

Fig. 4. Newman projections around the P(2)-S(4) and P(12)-S(4) bonds, showing torsion angles (°).

1.449 (11); (II) P=O 1.402 (14) and 1.426 (13); (III) P=O 1.45 (2) and 1.50 (5), and P=S 1.87 (5) and 1.78 (3). The comparatively long phosphoryl P(12)-O(12) and short thiophosphoryl P(2)-S(2) bonds of isomer (IV) are not accompanied by a shortening or elongation of the other P-O and P-S bonds in the  $\text{PO}_3\text{S}$  and  $\text{PO}_2\text{S}_2$  tetrahedra.

The mutual orientation of both the tetrahedra is shown in Fig. 4 which represents the Newman projection around the bridging P(2)-S(4) and P(12)-S(4) bonds. The bridging plane P(2)-S(4)-P(12) divides nearly symmetrically the largest dihedral angles of the tetrahedra.

The molecular packing did not show a distinct shortening of intermolecular distances.

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## References

- BUKOWSKA-STRZYŻEWSKA, M. & DOBROWOLSKA, W. (1978). *Acta Cryst.* **B34**, 1357-1360.
- BUKOWSKA-STRZYŻEWSKA, M. & DOBROWOLSKA, W. (1980). *Acta Cryst.* **B36**, 3169-3172.
- BUKOWSKA-STRZYŻEWSKA, M., MICHALSKI, J., MŁOTKOWSKA, B. & SKOWERANDA, J. (1976). *Acta Cryst.* **B32**, 2605-2608.
- CORBRIDGE, D. E. C. (1974). *The Structural Chemistry of Phosphorus*, p. 218. Amsterdam: Elsevier.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104-109.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368-376.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- WIECZOREK, M. W., SHELDICK, W. S., KAROLAK-WOJCIECHOWSKA, J., MIKOŁAJCZYK, M. & ZIEMNICKA, B. (1979). *Acta Cryst.* **B35**, 2339-2344.
- WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151-152.

*Acta Cryst.* (1981). **B37**, 727-729

## Structure of 17 $\beta$ -Hydroxy-7 $\alpha$ -methyl-5-androsten-3-one (RMI 12,936)

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**Abstract.**  $\text{C}_{20}\text{H}_{30}\text{O}_2$ ,  $M_r = 302.2$ ,  $D_m = 1.19$ ,  $D_x = 1.19 \text{ Mg m}^{-3}$ , orthorhombic,  $P2_{1}2_12_1$ ,  $Z = 4$ ,  $a = 5.970(2)$ ,  $b = 14.070(3)$ ,  $c = 20.015(3) \text{ \AA}$ ,  $U = 1681.2 \text{ \AA}^3$ . Final  $R = 0.029$  for 1294 independent reflexions. Rings A and C are observed in chair conformations whilst ring B approximates to the  $8\beta,9\alpha$ -half-chair form. Ring D approximates to an envelope conformation and an O(2)-H $\cdots$ O(1) hydrogen bond ( $2.85 \text{ \AA}$ ) provides the head-to-tail linkage between hydroxy and carbonyl O atoms of adjacent molecules.

**Introduction.** The X-ray crystal structure of the title compound was undertaken as part of a programme to determine the conformational features of a number of related antiprogestational steroids. RMI 12,936 is an antiprogestational and an antiestrogenic steroid and its antifertility activity has attracted attention (Kendle, 1979; Geddes, Kendle, Shanks & Steven, 1979). Of particular structural interest is the influence of the  $7\alpha$  methylation on ring conformation. Crystallographic data were obtained on an Enraf-Nonius CAD-4 automated diffractometer with Ni-filtered Cu  $K\alpha$

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) with e.s.d.'s and equivalent values of the anisotropic temperature factor coefficients ( $\times 10^3$ )

