

hydrogen atom was located approximately mid-way between the two oxygen atoms; $O(1)\cdots H=1.29$, $O(2)\cdots H=1.36$, $O(1)\cdots O(2)=2.64$ Å and $O(1)\cdots H\cdots O(2)=174.2^\circ$. The hydrogen bond, which is shown in Fig. 3, is the only intermolecular approach less than the van der Waals separations.

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Chlormadinone Acetate (6-Chloro-17-hydroxypregna-4,6-diene-3,20-dione Acetate)

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Abstract. $C_{23}H_{29}ClO_4$, orthorhombic, $P2_12_12_1$, $a=10.925$ (6), $b=12.068$ (6), $c=16.179$ (9) Å, $\rho_{obs}=1.26$, $\rho_{calc}=1.261$ g cm⁻³, $Z=4$. Chlormadinone acetate is isomorphous with cyproterone acetate *A*. but has markedly different biological activity. The structures of cyproterone acetate (I) and chlormadinone acetate (II) are identical except in ring *A*.

Table 1. Heavy-atom parameters and their standard deviations

The values have been multiplied by 10^4 . The temperature factor is in the form:

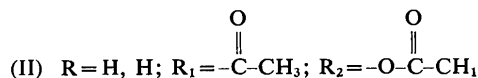
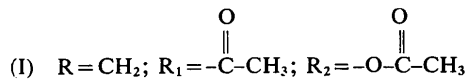
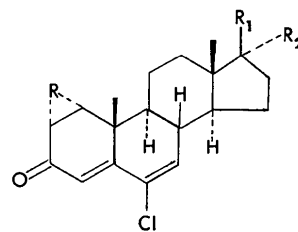
$$T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)].$$

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	3745 (5)	3130 (4)	4139 (2)	110 (6)	70 (4)	32 (2)	6 (9)	30 (6)	1 (5)
C(2)	3836 (5)	4234 (4)	3684 (3)	138 (6)	89 (4)	30 (2)	3 (10)	23 (7)	13 (5)
C(3)	2877 (4)	5051 (4)	3939 (3)	103 (6)	78 (4)	38 (2)	-33 (11)	-18 (6)	13 (6)
C(4)	2306 (4)	4900 (4)	4744 (2)	75 (4)	72 (4)	35 (2)	-2 (9)	-6 (5)	9 (5)
C(5)	2633 (4)	4091 (3)	5278 (2)	67 (4)	52 (3)	30 (2)	-23 (7)	-3 (5)	-5 (5)
C(6)	2053 (4)	3994 (3)	6102 (2)	79 (5)	51 (3)	34 (2)	-8 (8)	3 (5)	-14 (5)
C(7)	2246 (4)	3165 (3)	6622 (2)	97 (5)	54 (3)	26 (2)	-17 (8)	11 (5)	-4 (4)
C(8)	3051 (4)	2213 (3)	6422 (2)	77 (5)	46 (3)	27 (1)	10 (7)	-1 (5)	-6 (4)
C(9)	3289 (4)	2125 (3)	5480 (2)	68 (4)	57 (3)	25 (1)	-4 (7)	16 (5)	-6 (4)
C(10)	3632 (4)	3267 (3)	5092 (2)	78 (5)	56 (3)	29 (2)	-7 (8)	0 (5)	1 (4)
C(11)	4154 (4)	1174 (4)	5289 (3)	99 (5)	62 (4)	39 (2)	14 (8)	39 (6)	3 (5)
C(12)	3695 (4)	51 (4)	5620 (2)	85 (5)	61 (4)	40 (2)	19 (9)	38 (5)	-9 (5)
C(13)	3395 (4)	125 (3)	6545 (2)	74 (4)	50 (3)	34 (2)	-1 (7)	11 (5)	6 (5)
C(14)	2528 (4)	1094 (3)	6702 (2)	63 (5)	61 (3)	25 (1)	-2 (8)	2 (5)	-1 (4)
C(15)	2123 (5)	946 (3)	7605 (2)	107 (5)	58 (4)	32 (2)	0 (9)	12 (6)	-6 (5)
C(16)	2038 (4)	-319 (3)	7705 (2)	103 (5)	61 (4)	33 (2)	2 (8)	28 (6)	2 (4)
C(17)	2637 (4)	-850 (3)	6928 (2)	82 (5)	52 (3)	35 (2)	9 (8)	-15 (6)	-3 (4)
C(18)	4601 (4)	216 (4)	7043 (3)	80 (5)	74 (4)	58 (2)	6 (9)	-12 (7)	16 (6)
C(19)	4834 (4)	3715 (4)	5458 (3)	80 (5)	75 (4)	55 (2)	-29 (9)	-18 (7)	21 (6)
C(20)	3376 (4)	-1894 (4)	7104 (3)	91 (5)	64 (4)	43 (2)	-2 (8)	-3 (7)	14 (5)
C(21)	3692 (5)	-2667 (4)	6408 (3)	127 (7)	74 (4)	57 (3)	57 (9)	12 (8)	13 (6)
O(23)	3768 (3)	-2082 (3)	7791 (2)	139 (4)	89 (3)	49 (1)	44 (7)	-41 (5)	18 (4)
O(24)	1714 (2)	-1105 (2)	6302 (1)	76 (3)	53 (2)	37 (1)	-1 (5)	-7 (4)	9 (3)
C(25)	919 (4)	-1936 (3)	6464 (3)	87 (5)	47 (3)	52 (2)	2 (8)	-15 (7)	-2 (5)
C(26)	111 (5)	-2157 (4)	5732 (3)	123 (7)	73 (4)	64 (3)	-21 (10)	-56 (8)	6 (6)
O(27)	896 (3)	-2446 (2)	7100 (2)	130 (4)	65 (3)	51 (1)	-41 (6)	-3 (5)	21 (4)
O(28)	2614 (3)	5849 (3)	3510 (2)	161 (5)	124 (4)	49 (1)	40 (8)	-1 (6)	78 (5)
Cl(29)	1073 (1)	5066 (1)	6403 (1)	125 (1)	60 (1)	43 (1)	36 (2)	26 (1)	-10 (1)

