# The Crystal Structure and Absolute Configuration of the 2:1 Complex Between Testosterone and Mercuric Chloride

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The 2:1 complex between testosterone and mercuric chloride,  $(C_{19}H_{28}O_2)_2HgCl_2$ , was prepared by dissolving testosterone and mercuric chloride together in the minimum quantity of hot benzene. Crystallization took place in a sealed container at a constant temperature of 50 °C. The crystals are monoclinic, space group C2, with  $a=21\cdot339$ ,  $b=7\cdot784$ ,  $c=12\cdot640$  Å,  $\beta=120\cdot00^\circ$ . The crystal structure was solved from the three-dimensional Patterson and Fourier syntheses and was refined by block-diagonal least squares to R=0.064. The steroid molecules are hydrogen bonded 'head-to-tail' through the 3-oxo and 17-hydroxyl oxygen atoms. The two 17-hydroxyl groups of two steroid molecules and the two chlorine atoms, form an extremely distorted tetrahedral configuration about the mercury atom with the angle Cl-Hg-Cl equal to 165° and Hg-OH equal to 2.48 Å.

#### Introduction

The complex between testosterone and mercuric chloride was prepared during an attempt to establish methods for forming complexes between steroids and amino acids, a project which has been in progress in this laboratory as a starting point in the study of the interaction between steroids and proteins. Testosterone is a powerful androgen formed by the interstitial cells of the adult testis and is responsible for the development and growth of the male primary and secondary sex characteristics. It circulates in the blood, loosely bound to carrier proteins, and is catabolized mainly by the liver to form 17-ketosteroids which are excreted in the urine. Testosterone has been used as a drug in the treatment of testicular failure due to primary disease of the gonad or to anterior pituitary insufficiency, in the treatment of patients with disseminated breast carcinoma, in osteoporosis, and for its ability to stimulate protein synthesis.

#### **Experimental data**

The complex was prepared by dissolving together testosterone and mercuric chloride in equal molar proportions in the minimum quantity of hot benzene. The container was sealed and maintained at a constant temperature of 50 °C whereupon large, irregular, striated crystals were obtained.

Unit-cell parameters and space-group determinations were carried out on a General Electric single crystal orienter. The unit cell was found to be monoclinic and systematic X-ray extinctions were observed for all spectra with h+k=2n+1. The non-centrosymmetric space-group C2 was chosen so as to be compatible with the asymmetry of the steroid molecules. Density measurements indicated one molecule of mercuric chloride per two molecules of steroid, with two such units per unit cell. The crystal data were:  $(C_{19}H_{28}O_{2})_2HgCl_2$ ,  $M=848\cdot3$ ,  $a=21\cdot339\pm0\cdot003$ , b= $7\cdot84\pm0\cdot002$ ,  $c=12\cdot640\pm0\cdot006$  Å,  $\beta=120\cdot00\pm0\cdot05^\circ$ ,  $V_0=1818\cdot8$  Å<sup>3</sup>,  $D_m=1\cdot539\pm0\cdot011$  (by flotation), Z=2,  $D_c=1\cdot549$  g.cm<sup>-3</sup>, F(000)=860. Space group C2 ( $C_{2}^{3}$ , no. 5). Cu K $\alpha$  single-crystal diffractometry. (The equivalent body-centered unit cell has space group I2 and cell dimensions  $a=18\cdot585$ ,  $b=7\cdot784$ ,  $c=12\cdot640$  Å,  $\beta=96\cdot1^\circ$ .)

A roughly cubic crystal was selected for intensity measurements and this was ground into a sphere so that absorption of X-rays in the specimen would be uniform in all directions (no corrections were made for this absorption). The intensities of 1940 independent spectra with  $2\theta \le 140^{\circ}$  were measured on the single crystal orienter by the stationary crystal/stationary counter method, using balanced nickel/cobalt filters. The intensities were each counted for ten seconds with each filter.