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$ ( $\text{\AA}^2$ )
O(1)	1885 (5)	3057 (2)	5424 (1)	70
O(2)	-257 (4)	-330 (1)	10282 (1)	54
C(1)	-143 (4)	1432 (2)	6610 (1)	46
C(2)	552 (5)	1599 (2)	5881 (1)	51
C(3)	2127 (5)	2417 (2)	5823 (1)	45
C(4)	4072 (5)	2384 (2)	6294 (1)	47
C(5)	3376 (5)	2174 (2)	7008 (1)	38
C(6)	4092 (5)	2711 (2)	7507 (1)	47
C(7)	3538 (5)	2576 (2)	8232 (1)	42
C(8)	2635 (4)	1563 (2)	8352 (1)	32
C(9)	851 (4)	1300 (2)	7824 (1)	33
C(10)	1842 (4)	1321 (2)	7103 (1)	33
C(11)	-367 (4)	363 (2)	7973 (1)	43
C(12)	-1162 (4)	263 (2)	8701 (1)	41
C(13)	786 (4)	426 (2)	9184 (1)	33
C(14)	1700 (4)	1428 (2)	9054 (1)	34
C(15)	3203 (5)	1627 (2)	9659 (1)	44
C(16)	2069 (5)	1082 (2)	10239 (1)	45
C(17)	116 (5)	526 (2)	9922 (1)	39
C(18)	2567 (5)	-353 (2)	9110 (1)	42
C(19)	3155 (5)	411 (2)	6937 (1)	45
C(20)	2000 (7)	3378 (2)	8464 (2)	61
H(1A)	-1104 (48)	2002 (17)	6770 (15)	
H(1B)	-1107 (49)	853 (16)	6642 (15)	
H(2A)	-780 (51)	1782 (25)	5605 (18)	
H(2B)	1464 (47)	1026 (19)	5684 (14)	
H(4A)	5058 (52)	1853 (19)	6109 (16)	
H(4B)	4960 (56)	3006 (18)	6263 (16)	
H(6)	4980 (52)	3276 (16)	7393 (15)	
H(7)	4958 (42)	2613 (21)	8508 (13)	
H(8)	3918 (38)	1133 (16)	8246 (13)	
H(9)	-300 (44)	1803 (16)	7845 (14)	
H(11A)	659 (44)	-201 (17)	7839 (13)	
H(11B)	-1735 (43)	300 (21)	7669 (14)	
H(12A)	-1822 (52)	-392 (16)	8773 (15)	
H(12B)	-2331 (45)	770 (16)	8789 (13)	
H(14)	316 (35)	1829 (16)	9104 (13)	
H(15A)	4781 (43)	1377 (21)	9571 (18)	
H(15B)	3083 (53)	2329 (16)	9778 (13)	
H(16A)	3058 (52)	606 (18)	10445 (15)	
H(16B)	1459 (52)	1519 (18)	10609 (13)	
H(17)	-1255 (41)	930 (19)	9949 (15)	
H(18A)	3907 (47)	-186 (22)	9412 (14)	
H(18B)	3229 (50)	-341 (19)	8633 (11)	
H(18C)	1847 (55)	-988 (19)	9198 (15)	
H(19A)	2066 (46)	-175 (18)	6880 (15)	
H(19B)	4176 (49)	254 (22)	7332 (13)	
H(19C)	4085 (42)	490 (17)	6511 (11)	
H(20A)	1606 (55)	3374 (21)	8967 (11)	
H(20B)	471 (45)	3319 (22)	8227 (15)	
H(20C)	2747 (52)	3999 (18)	8345 (15)	
HO(2)	-856 (64)	-803 (21)	10005 (17)	

radiation. The systematic absences determined the space group to be  $P2_12_12_1$ . The cell dimensions were adjusted by least squares from the angular settings of 25 reflexions measured at  $\theta \approx 30^\circ$ . Integrated relative intensities for 1894 independent reflexions with  $\theta < 70^\circ$  were measured as  $2\theta - \omega$  scans; 1294 reflexions had  $I > 3\sigma(I)$ .

The structure was solved with MULTAN (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All H atoms were located in difference maps calculated at intermediate stages of refinement. In the final cycles of full-matrix least-squares refinement the positional parameters for all atoms, anisotropic thermal parameters for the C and O atoms and isotropic for H were varied. Convergence was reached at  $R = 2.9\%$  and the weighting scheme in the final calculation was  $w = (\sigma^2 F_o + 0.0014 F_o^2)^{-1}$ . Final positional parameters are listed in Table 1,\* torsion angles in Table 2.

**Discussion.** The molecular structure and the packing of the molecules are shown in Figs. 1 and 2. Fig. 3 shows the bond lengths and angles involving non-hydrogen atoms; e.s.d.'s range from 0.003 to 0.004 Å for the bond distances and from 0.2 to 0.3° for the angles.

