2)
C(2)	7312 (6)	10192 (3)	6510 (1)	52 (2)
C(3)	6435 (5)	9630 (3)	6982 (1)	49 (2)
C(4)	7204 (5)	8266 (3)	7149 (1)	49 (2)
C(5)	8709 (4)	7533 (3)	6916 (1)	41 (2)
C(6)	9707 (6)	6294 (3)	7159 (1)	52 (2)
C(7)	9845 (5)	4992 (3)	6824 (1)	45 (2)
C(8)	10894 (4)	5406 (3)	6331 (1)	37 (2)
C(9)	9709 (4)	6624 (3)	6080 (1)	33 (2)
C(10)	9542 (4)	7969 (3)	6409 (1)	37 (2)
C(11)	10519 (5)	6060 (3)	5553 (1)	46 (2)
C(12)	10775 (5)	5666 (3)	5225 (1)	46 (2)
C(13)	12128 (4)	4579 (3)	5479 (1)	38 (2)
C(14)	11092 (4)	4172 (3)	5975 (1)	37 (2)
C(15)	12227 (5)	2825 (3)	6132 (1)	46 (2)
C(16)	12458 (5)	2029 (3)	5641 (1)	52 (2)
C(17)	12341 (4)	3140 (3)	5236 (1)	45 (2)
C(18)	14391 (4)	5103 (3)	5538 (1)	49 (2)
C(19)	11688 (5)	8674 (3)	6486 (1)	54 (2)
C(20)	7705 (6)	4308 (3)	6771 (1)	60 (2)
H(1A)	6798 (37)	8445 (30)	6054 (11)	61 (9)
H(1B)	8669 (42)	9437 (27)	5862 (8)	42 (7)
H(2A)	6415 (50)	10888 (32)	6342 (12)	84 (12)
H(2B)	8531 (46)	10800 (36)	6611 (13)	88 (13)
H(4)	6711 (42)	7921 (28)	7474 (7)	43 (8)
H(6A)	11177 (34)	6531 (37)	7261 (12)	72 (10)
H(6B)	9033 (39)	6066 (28)	7486 (7)	46 (8)
H(7)	10756 (38)	4290 (25)	7002 (9)	44 (8)
H(8)	12337 (32)	5725 (30)	6421 (10)	50 (8)
H(9)	8261 (30)	6257 (27)	6020 (10)	45 (8)
H(11A)	11882 (34)	7471 (29)	5596 (10)	55 (9)
H(11B)	9548 (49)	7625 (32)	5376 (11)	79 (11)
H(12A)	11416 (48)	5966 (30)	4908 (8)	56 (9)
H(12B)	9389 (34)	5254 (31)	5152 (11)	60 (9)
H(14)	9709 (30)	3877 (28)	5872 (9)	40 (7)
H(15A)	13584 (36)	3100 (36)	6280 (11)	72 (10)
H(15B)	11550 (43)	2272 (27)	6393 (8)	48 (8)
H(16A)	11324 (41)	1365 (29)	5579 (12)	63 (10)
H(16B)	13741 (42)	1439 (34)	5591 (13)	79 (11)
H(18A)	15264 (44)	4380 (22)	5699 (8)	62 (10)
H(18B)	14418 (50)	5991 (20)	5746 (8)	65 (10)
H(18C)	14918 (46)	5348 (26)	5202 (6)	53 (8)
H(19A)	12236 (46)	8971 (28)	6156 (6)	65 (10)
H(19B)	11597 (55)	9511 (23)	6710 (8)	75 (11)
H(19C)	12629 (48)	7945 (26)	6631 (9)	78 (11)
H(20A)	7164 (56)	3935 (30)	7092 (7)	91 (13)
H(20B)	7714 (56)	3490 (23)	6525 (8)	72 (11)
H(20C)	6731 (49)	5034 (27)	6630 (10)	83 (12)

chromatized Mo $K\alpha$ radiation. The cell dimensions were adjusted by least squares from the angular settings of 25 reflexions measured at θ ca 14° . Integrated relative intensities for 2085 independent reflexions with $\theta < 27^\circ$ were measured as $2\theta-\omega$ scans; 1452 reflexions had $I > 2.5\sigma(I)$.