Using these data, a three-dimensional Patterson synthesis was computed in which the  $|F^2|$  terms were modified by the factor  $1/f_{Hg}^2$ . The mercury atom, which lies on the twofold symmetry axis, was assigned the coordinates (000), and the chlorine atom was easily located. Owing to the domination of the phases of the structure factors by the mercury atom, and to the relatively heavy vectors between this atom and lighter ones, the Patterson synthesis could be regarded as being equivalent to the Fourier synthesis obtained using the phases due to the mercury atom at the origin, and so the thirty-two large Patterson vectors represented tentative atomic locations. By examining the distances between these 'atoms' and allowing for known

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stereochemical features of the steroid molecule, only seven atomic positions could be confirmed. A Fourier synthesis phased on the mercury, chlorine and seven atoms which were assigned carbon form factors, showed a pseudo-mirror plane at  $y=\frac{1}{2}$ , but the outline of the steroid molecule could be seen lying roughly parallel to (100) and straddling the pseudo-mirror plane. Once again using the known stereochemistry of the steroid molecule, all the remaining atoms were placed, but with some uncertainty over the positions of C(8), C(14) and C(16) which lay close to the 'mirror plane' and over the positions of atoms C(7), C(9) and C(6), C(10), the members of each pair being closely related in position by the 'mirror plane'. A set of structure factors calculated for these atoms, with an overall isotropic temperature factor of  $4 \text{ Å}^2$  gave an R value of 0.23, compared with 0.31 for the mercury and chlorine atoms alone. Four cycles of block-diagonal least-squares refinement of the positional and isotropic thermal parameters (holding the mercury atom fixed at the origin) yielded an R value of 0.18. After examination of the interatomic distances it was found that C(8) and C(14) had each been placed on the wrong side of the 'mirror plane'; however, even with all the scattering matter in

### Table 1. Positional and thermal parameters

Standard deviations, which refer to the last two digits of each number, are given in parentheses.

	x/a	y/b	z/c	B(iso)
C(1)	0.1714 (10)	0.7806 (28)	0.7981 (17)	4.56 (31)
C(2)	0.1976 (11)	0.7595 (33)	0.9358 (20)	5.32 (32)
C(3)	0.1620(10)	0.6079 (27)	0.9526 (17)	4.43 (31)
C(4)	0.1415 (8)	0.4559 (21)	0.8631 (14)	4·00 (27)
C(5)	0.1585 (7)	0.4631 (20)	0.7751 (12)	3.47 (24)
C(6)	0.1540 (10)	0.3048 (26)	0.7077 (16)	4.16 (29)
C(7)	0.1097 (11)	0.3295 (27)	0.5681 (18)	4.18 (32)
C(8)	0.1367 (5)	0.4818(29)	0.5285 (9)	2.84 (19)
C(9)	0.1372 (9)	0.6472 (21)	0.5954 (14)	3.10 (24)
C(10)	0.1852 (8)	0.6277 (22)	0.7394 (14)	3.26 (23)
C(11)	0.1597 (10)	0.8028 (30)	0.5507 (19)	5.00 (32)
C(12)	0.1135 (9)	0.8269 (26)	0.4142 (16)	4.23 (28)
C(13)	0.1171 (7)	0.6692 (21)	0.3464 (13)	3.18 (22)
C(14)	0.0913 (5)	0.5124 (28)	0.3911 (10)	2.78 (21)
C(15)	0.0819 (9)	0.3712 (28)	0.3027 (17)	4.57 (33)
C(16)	0.0542 (9)	0.4653 (30)	0.1794 (16)	5.01 (33)
C(17)	0.0618 (8)	0.6574 (23)	0.2090 (14)	3.58 (24)
C(18)	0.1940 (10)	0.6361 (28)	0.3675 (17)	4.41 (29)
C(19)	0.2643 (10)	0.6078 (29)	0.7807 (18)	4.74 (32)
O(3)	0.1507 (9)	0.5863 (27)	1.0413 (17)	6.40 (36)
O(17)	0.0799 (7)	0.7698 (20)	0.1359 (12)	4.88 (24)
Cl	0.0588 (3)	1.0399 (6)	-0.1083 (5)	8·34 (́—́)*
Hg	0.0000 ()	1.0000(-)	0·0000 ()	5·26 (—)*

are:

\* Equivalent B(iso). The anisotropic thermal parameters for the thermal motion of these atoms, in the form  $T = \exp - \left[ (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}kl + 2b_{23}hl) \times 10^{-5} \right]$ 





Fig.1. A perspective view of the complex, in the correct absolute configuration. The atoms are numbered according to the standard scheme for steroids. Interatomic distances (Å) and angles (°) have standard deviations in the ranges 0.02–0.03 Å and 1–2° respectively.