Table 2. *Hydrogen atom parameters*

The values for the coordinates have been multiplied by 10^4 .
The value for the isotropic temperature factor is 3.4.

Atom bearing	H	x/a	y/b	z/c
H(30)	1	4562	2600	4011
H(31)	2	4766	4587	3821
H(32)	2	3818	4086	3022
H(33)	11	4309	1114	4612
H(34)	11	5048	1339	5566
H(35)	12	2823	-155	5284
H(36)	12	4326	-609	5494
H(37)	15	2770	1319	8025
H(38)	15	1224	1332	7712
H(39)	16	2562	-595	8244
H(40)	16	1113	-607	7763
H(41)	4	1587	5485	4960
H(42)	7	1797	3157	7225
H(43)	8	3922	2338	6726
H(44)	9	2379	1918	5194
H(45)	14	1695	1086	6327
H(46)	19	5540	3080	5370
H(47)	19	4660	3850	6110
H(48)	19	5000	4490	5170
H(49)	18	5080	-449	6920
H(50)	18	5040	1000	6840
H(51)	18	4350	300	7680
H(52)	21	4640	-2499	6250
H(53)	21	3150	-2359	5870
H(54)	21	3460	-3479	6560
H(55)	26	560	-2689	5350
H(56)	26	-79	-1379	5470
H(57)	26	-779	-2489	6020
H(58)	1	2956	2673	3917



Introduction. Cyproterone acetate displays progestenic and antiandrogenic properties (Brennan & Kraay, 1963). Chlormadinone acetate, which was obtained through the courtesy of Mr James D. Match of the Syntex Corp., is chemically similar to cyproterone acetate without the 1,2 methylene bridge. However, the omission of this single carbon atom results in the loss of the antiandrogenic activity. The crystal structure of cyproterone acetate has been recently reported (Chandross & Bordner, 1974). Since the crystal survey, data collection and refinement procedures for chlormadinone acetate were identical with this previously reported compound, details of these procedures will not be reported here. Of the 1561 independent reflections (collected on a Syntex $P\bar{T}$ with copper radiation

