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Oxido Steroids. III. X-ray Structure Analysis of 5α-Bromo-6β,19-oxido-pregnan-3β-ol-20-one

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The crystal and molecular structure of the steroid 5α-bromo-6β,19-oxido-3β-hydroxy-pregnan-20-one, $C_{21}H_{31}O_3Br$, has been determined by X-ray diffraction methods. The steroid crystallizes in the orthorhombic space group $P2_12_12_1$ with two molecules in the asymmetric unit, and with unit-cell dimensions $a=14{\cdot}123$, $b=39{\cdot}519$ and $c=6{\cdot}925$ Å. The positional and thermal parameters of all atoms, including hydrogens, have been refined using the intensity data from 4475 independent reflections, to a final R index of 6·5%. Rings *A*, *B* and *C* are chair-shaped, and the *D* ring is a slightly distorted β-envelope. The 6β,19-oxido bridge has subjected the *A* ring to a certain amount of strain, causing the ring to be rotated by about 5° from the mean plane of the steroid nucleus. The 3-hydroxyl group of molecule 1 of the asymmetric unit acts both as a proton donor and as a proton acceptor in forming hydrogen bonds with two molecules of the second type.

Introduction

The presence of an oxido bridge between C(6) and C(19) imposes a certain amount of distortion in the nucleus of the steroid, 5α-bromo-6β,19-oxido-3β-hydroxy-pregnan-20-one ($C_{21}H_{31}O_3Br$). The present structure analysis was undertaken as a continuation of our study of steroid nuclear distortion. Fig. 1 is a schematic representation of the molecule showing its main stereochemical features and the numbering which will be used in the text to identify the atoms.

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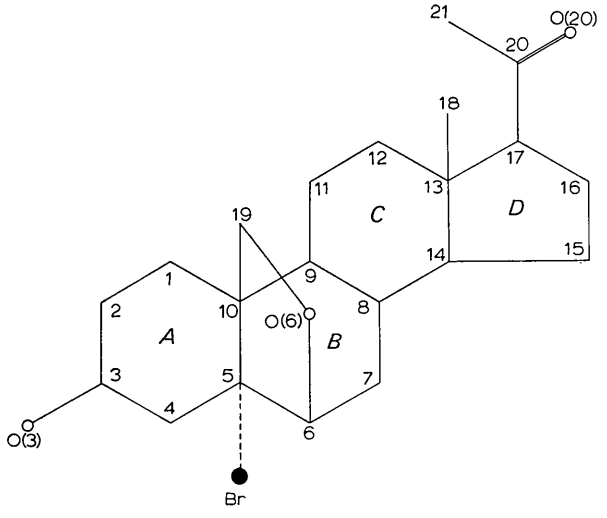


Fig. 1. 5α-Bromo-6β,19-oxido-pregnan-3β-ol-20-one. Schematic drawing of the molecule with atoms numbered for reference in the text.

Experimental

Crystals of 5α-bromo-6β,19-oxido-3β-hydroxy-pregnan-20-one were grown from a solution in a mixture of isopropanol and hexane. The crystals were acicular, elongated along the *c*-axis, with the (110) face dominating. A specimen of length 0·25 mm was cut from a longer crystal, of cross-sectional dimensions 0·18 × 0·24 mm. All X-ray measurements were made on a General Electric single crystal diffractometer with Cu $K\alpha$ radiation. The crystal was mounted with its *b* axis parallel to the φ axis of the Eulerian cradle.

The observed systematic extinctions ($h00$, $0k0$ and $00l$ for h, k and l odd) placed the crystal in the orthorhombic space group $P2_12_12_1$. The unit-cell dimensions obtained from a least-squares refinement of 40 observations of 2θ are $a=14{\cdot}121\pm0{\cdot}002$, $b=39{\cdot}380\pm0{\cdot}008$ and $c=6{\cdot}924\pm0{\cdot}001$ Å (measured at 20°C; Cu $K\alpha_1=1{\cdot}54051$ Å). There are eight molecules in the unit cell, and hence two molecules in the asymmetric unit. The crystal density, determined by flotation in an aqueous solution of potassium iodide, is 1·416 g.cm^{-3}, compared with a calculated density of 1·420 g.cm^{-3}.