# Table 2. Comparison between the observed structure amplitudes and those calculated with use of the final atomic parameters as obtained in this analysis

The *hkl* indices listed here are for the correct absolute configuration of the molecule. The listed values of *FOBS* and *FCAL* are ten times absolute scale.

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Table 2 (cont.)

нк	L FOR	S FCAL	н	K LI	FOBS F	CAL	н	K L FI	US FCA	ь н	K L	FOBS FCA	. н	K L	FOBS	FCAL	1 8 1	FJBS	FCAL	.н	K L FO	S FCAL	. н	K L F	OBS FCA	ь н		FOBS P	FCAL	нк	L FORS	FCAL
H K 15 7 15 7 15 7 15 7 15 7 15 7 16 0 -16	L FUE -6 28 -7 29 -8 12 -9 21 -1 49 -2 51 -1 49 -2 51 -3 39 -4 44 -5 32 -6 19 -6 19	35         FCAL           18         267           33         268           155         160           11         205           150         471           100         367           25         232           100         367           100         367           100         367           100         367           100         316           100         316           100         316           100         316           100         316           100         173           100         176	H 166 -166 -166 -166 -166 -166 -166 -166	K 2-13 22-14 22-15 24 -1 15 24 -1 15 24 -1 15 24 -1 22 15 24 -1 15 22 15 24 -1 15 24 -1 25 24 -1 25 24 24 -1 25 24 24 -1 25 24 24 -1 25 24 24 -1 25 24 24 -1 25 24 24 24 -1 25 24 24 -1 25 24 24 24 -1 25 24 24 24 24 24 24 24 24 24 24 24 24 24	FD85 F 147 124 75 281 357 320 491 256 260 163 199 265 231	CAL 153 111 68 230 332 306 444 284 121 - 428 222 2225 - 277	H 17 17 17 17 17 17 17 17 17 17 17 17 17	K L FI 1 -5 1 -6 1 -7 1 -8 1 -7 1 -10 1 -10 1 -11 1 -12 1 -13 3 -1 3 -1 3 -1 3 -2 3 -2	BUS         FCA           00         30           99         13           443         35           81         48           99         28           992         28           45         12           39         2           39         2           39         2           39         2           39         2           39         2           39         2           39         2           39         2           39         2           39         2           39         2           30         2           31         27           35         29           35         27           36         27	L H 5 177 7 177 3 187 3 177 3 187 3 177 3 187 3 187 1	K L 5-12 7-3 7-5 7-5 7-6 0-1 0-1 0-2 0-3 0-4 -4	FGBS FCAI 70 77 136 177 137 177 138 127 138 127 138 127 138 120 130 277 489 43 209 20 312 274 200 160 335 311 157	H 15 15 16 16 18 18 18 18 18 18 18 18 18 18 18 18 18	X L 2-12 2-13 2-14 4 -1 4 -2 4 -3 4 -5 4 -6 4 -7 4 -9 4 -10	F085 204 126 61 234 257 265 231 267 265 261 265 261 265 261 265 261 265 261	FCAL 159 100 101 241 202 164 190 231 273 294 222 292 292 292 293 246 223	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F J85 184 152 111 230 246 246 263 158 426 158 426 245 245 190	FCAL 139 110 101 217 187 207 241 143 392 251 244 153 392 251 244	H	K L FO 0-13 1 0-13 2 0-13 2 0-2 2 0 0-2 2 0-2 2 0-2 2 0 0-2 2 0-2 2 0 0-2 2 0 0-2 2 0 0 0 0	35 FCAL 35 ID8 35 ID8 36 B4 46 B4 55 217 57 51 57 51 52 249 52 249 52 249 52 249 54 224 59 224 59 224 59 224 59 224 59 224 59 224 59 224 59 224 59 23 50 133 50 133 50 133 50 138 50 249 50 224 50 23 50 23 50 23 50 23 50 23 50 23 50 24 50 23 50 23 50 23 50 23 50 24 50 24 50 23 50 24 50 20	H 21 21 21 21 21 21 21 21 21 21 21 21 21	K L F 1 -3 1 -5 1 -5 1 -6 1 -7 1 -9 1 -10 1 -11 1 -12 1 -13 3 -1 3 -1 3 -3 3 -3	OBS         FCA           182         15           290         26           293         26           288         19           289         26           288         19           289         26           288         19           289         25           181         14           207         18           127         18           122         7           70         3           180         17           101         12           122         15           136         13           191         16	L H 222 223 225 222 222 