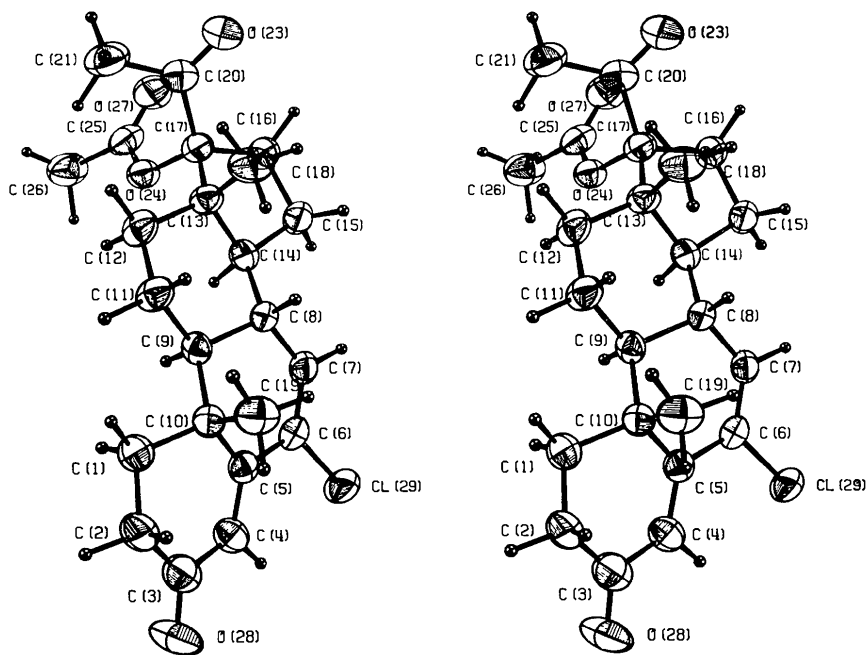


Fig. 1. Stereoscopic view down the a axis of chlormadinone acetate.

Table 3. Comparison of bond distances

	I	II		I	II
C(1)–C(2)*	1.474 (9)	1.526 (7)	C(10)–C(19)	1.533 (9)	1.538 (7)
C(1)–C(10)*	1.544 (8)	1.555 (6)	C(11)–C(12)	1.547 (9)	1.541 (7)
C(1)–C(22)	1.451 (9)		C(12)–C(13)	1.555 (9)	1.535 (6)
C(2)–C(3)*	1.471 (10)	1.497 (8)	C(13)–C(14)	1.533 (8)	1.527 (6)
C(2)–C(22)	1.486 (10)		C(13)–C(17)	1.578 (8)	1.567 (6)
C(3)–C(4)*	1.481 (9)	1.455 (7)	C(13)–C(18)	1.530 (9)	1.548 (7)
C(3)–O(28)*	1.235 (9)	1.221 (7)	C(14)–C(15)	1.530 (9)	1.537 (6)
C(4)–C(5)*	1.346 (9)	1.352 (7)	C(15)–C(16)	1.548 (8)	1.539 (7)
C(5)–C(6)	1.453 (9)	1.481 (6)	C(16)–C(17)	1.546 (9)	1.556 (7)
C(5)–C(10)*	1.523 (9)	1.508 (6)	C(17)–C(20)	1.534 (9)	1.522 (7)
C(6)–C(7)	1.327 (9)	1.323 (6)	C(17)–O(24)	1.458 (7)	1.463 (6)
C(6)–Cl(29)	1.758 (7)	1.747 (5)	C(20)–C(21)	1.494 (10)	1.502 (8)
C(7)–C(8)	1.476 (9)	1.482 (6)	C(20)–O(23)	1.203 (8)	1.213 (7)
C(8)–C(9)	1.525 (8)	1.549 (6)	O(24)–C(25)	1.373 (8)	1.352 (6)
C(8)–C(14)	1.525 (8)	1.535 (6)	C(25)–C(26)	1.461 (10)	1.502 (8)
C(9)–C(10)	1.564 (9)	1.561 (6)	C(25)–O(27)	1.198 (8)	1.199 (6)
C(9)–C(11)	1.535 (9)	1.518 (7)			

* Atoms in ring A.