The structure was elucidated by direct methods with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms were observed in

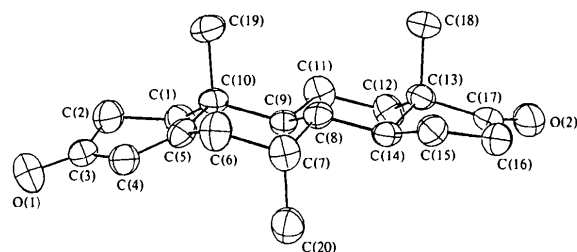


Fig. 1. The molecular structure.

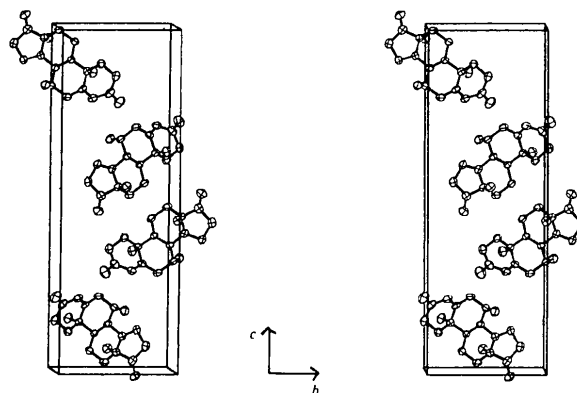
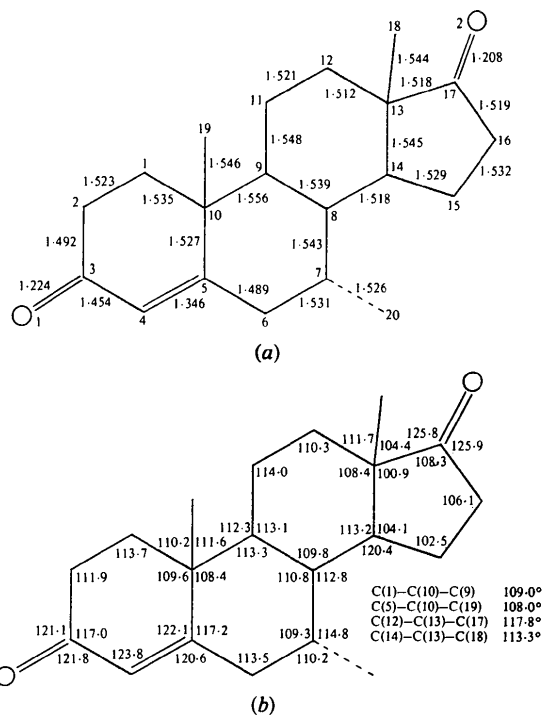


Fig. 2. A stereoscopic view of the molecular packing.

Fig. 3. (a) Bond lengths (Å). (b) Interbond angles ($^\circ$).

electron density maps obtained at intermediate stages of structure refinement. In the final cycles of full-matrix least-squares refinement the positional parameters for

Table 2. *Torsion angles* ($^{\circ}$)