The conformations of *B* rings of steroids having a C(5)–C(6) double bond normally vary about the symmetric  $8\beta,9\alpha$ -half-chair form (Duax & Norton, 1975). The asymmetry parameters for this ring in RMI

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35776 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

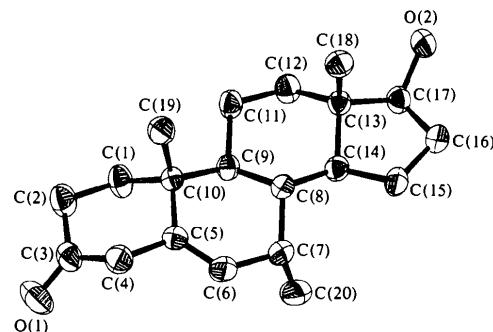


Fig. 1. The atomic arrangement in the molecule.

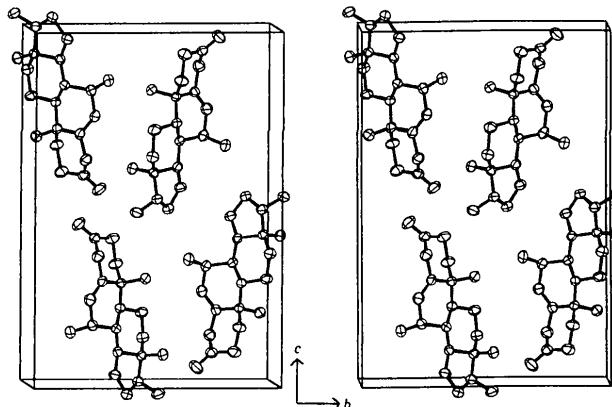
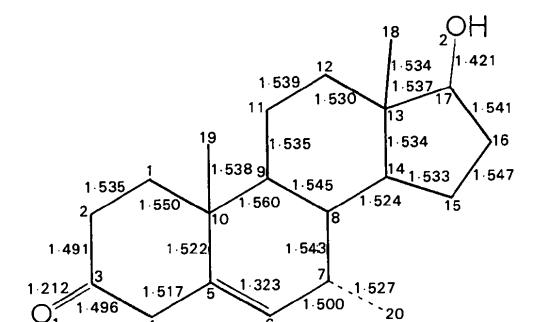


Fig. 2. A stereoscopic view of the molecular packing.

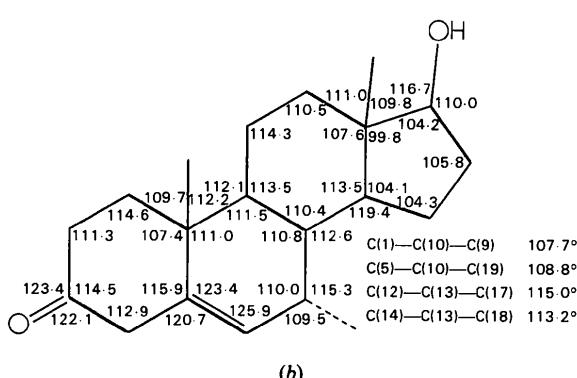
Table 2. Torsion angles ( $^{\circ}$ )

The sign convention used for an angle (1)–(2)–(3)–(4) is such that the sign is negative if an anticlockwise rotation of atom (1) is required to eclipse atom (4) whilst looking down the (2)–(3) bond.