222 222 222	K L 1 0-10 0-11 0-12 0-12 2 -12 2 -3 2 -4 2 -3 2 -4 2 -3 2 -4 2 -7 2 -8 2 -7 2 -8 2 -11	FUBS 7 46 160 161 161 161 161 161 161 160 168 190 168 190 168 190 168 2355 227 130 110	FC4L 32 142 145 122 128 201 157 146 200 189 189 104 127	H K 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	L F085 -4 185 -5 171 -5 181 -7 218 -7 218 -8 73 -9 150 10 92 -10 92 -11 92 -2 135 -3 114 -5 199 -6 213 -7 173 -8 147 -6 213 -7 19 -6 213 -7 19 -6 213 -7 19 -6 213 -7 19 -6 213 -6 19 -6 19 -7 19 -6 19 -7 19 -6 19 -7 19 -6 19 -7 19 -7 19 -6 19 -7 19 -7 19 -7 19 -6 213 -7 19 -7 19 -7 19 -6 213 -7 19 -7 19 -6 213 -7 19 -7 19 -7 19 -6 213 -7 19 -7 19 -7 19 -7 19 -7 19 -7 19 -6 213 -7 19 -7 -9 40 -10 -10 -10 -10 -10 -10 -10 -10 -10 -10	FCAL 143 158 145 145 145 145 145 145 145 113 76 113 129 113 139 139 139 139 139 139 13
16 0	-7 28	V 268	16	4-13 4-11	316 201	311 -	17	3 -3	66 16 23 14	0 18	0 -5	385 39	18	4-12	170	143	19 3-1	95	64 94	20	2-10 1.	28 143	21	3 - 5	248 19		2-12	70	51 102	24 0-	11 69	42
16 0- 16 0-	-9 46 10 42 11 44	5 442 3 380 2 400	16 16	4-12 4-13 6 3	162 75 267	161 98 255	17 17	3 -4	96 25	0 18	0 -7 0 -8	302 28	18	6 -1	190	187	19 3-19	125	100	20	2-12 2-13 2-14	0 103 88 49	21	3 -7 3 -8	163 17	22	4 -2	159	137 89	24 2 24 2 24 2	-3 115 -4 121 -5 148	129
16 0-	12 37	1 372	-16	6 -1 6 -1	210	247 237	17	3 -7	67 33 05 40	7 18	0-10 0-11	345 36	18	6 -4	224	181	19 5 -	256	214	20 20	4 0 L 4 -L 1	6 184 6 116	21	3-10 3-11	181 14 132 8	22	4 -5	190	176	24 2 24 2	-6 206	189
16 0-	14 11	8 189	16	6 - 2	274	241 182	17	3 -9 3-10	94 35 65 23	1 18	0-12 0-13	174 141	18	6 -6 6 -7	226 270	197 250	19 5 -	178	183	20	4 -2 2 4 -3 2	11 171	21	3-12	106 8 65 6	22	4 -7	162	128	24 2 24 2	-8 116	107
16 Z	-1 45	i4 369	16	8 -5	333	237	17	3-12	41 24	2 18	0-14	81 8	18	6 -8	187	199	19 5 -6	263	220	20	4 - 4 2	4 228	21	3 - 3	56 14	9 22 5 22	4-10	83 34	100 61	24 2-	10 161	123
-16 2	-1 -1	10 397	16	6 -6	339	273	17	3-13	81 7	4 18	2 0	310 25	18	6-10	98	88	19 5 -1	272	214	20	4 -0 1	15 153	21	5 - 4	158 14	5 22	4-11	85	68	24 4	-7 29	52
-16 2 ·	2 39	8 368	16	6 - 8	239	202	ii ·	5 0	40 27	3 -18	2.1	392 41	19	1 -1	288	276	19 5-10	134	140	20	4 -8 1	15 132	21	5 - 6	202 19	5 23	1 -2		54	25 1	-5 109	144
-16 2	-3 22	17 179	16	6 - 9	203	218	17	5-i i	33 20	7 18	2 - 2	319 29	-19	i -i	256	209	19 5-11	50	62	20	4 -9 1	16 151	21	5 -7	145 14	2 23	i - 3	145	138	25 1	-6 114	105
-16 2	-3 33	5 335	16	6-10	145	131 -	17	2 -1	30 20	5 -18	2 - 2	197 15	-19	1 - 2	335	287	-2, 0 0	270	262	20	4-10 1	100	21	5 -8	216 20	2 23	1.11	193	173	25 1	-7 172	176
16 2		540	17	1 0	540	494	17		70 21	5 18	523	204 24		1.15	250	220	20 0 -1	222	208	20	A-12 1	11 90		5-10	75 5		1 - 4	141	111	25 1	-0 80	
-16 2 -	-5 10	3 103	17	i -i	397	409	17	5 -3	25 27	9 -18	2 -4	106 15	19	i - i	287	265	-2 0 -	238	219	20	6 -4 · 1	13 120	-22	0 0	161 12	3 23	1 -7	217	156	25 1.	10 71	133
16 2 .	-5 24	6 221	-17	1 - i	350	330	17	5 -4 3	56 19	8 18	2 - 4	232 18	5 19	- i - i	178	200	20 5 -	237	212	δŝ	6 -5 1	54 180	22	0 - i	109 8	5 Ž3	1 -8	104	113	25 i-	-11 66	63
16 2	- 53	5 524	-17	1 -2	340	361	17	5 - 5	53 22	1 18	2 -5	392 281	19	1 -5	205	169	20 0 -	227	200	20	6 -6 1	0 178	22	0 -2	164 13	23	1 -9	212	183	25 3	-7 11	104
16 2		14 303 70 304	-17	1 -2	403	436	17		24 23	5 18	2 - 6	349 39	2 19	1 -6	380	358	23 0 -4	150	156	20	6 -7 1	8 194	22	0 -3	99 7	2 23	1-10	*2	24	25 3	-8 81	73
16 2		1 188	-17	: 3		105	12	5 - 6	84 21	2 18	5	315 27	19	1 - 7	366	373	20.0-0	182	191	21	1 0 1	4 121			222 20	2 23	1-12		60	20 0	-7 37	41
16 2-	10 31	4 291	-17	i -4	169	173	17	5 - 9	15 20	5 18	2 - 9	263 25	19	i -9	209	210	20 0 -	314	261	21	1 -1 ž	191	22	0 -6	355 39	žž	1-13	54	72	26 0	-8 67	88
16 2-	11 32	10 310	17	i -4	166	167	17 .	5-10	28 19	5 18	2-10	891 26	19	1-10	218	197	20 0 -8	258	237	-21	1 -1 2	59 236	22	ó -7	319 29	i 23	3 -2	116	142	26 0	-9 111	103
16 2-	12 18	1 176	-17	1 -5	118	151	17 :	5-ti 🗄	73 17	2 18	2-11	143 125	19	1-11	238 -	229	2.0-1	192	181	21	1 -2 1.	21 114	22	0 -8	239 23	N 23	3 - 3	125	135	26 0-	10 29	38