C(10)–C(1)–C(2)–C(3)	–53.5 (3)	C(2)–C(1)–C(10)–C(5)	46.9 (3)
C(2)–C(1)–C(10)–C(9)	165.4 (2)	C(2)–C(1)–C(10)–C(19)	–71.7 (3)
C(1)–C(2)–C(3)–O(1)	–156.1 (3)	C(1)–C(2)–C(3)–C(4)	27.5 (4)
O(1)–C(3)–C(4)–C(5)	–173.1 (3)	C(2)–C(3)–C(4)–C(5)	3.3 (5)
C(3)–C(4)–C(5)–C(6)	167.8 (3)	C(3)–C(4)–C(5)–C(10)	–9.0 (5)
C(4)–C(5)–C(6)–C(7)	132.1 (3)	C(10)–C(5)–C(6)–C(7)	–50.9 (3)
C(4)–C(5)–C(10)–C(1)	–16.3 (4)	C(4)–C(5)–C(10)–C(9)	–135.2 (3)
C(4)–C(5)–C(10)–C(19)	103.7 (3)	C(6)–C(5)–C(10)–C(1)	166.7 (2)
C(6)–C(5)–C(10)–C(9)	47.8 (3)	C(6)–C(5)–C(10)–C(19)	–73.2 (3)
C(5)–C(6)–C(7)–C(8)	52.7 (3)	C(5)–C(6)–C(7)–C(20)	–74.3 (3)
C(6)–C(7)–C(8)–C(9)	–56.4 (3)	C(6)–C(7)–C(8)–C(14)	–179.9 (2)
C(20)–C(7)–C(8)–C(9)	68.0 (3)	C(20)–C(7)–C(8)–C(14)	–55.5 (3)
C(7)–C(8)–C(9)–C(10)	58.0 (3)	C(7)–C(8)–C(9)–C(11)	–172.7 (2)
C(14)–C(8)–C(9)–C(10)	–176.8 (2)	C(14)–C(8)–C(9)–C(11)	–47.4 (3)
C(7)–C(8)–C(14)–C(13)	179.6 (2)	C(7)–C(8)–C(14)–C(15)	–56.5 (3)
C(9)–C(8)–C(14)–C(13)	55.6 (3)	C(9)–C(8)–C(14)–C(15)	179.5 (2)
C(8)–C(9)–C(10)–C(1)	–170.2 (2)	C(8)–C(9)–C(10)–C(5)	–51.0 (3)
C(8)–C(9)–C(10)–C(19)	67.8 (3)	C(11)–C(9)–C(10)–C(1)	60.1 (3)
C(11)–C(9)–C(10)–C(5)	179.3 (2)	C(11)–C(9)–C(10)–C(19)	–61.9 (3)
C(8)–C(9)–C(11)–C(12)	48.2 (3)	C(10)–C(9)–C(11)–C(12)	178.0 (2)
C(9)–C(11)–C(12)–C(13)	–54.0 (3)	C(11)–C(12)–C(13)–C(14)	58.9 (3)
C(11)–C(12)–C(13)–C(17)	172.6 (2)	C(11)–C(12)–C(13)–C(18)	–66.7 (3)
C(12)–C(13)–C(14)–C(8)	–62.1 (3)	C(12)–C(13)–C(14)–C(15)	165.5 (2)
C(17)–C(13)–C(14)–C(8)	173.5 (2)	C(17)–C(13)–C(14)–C(15)	41.1 (2)
C(18)–C(13)–C(14)–C(8)	62.5 (3)	C(18)–C(13)–C(14)–C(15)	–69.9 (3)
C(12)–C(13)–C(17)–O(2)	37.6 (4)	C(12)–C(13)–C(17)–C(16)	–144.1 (3)
C(14)–C(13)–C(17)–O(2)	155.3 (3)	C(14)–C(13)–C(17)–C(16)	–26.3 (3)
C(18)–C(13)–C(17)–O(2)	–86.9 (3)	C(18)–C(13)–C(17)–C(16)	91.5 (3)
C(8)–C(14)–C(15)–C(16)	–186.4 (2)	C(13)–C(14)–C(15)–C(16)	–40.3 (3)
C(14)–C(15)–C(16)–C(17)	23.4 (3)	C(15)–C(16)–C(17)–O(2)	–179.5 (3)
C(15)–C(16)–C(17)–C(13)	2.1 (3)		

all atoms, anisotropic thermal parameters for the C and O atoms and isotropic thermal parameters for the H atoms were varied. Convergence was reached at R 3.8% and the weighting scheme used in the final calculation was $w = 1/(\sigma^2 F_o)$.

Final positional parameters are listed in Table 1 and torsion angles in Table 2.*

Discussion. The molecular structure and the packing of the molecules in the unit cell are shown in Figs. 1 and 2. Fig. 3 shows the bond lengths and valency angles involving non-hydrogen atoms; e.s.d.'s range from 0.003 to 0.005 Å for the bond distances and from 0.2 to 0.3° for the valency angles. Table 3 shows that the conformation of the molecule is very similar to that of 4-androstene-3,17-dione (Busetta, Comberton, Courseille & Hospital, 1972). This suggests that 7 α -methylation does not influence conformation in the solid state. When differences have been observed, such as in the A rings of 19-norandrostenediol and 7 α -methyl-19-norandrostenediol (Duchamp, 1979), such features can often be rationalized in terms of the effect of crystal packing on conformation flexibility. Fig. 1 shows that the 7 α -methyl C atom protrudes out from the plane of the molecule, a factor which may be significant in

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36342 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Asymmetrical* (ΔC_s), *geometrical* (φ_m) and *conformational parameters* (Δ) (Duax & Norton, 1975)

	4-Androstene-3,17-dione	This study
$\Delta C_s(1)$ (ring A)	8.7°	8.2°
$\Delta C_s(5)$ (ring B)	1.3	2.2
$\Delta C_s(9)$ (ring C)	3.7	2.1
Δ } (ring D)	–24.2	–31.2
φ_m }	41.9	42.7

rationalizing its antifertility activity. The intramolecular separation between O(1) and O(2) is 10.673 (3) Å.

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