Table 4. Comparison of bond angles

	I	II		I	II
C(10)–C(1)–C(2)*	120.2 (6)	113.0 (4)	C(19)–C(10)–C(9)	111.5 (5)	111.2 (4)
C(22)–C(1)–C(2)	61.1 (5)		C(12)–C(11)–C(9)	112.0 (5)	113.0 (4)
C(22)–C(1)–C(10)	121.5 (6)		C(13)–C(12)–C(11)	110.8 (5)	110.9 (4)
C(3)–C(2)–C(1)*	119.7 (6)	113.4 (4)	C(14)–C(13)–C(12)	108.9 (5)	109.8 (4)
C(22)–C(2)–C(1)	58.7 (4)		C(17)–C(13)–C(12)	115.8 (5)	117.1 (4)
C(22)–C(2)–C(3)	117.0 (6)		C(18)–C(13)–C(12)	109.8 (5)	109.3 (4)
C(4)–C(3)–C(2)*	116.4 (6)	117.6 (4)	C(17)–C(13)–C(14)	100.4 (5)	100.5 (3)
O(28)–C(3)–C(2)*	124.4 (6)	121.8 (5)	C(18)–C(13)–C(14)	112.7 (5)	112.7 (4)
O(28)–C(3)–C(4)*	119.2 (6)	120.5 (5)	C(18)–C(13)–C(17)	109.1 (5)	107.3 (4)
C(5)–C(4)–C(3)*	123.8 (6)	123.3 (5)	C(13)–C(14)–C(8)	112.8 (5)	113.2 (4)
C(6)–C(5)–C(4)	122.6 (6)	121.3 (4)	C(15)–C(14)–C(8)	121.0 (5)	119.4 (4)
C(10)–C(5)–C(4)*	122.2 (6)	122.7 (4)	C(15)–C(14)–C(13)	104.2 (5)	104.3 (4)
C(10)–C(5)–C(6)	115.1 (5)	115.9 (4)	C(16)–C(15)–C(14)	103.3 (5)	103.5 (4)
C(7)–C(6)–C(5)	124.9 (6)	124.3 (4)	C(17)–C(16)–C(15)	107.7 (5)	107.4 (4)
Cl(29)–C(6)–C(5)	116.2 (5)	117.0 (3)	C(16)–C(17)–C(13)	103.1 (4)	103.5 (4)
Cl(29)–C(6)–C(7)	118.9 (5)	118.7 (4)	C(20)–C(17)–C(13)	112.1 (5)	114.5 (4)
C(8)–C(7)–C(6)	122.3 (6)	122.8 (4)	O(24)–C(17)–C(13)	105.2 (4)	104.4 (3)
C(9)–C(8)–C(7)	111.7 (5)	111.6 (4)	C(20)–C(17)–C(16)	114.8 (5)	114.4 (4)
C(14)–C(8)–C(7)	113.8 (5)	113.4 (4)	O(24)–C(17)–C(16)	111.4 (5)	110.9 (4)
C(14)–C(8)–C(9)	109.3 (5)	107.0 (3)	O(24)–C(17)–C(20)	109.7 (5)	108.7 (4)
C(10)–C(9)–C(8)	111.7 (5)	112.0 (4)	C(21)–C(20)–C(17)	119.4 (6)	119.7 (5)
C(11)–C(9)–C(8)	111.4 (5)	110.9 (4)	O(23)–C(20)–C(17)	120.2 (6)	120.9 (5)
C(11)–C(9)–C(10)	114.6 (5)	115.8 (4)	O(23)–C(20)–C(21)	120.4 (6)	119.3 (5)
C(5)–C(10)–C(1)	111.8 (5)	109.0 (4)	C(2)–C(22)–C(1)	60.2 (5)	
C(9)–C(10)–C(1)*	109.0 (5)	108.9 (4)	C(25)–O(24)–C(17)	117.5 (5)	117.6 (4)
C(19)–C(10)–C(1)	108.4 (5)	110.6 (4)	C(26)–C(25)–O(24)	110.5 (6)	110.8 (4)
C(9)–C(10)–C(5)	107.5 (5)	109.2 (4)	O(27)–C(25)–O(24)	122.8 (6)	124.2 (5)
C(19)–C(10)–C(5)	108.7 (5)	108.0 (4)	O(27)–C(25)–C(26)	126.7 (6)	124.9 (5)

* Atoms in ring A.

to a resolution of 1 Å), 81 had intensities less than 2σ . These weak reflections were assigned a weight and intensity of zero. Since the two compounds appeared to be isomorphous, the refined coordinates of cyproterone acetate (minus the methylene bridge carbon) served as the trial structure for chlormadinone acetate. Full-matrix least-squares refinement proceeded smoothly to a final R index of 0.045; $\sum||F_o| - |F_c|| / \sum|F_o|$.* The goodness of fit was 2.56; $[w(F_o^2 - F_c^2)^2 /$

$(m - s)]^{1/2}$ (where m is the number of observations and s is the number of parameters refined). Both data-fit criteria were based on non-zero reflections. The final shifts were all less than 0.1 of their corresponding standard deviations. A final difference Fourier revealed no missing or misplaced electron density.

Discussion. The atomic parameters for chlormadinone acetate along with their standard deviations are presented in Tables 1 and 2. A stereo view of the molecule is given in Fig. 1. The molecular structure of chlormadinone acetate (II) is very similar to that of cyproterone acetate (I). The only significant differences occur in ring A. The similarities and differences can best be seen by examination of Tables 3–5.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30775 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. Comparison of dihedral angles