#### Table 3(a). Least-squares planes through the atoms

These planes are of the form lX+mY+nZ=p, where X, Y, Z and p are in Å relative to the orthogonal axes with X||a, Y||b and  $Z||c^*$ .

Plane	Atoms	1	m	n	р
A1	C(2), C(3), C(4)	0.6918	-0.4152	0.5908	2.424
A2	C(1), C(2), C(4), C(5)	0.8859	-0.2477	0.3921	0.876
A3B1	C(1), C(5), C(6), C(10)	0.6186	-0.1703	0.7671	4.875
<i>B</i> 2	C(6), C(7), C(9), C(10)	<i>−</i> 0·9837	0.1640	0.0742	2.122
<i>B</i> 3 <i>C</i> 1	C(7), C(8), C(9), C(11)	0.6845	-0.1824	0.7058	3.087
<i>C</i> 2	C(8), C(11), C(12), C(14)	-0.9877	0.1264	0.0919	1.420
C3D1	C(12), C(13), C(14), C(15)	0.7204	-0.2202	0.6577	1.495
D2	C(13), C(15), (16), C(17)	-0.9897	0.1247	0.0710	0.685
D3	C(14), C(15), C(16), C(17)	0.9721	0.0277	0.2329	0.636
A	C(1), C(2), C(3), C(4), C(5), C(10)	0.8026	-0.2662	0.5338	2.276
В	C(5), C(6), C(7), C(8), C(9), C(10)	-0.9580	0.1984	-0.2070	0.204
С	C(8), C(9), C(11), C(12), C(13), C(14)	0.9626	-0.1531	0.2234	0.090
D	C(13), C(14), C(15), C(16), C(17)	-0.9787	-0.1631	0.1251	0.358
C(1)-C(17)		0.9464	-0.1641	0.2783	0.217