C(10)–C(1)–C(2)–C(3)	−53.5 (3)	C(11)–C(12)–C(13)–C(17)	169.2 (2)	C(6)–C(7)–C(8)–C(14)	−171.0 (2)
C(2)–C(1)–C(10)–C(9)	172.3 (2)	C(12)–C(13)–C(14)–C(8)	−62.3 (2)	C(20)–C(7)–C(8)–C(14)	−46.6 (3)
C(1)–C(2)–C(3)–O(1)	−130.6 (3)	C(17)–C(13)–C(14)–C(8)	177.4 (2)	C(7)–C(8)–C(9)–C(11)	−171.3 (2)
O(1)–C(3)–C(4)–C(5)	132.3 (3)	C(18)–C(13)–C(14)–C(8)	60.7 (2)	C(14)–C(8)–C(9)–C(11)	−45.9 (2)
C(3)–C(4)–C(5)–C(6)	−130.1 (3)	C(12)–C(13)–C(17)–O(2)	81.7 (3)	C(7)–C(8)–C(14)–C(15)	−56.8 (3)
C(4)–C(5)–C(6)–C(7)	−179.7 (2)	C(14)–C(13)–C(17)–O(2)	−163.6 (2)	C(9)–C(8)–C(14)–C(15)	178.7 (2)
C(4)–C(5)–C(10)–C(1)	−50.8 (3)	C(18)–C(13)–C(17)–O(2)	−44.4 (3)	C(8)–C(9)–C(10)–C(5)	−41.6 (2)
C(4)–C(5)–C(10)–C(19)	67.8 (3)	C(8)–C(14)–C(15)–C(16)	−159.8 (2)	C(11)–C(9)–C(10)–C(1)	72.6 (2)
C(6)–C(5)–C(10)–C(9)	11.9 (3)	C(11)–C(15)–C(16)–C(17)	5.2 (3)	C(11)–C(9)–C(10)–C(19)	−48.1 (3)
C(5)–C(6)–C(7)–C(8)	17.7 (4)	C(15)–C(16)–C(17)–C(13)	23.3 (2)	C(10)–C(9)–C(11)–C(12)	173.9 (2)
C(6)–C(7)–C(8)–C(9)	−46.9 (3)	C(2)–C(1)–C(10)–C(5)	52.6 (3)	C(11)–C(12)–C(13)–C(14)	59.0 (2)
C(20)–C(7)–C(8)–C(9)	77.5 (3)	C(2)–C(1)–C(10)–C(19)	−65.4 (3)	C(11)–C(12)–C(13)–C(18)	−65.4 (3)
C(7)–C(8)–C(9)–C(10)	60.9 (2)	C(1)–C(2)–C(3)–C(4)	49.8 (3)	C(12)–C(13)–C(14)–C(15)	166.3 (2)
C(14)–C(8)–C(9)–C(10)	−173.7 (2)	C(2)–C(3)–C(4)–C(5)	−48.2 (3)	C(17)–C(13)–C(14)–C(15)	45.9 (2)
C(7)–C(8)–C(14)–C(13)	179.8 (2)	C(3)–C(4)–C(5)–C(10)	50.0 (3)	C(18)–C(13)–C(14)–C(15)	−70.7 (2)
C(9)–C(8)–C(14)–C(13)	55.4 (2)	C(10)–C(5)–C(6)–C(7)	0.1 (4)	C(12)–C(13)–C(17)–C(16)	−156.9 (2)
C(8)–C(9)–C(10)–C(1)	−158.9 (2)	C(4)–C(5)–C(10)–C(9)	−168.3 (2)	C(14)–C(13)–C(17)–C(16)	−42.2 (2)
C(8)–C(9)–C(10)–C(19)	80.4 (2)	C(6)–C(5)–C(10)–C(1)	129.4 (3)	C(18)–C(13)–C(17)–C(16)	77.0 (2)
C(11)–C(9)–C(10)–C(5)	−170.1 (2)	C(6)–C(5)–C(10)–C(19)	−112.0 (3)	C(13)–C(14)–C(15)–C(16)	−32.0 (2)
C(8)–C(9)–C(11)–C(12)	46.5 (3)	C(5)–C(6)–C(7)–C(20)	−110.1 (3)	C(15)–C(16)–C(17)–O(2)	149.1 (2)
C(9)–C(11)–C(12)–C(13)	−53.4 (3)				



(a)



(b)

Fig. 3. (a) Intramolecular bonded distances (Å). (b) Valency angles (°).

12,936 are  $\Delta C_2(5–6)$  5.6°,  $\Delta C_s(5)$  17.4°,  $\Delta C_s(6)$  25.3°. Alternatively, a mean plane through C(10)–C(5)–C(6)–C(7), torsion angle = 0.1 (3)°, shows that C(8) and C(9) are displaced to opposite sides by 0.44 and 0.30 Å respectively. This conformation is similar to that found in some 5-ene steroids that are not substituted in their B rings. Rings A and C adopt chair conformations although ring A is more symmetrical than ring C. The D ring adopts a 13 $\beta$ -envelope conformation, the smallest endocyclic torsion angle being 5.2°. The intramolecular distance between O(1) and O(2) is 10.902 (3) Å.

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## References

- DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*, Vol. I. New York: Plenum.
- GEDDES, C., KENDLE, K. E., SHANKS, C. W. & STEVEN, M. J. (1979). *J. Reprod. Fertil.* **49**, 231–235.
- KENDLE, K. E. (1979). *Current Investigations of Antiprogestational Steroids in Antihormones*, edited by M. K. AGARWAL. Amsterdam: Elsevier/North-Holland.
- 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.