Ring A	I	II	Ring B	I	II
C(1)–C(2)	–6.2	–49.1	C(5)–C(6)	–11.5	–9.0
C(2)–C(3)	–12.7	22.1	C(6)–C(7)	–2.3	–1.7
C(3)–C(4)	14.1	2.6	C(7)–C(8)	–16.3	–17.7
C(4)–C(5)	4.9	0.5	C(8)–C(9)	47.3	46.6
C(5)–C(10)	–22.8	–26.6	C(9)–C(10)	–59.2	–56.2
C(1)–C(10)	23.0	50.0	C(5)–C(10)	40.5	37.0
Ring C			Ring D		
C(8)–C(9)	–56.3	–57.7	C(13)–C(14)	46.6	46.1
C(9)–C(11)	55.2	56.5	C(14)–C(15)	–36.4	–35.9
C(11)–C(12)	–54.3	–53.3	C(15)–C(16)	11.4	11.0
C(12)–C(13)	54.7	52.5	C(16)–C(17)	16.7	16.8
C(13)–C(14)	–58.4	–58.6	C(13)–C(17)	–38.1	–38.0
C(14)–C(8)	59.3	60.2			

Table 5 (cont.)

Side chain	I	II
C(13)–C(17)–C(20)–O(23)	96.0	97.6
C(16)–C(17)–C(20)–O(23)	–21.2	–21.5
C(13)–C(17)–O(24)–C(25)	178.5	179.5
C(16)–C(17)–O(24)–C(25)	–70.4	–69.7
C(17)–O(24)–C(25)–O(27)	5.6	2.9
C(17)–O(24)–C(25)–C(26)	–171.8	–174.9
C(13)–C(17)–C(20)–C(21)	–83.1	–78.5
C(16)–C(17)–C(20)–C(21)	159.7	162.3

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(–)₅₈₉-Tris-(*R*-propylenediamine)cobalt(III) Bromide

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Abstract. (–)₅₈₉-[Co(*R*-pn)₃]Br₃, *M. W.* 518.0, hexagonal, *P*6₃, *a* = 11.012 (2), *c* = 8.582 (1) Å, *Z* = 2, *D*_m = 1.911, *D*_x = 1.908 g cm^{–3}, *U* = 901.4 Å³, *μ*(Mo *Kα*, λ = 0.7107 Å) = 80.0 cm^{–1}. The crystal structure was redetermined on the basis of the intensity data collected by diffractometry in order to obtain more accurate information on the conformational details. The results are essentially the same as those previously reported; however, the standard deviations of the atomic parameters were reduced to about one third of the previous values. Methyl groups were revealed to take two alternative azimuthal orientations around the C–CH₃ bonds.

Introduction. *A*(*le*₃)-[Co(*R*-pn)₃]³⁺ ion is one of the most familiar and fundamental complex ions in coordination chemistry and has been extensively studied, including the absolute configuration (Iwasaki & Saito, 1966). Recently the *A*(*ob*₃) isomer of this complex ion was isolated and the crystal structure of the hexacyanocobaltate was determined accurately by diffractometer methods (Kuroda & Saito, 1974).

The crystal structure of the *A*(*le*₃)-[Co(*R*-pn)₃]Br₃ was redetermined by the diffractometer method, since the previous work was based on the intensity data collected by the photographic method. The redetermination will enable us to compare the detailed conformations of the two isomeric complex ions and, moreover, such accurate knowledge of the crystal struc-

ture would be of a great help in constructing a theoretical model for optical activity.

Crystals were prepared according to the method described by Iwasaki & Saito (1966). They are dark-red hexagonal prisms elongated along the *c* axis. Unit-cell dimensions were determined from Weissenberg photographs and were later refined on a diffractometer. The crystal specimen was shaped into a sphere with a radius of 0.15 mm. The intensity data were measured on a Rigaku automated four-circle diffractometer using Mo *Kα* radiation monochromated by a graphite plate. The ω–2θ scan technique was employed. The data were corrected for Lorentz and polarization factors but not for absorption and extinction. Among 1067 accessible reflexions below 2θ = 60°, 888 with |*F*_o| ≥ 3σ were used for structure determination.

The atomic coordinates previously reported by Iwasaki & Saito (1966) were used as a starting set in the least-squares refinement. After several cycles of least-squares refinement with isotropic thermal parameters, the *R* value became 0.099. A difference Fourier map at this stage showed some of the hydrogen atoms. Successive difference Fourier synthesis and least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms finally revealed all the hydrogen atoms in an asymmetric unit. The *R* value decreased to 0.037 for 888 independent reflexions. At the final stage all the positional shifts of non-hydrogen atoms were less than one half of the standard deviations of the positional parameters. The weighting scheme used was *w* = 1.0 for |*F*_o| ≥ 19.67, *w* = 0.5 for 0 ≤ |*F*_o| ≤ 19.67. The scattering factors for the atoms apart from hydro-

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