the unit cell accounted for, the pseudo-mirror plane persisted very strongly. For example, a Fourier synthesis computed with any one atom removed (except the mercury or chlorine atom) always showed almost equal electron density at the supposed atomic position and at the mirror related position. This effect could be expected to influence strongly the parameters of the atoms C(7), C(9) and C(6), C(10) which appeared to be related in pairs by the 'mirror plane'. Hence, the interactions between these atoms were taken into account in the least-squares normal equations by placing the respective pairs of atoms in two separate  $(8 \times 8)$ matrix blocks instead of in individual  $(4 \times 4)$  blocks as for the other atoms. The mercury and chlorine atoms were assigned anisotropic thermal parameters in separate  $(9 \times 9)$  blocks. Five cycles of least-squares refinement were now carried out with weights allotted as  $1/(13 - 0.4|F_o| + 0.01|F_o|^2)$ , derived so that the values of  $\langle |w\Delta^2| \rangle$  remained invariant with the magnitude of  $\langle |F_{o}| \rangle$ . Refinement ceased with R = 0.068. It is interesting to note that a structure factor calculation for the mercury and chlorine atoms alone, each atom having anisotropic thermal parameters, gave an R value of

0.19. During all the refinement so far the scattering factors for mercury had been corrected for the real part of the anomalous dispersion correction only  $(\Delta f' = 4.8)$ . The last three cycles of refinement were now repeated, first with the imaginary anomalous dispersion correction positive, and again with it negative  $(\Delta f'' = 7.0$  for Cu Ka), which was equivalent to refining separately the two possible absolute configurations of the structure. The refinement using  $\Delta f''$  negative appeared to be the better of the two, the minimization functions ( $\Sigma w \Delta^2 / [m-n]$ ) and the R indices ( $\Sigma ||F_0| |F_c|/\Sigma |F_o|$  for the negative and positive cases being respectively 9.10, 10.19, 0.064 and 0.072. Hence the absolute configuration of the molecule was taken as that obtained using  $\Delta f'' = -7.0$ ; that is, the atomic coordinates should be converted to  $\bar{x}\bar{y}\bar{z}$ . However, examination of the geometry of the diffractometer showed that the spectra had been indexed with respect to a left-handed set of reciprocal axes, so that the indexing must be changed to hkl, and in order to be compatible with the configuration as already determined, the correct absolute configuration of the structure is given by the original set of xyz, together with the

altered indexing  $h\bar{k}\bar{l}$ . The configuration so obtained agrees with that normally found in naturally occurring steroids. A perspective view of the complex in the correct configuration is given in Fig. 1.

The final atomic parameters for the correct absolute configuration, in a right-handed coordinate system, are given in Table 1, along with standard deviations obtained from the inverses of the full least-squares normal equations blocks for each atom. Table 2 lists the comparison between the observed and calculated structure amplitudes for all measured reflections (all reflections were used in the least-squares refinement, irrespective of the observed magnitudes of their intensities). In this Table, the signs of the indices hkl have been changed as described above, so that the correct absolute configuration of the molecule is given thereby.

#### Description of the steroid molecules

With the exception of the Hg–Cl bond, the standard deviations of all interatomic distances and angles lie in the ranges 0.02–0.03 Å and 1–2° respectively. With these observed errors, none of the bond distances differ significantly from their normally expected values. The distances found for bonds C(4)–C(5) and C(3)–O(3) are consistent with their chemically established double bond characters. The bond angles in rings A, B and C are generally larger than expected for tetrahedral carbon atoms, but are in accord with similar angles found in other steroids (Norton, 1965). The enlargement of the angle C(2)–C(1)–C(10) to 115° assists in relieving the strain imposed on ring A by the  $\Delta^{4,5}$  bond. The bond distances and angles are summarized in Fig.1.

Rings *B*, *C* and *D* are *trans* fused. Rings *B* and *C* have normal configurations and are chair shaped, but ring *A* is distorted by the double bond between atoms C(4) and C(5), which also affects the A/B ring junction. The dihedral angles at the junctions of rings *B*, *C* and *D* are in the region of 130° whereas that at the A/B junction is 125°; however, the A/B junction itself retains its planarity [see Table 3(b)]. The conjugated

system O(3)=C(3)-C(4)=C(5)-C(6) is, with the exception of C(4) which lies 0.15 Å out of the plane, planar to within 0.04 Å. Atom C(10) also lies in this plane. Ring D is a  $\beta$ -envelope and has normal configuration with atoms C(14), C(15), C(16) and C(17) planar to within 0.04 Å. The 17-hydroxyl group has the  $\beta$ -configuration with a torsional angle C(18)-C(13)-C(17)-OH of 54°.

Fable 3(b). Interplanar and	zles
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Planes	Angle
A/B	134°
B/C	177
C/D	174
A1/A2	161
A2/A3B1	153
B2/A3B1	125
<i>B</i> 2/ <i>B</i> 3 <i>C</i> 1	131
C2/B3C1	129
C2/C3D1	133
D2/C3D1	134
C(1)-C(17)/(100)	19
C(1)-C(17)/(010)	100
C(1)-C(17)/(001)	74

The steroid nucleus has been analysed in terms of the usual least-squares planes and interplanar angles and these are summarized in Table 3. The torsional angles in the steroid nucleus are summarized in Table 4.

#### Coordination of the mercury atoms

The mercury atom is positioned on a twofold symmetry axis with the Hg–Cl bond at  $82.5^{\circ}$  to this axis. That is, the mercuric chloride molecule, instead of being linear, is bent to give a Cl–Hg–Cl angle of 165°. The 17-hydroxy oxygen atom is 2.48 Å from the mercury atom with an OH–Hg–OH angle of 87°. The plane of these last three atoms is nearly perpendicular to the Cl–Hg–Cl plane (92°), so that the hydroxyl groups from two steroid molecules and the two chlorine atoms form a very distorted tetrahedral configuration about the mercury atom (Figs. 1, 2 and 3). This

Table 3(c). Deviations (Å) from the least-squares planes

C(1) C(2) C(3)	A = -0.34 = 0.26 = -0.03	В	С	D	A2 - 0.18 0.17 - 0.23	A3B1 0·07	<i>B</i> 2	<i>B</i> 3 <i>C</i> 1	C2	C3D1	D2	D3	C(1)-C(17) -0.10 0.06 -0.52
C(4) C(5) C(6) C(7)	-0.13 0.08	-0.21 0.20 -0.22			-0.21 0.22	0·08 -0·07	0·59 0·01 -0·01	-0.02					-0.48 0.12 0.43 -0.09
C(8) C(9) C(10)	0.16	0.25 - 0.25 0.22	$0.22 \\ -0.21$		0.45	0.06	-0.66 0.01 -0.01	0·02 0·02	0·01 0·64				0.38 - 0.02 0.55
C(11) C(12) C(13) C(14)			$0.23 \\ -0.25 \\ 0.26 \\ -0.25$	0·29 0·27				-0.05	-0.01 0.01 -0.72 -0.01	-0.07 0.08 0.07 -0.07	-0.07 0.63	0·69 -0·04	$ \begin{array}{r} 0.37 \\ -0.20 \\ 0.28 \\ -0.18 \end{array} $
C(15) C(16)				0·14 0·04 0·19							0·07 -0·12 0·12	0·06 0·06 0·04	$0.07 \\ -0.24 \\ -0.42$

# Table 4. Torsional angles in the rings

 $\varphi_{A-B}$  is the torsional angle about the A-B bond, in which the other two atoms required to define the angle are those attached to either end of the bond and are in the ring in question.

A ring		B ring		C ring		D ring	
Bond	$\varphi_{A-B}^*$	Bond	<i>Ф</i> А-В	Bond	Фа-в	Bond	<i>Ф</i> А-в
C(1) - C(2)	- 58	C(5) - C(6)	- 52	C(8) - C(9)	-52	C(13) - C(14)	+47
C(2) - C(3)	+31	C(6) - C(7)	+ 52	C(9) - C(11)	+55	C(14) - C(15)	-35
C(3) - C(4)	+2	C(7) - C(8)	- 55	C(11) - C(12)	- 58	C(15) - C(16)	+9
C(4) - C(5)	-12	C(8) - C(9)	+ 58	C(12) - C(13)	+ 58	C(16) - C(17)	+20
C(5) - C(10)	-13	C(9) - C(10)	- 52	C(13) - C(14)	- 59	C(13)-C(17)	-40
C(10) - C(1)	+49	C(10) - C(5)	+ 52	C(8) - C(14)	+ 56		

\* The sign convention for the direction of the torsional angle is that of Klyne & Prelog (1960).



Fig.2. Projection onto the plane (010) of the unit cell. The hydrogen bonding between the steroid molecules is indicated by the dotted lines between the 17-hydroxyl oxygen (○) and the 3-one oxygen (●) atoms.



Fig. 3. Projection onto the plane (001) of the unit cell, showing the distorted tetrahedral environment of the mercury atoms and the staggered bilayer packing of the steroid molecules.

tetrahedral coordination to the mercury atom is more distorted than that found in other similar examples (e.g. bis(triphenylarsine oxide)mercuric chloride, in which the angles Cl-Hg-Cl and O-Hg-O are 147° and 93° and the distance Hg-O is 2.35 Å) (Brändén, 1963).

The Hg–Cl bond length of  $2.296 \pm 0.006$  Å falls within the range of distances observed by other investigators between these two atoms (2.20-2.34 Å) but the Hg–O distance of  $2.48 \pm 0.02$  Å is significantly greater than the range of observed covalent bond lengths for mercury and oxygen (2.03-2.28 Å), (Grdenic, 1965). The observed distance is however, significantly less than the sum of the van der Waals radii of these two atoms (2.9 Å), which indicates that some form of bonding exists between them.

# Packing of the molecules

The steroid molecules are hydrogen bonded 'head-to tail' via the 3-keto and 17-hydroxyl groups, the OH····O distance and the C(17)-OH····O(3) angle

Tal	ble	5.	Intermol	'ecular	distances	less	than	4·0	Å	٢
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Contact	Position*	Distance
Cl - C(1)	1/001	3·75 Å
Cl - C(2)	1/00T	3.49
Cl - C(3)	1/00T	3.88
ClC(4)	1/01T	3.79
Cl - C(15)	2/010	3.79
Cl——C(16)	2/010	3.93
O(1) - C(3)	1/001	3.75
O(1)O(2)	1/00T	2.75
O(2) - C(16)	1/001	3.43
O(2) - C(17)	1/001	3.53
O(2) - C(18)	1/001	3.77
C(4) - C(16)	2/001	3.94
C(11)-C(18)	3/001	3.78

\* Equivalent position nomenclature: the symbol  $1/01\overline{1}$  is taken to mean that the second atom mentioned in the contact is in the molecule at equivalent position 1, translated 0, 1 and -1 unit cells in the **a**, **b** and **c** directions respectively. The equivalent positions are  $1 = (x, y, z); \ 2 = (\bar{x}, y, \bar{z}); \ 3 = (\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}).$ 

being 2.75 Å and 110° respectively. A very interesting point is that the angle Hg-OH···O is 113°, indicating that the environment of the hydroxyl oxygen atom is almost tetrahedral, as for example, in ice (Peterson & Levy, 1957). The steroid molecules are approximately planar and lie almost parallel to the (100) face of the crystal, with the hydrogen bonded molecules stacked in pairs 'bottom-to-bottom' along the twofold symmetry axes. The layers, which include the mercuric chloride molecules, are propagated through the unit cells by means of the  $2_1$  axes which translate them so as to minimize interference between adjacent methyl groups (Fig. 3). This packing is similar to that found in 4-bromoestrone (Norton, Kartha & Lu, 1963).

Apart from the hydrogen bonding, there are only thirteen intermolecular distances less than 4.0 Å (Table 5). Eleven of these are between chlorine atoms and rings A and D, and between O(3) and ring D. There are, in addition, twenty-seven longer 'contacts' in the range 4.0-4.5 Å between molecules related by the twofold axes and between methyl groups of one molecule and the ring system of the  $2_1$  related molecules.

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