Intensities of 4475 reflections with 2θ less than 148° were measured by the stationary-crystal stationary-counter technique with balanced nickel and cobalt filters. Each reflection was measured for ten seconds with each filter. Of the 4475 measured intensities, 272 were found to be less than twice their estimated standard deviations, and were omitted from the refinement of the structure. The observed structure amplitudes were scaled by Wilson's (1942) method; the scale factor thus found increased by 6% during the least-squares refinement of the structure.

Table 1. *Comparison of the observed structure amplitudes with those calculated from the refined atomic parameters*

The values of *F*OBS and *F*CAL are given on ten times absolute scale.

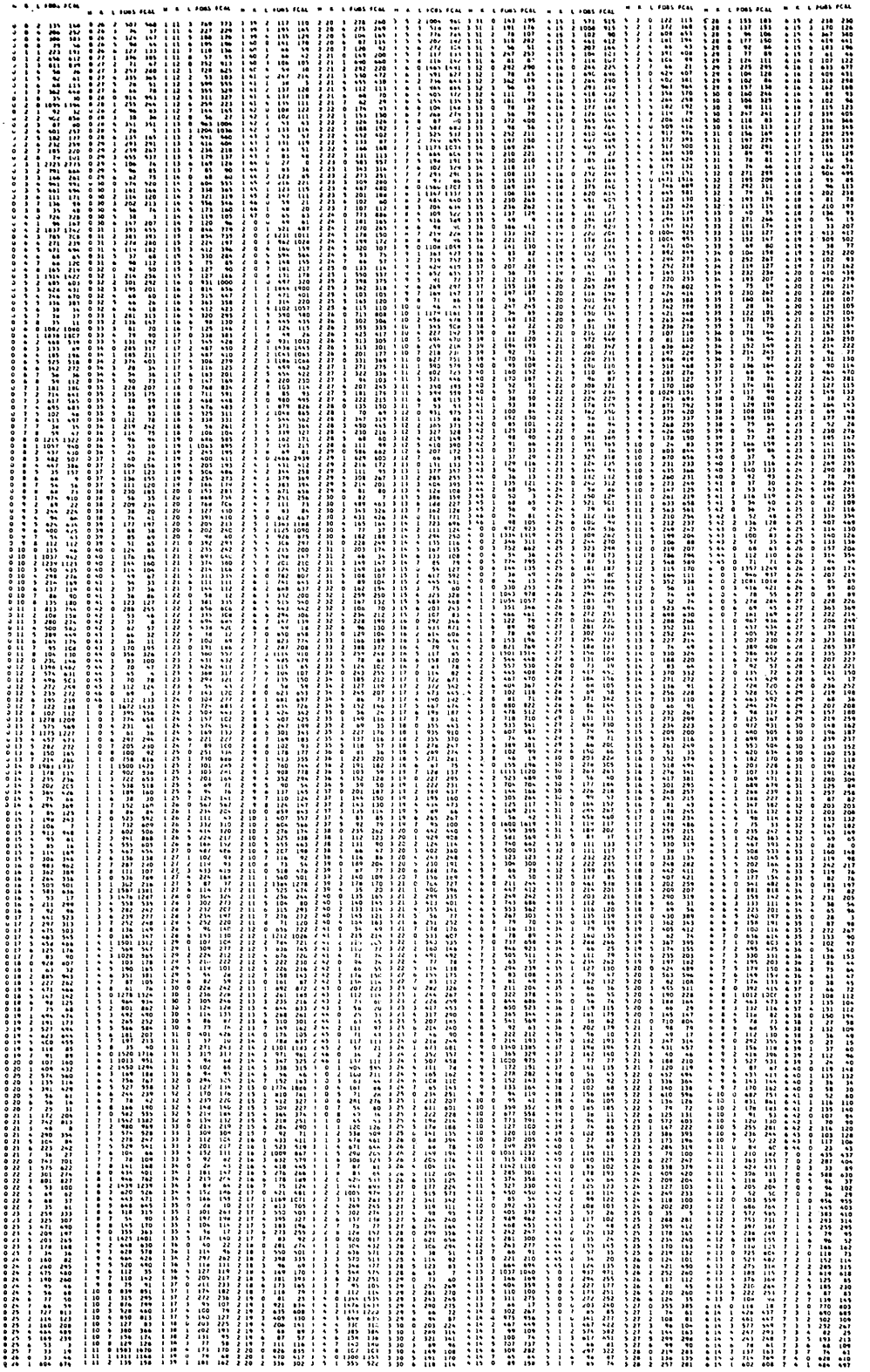
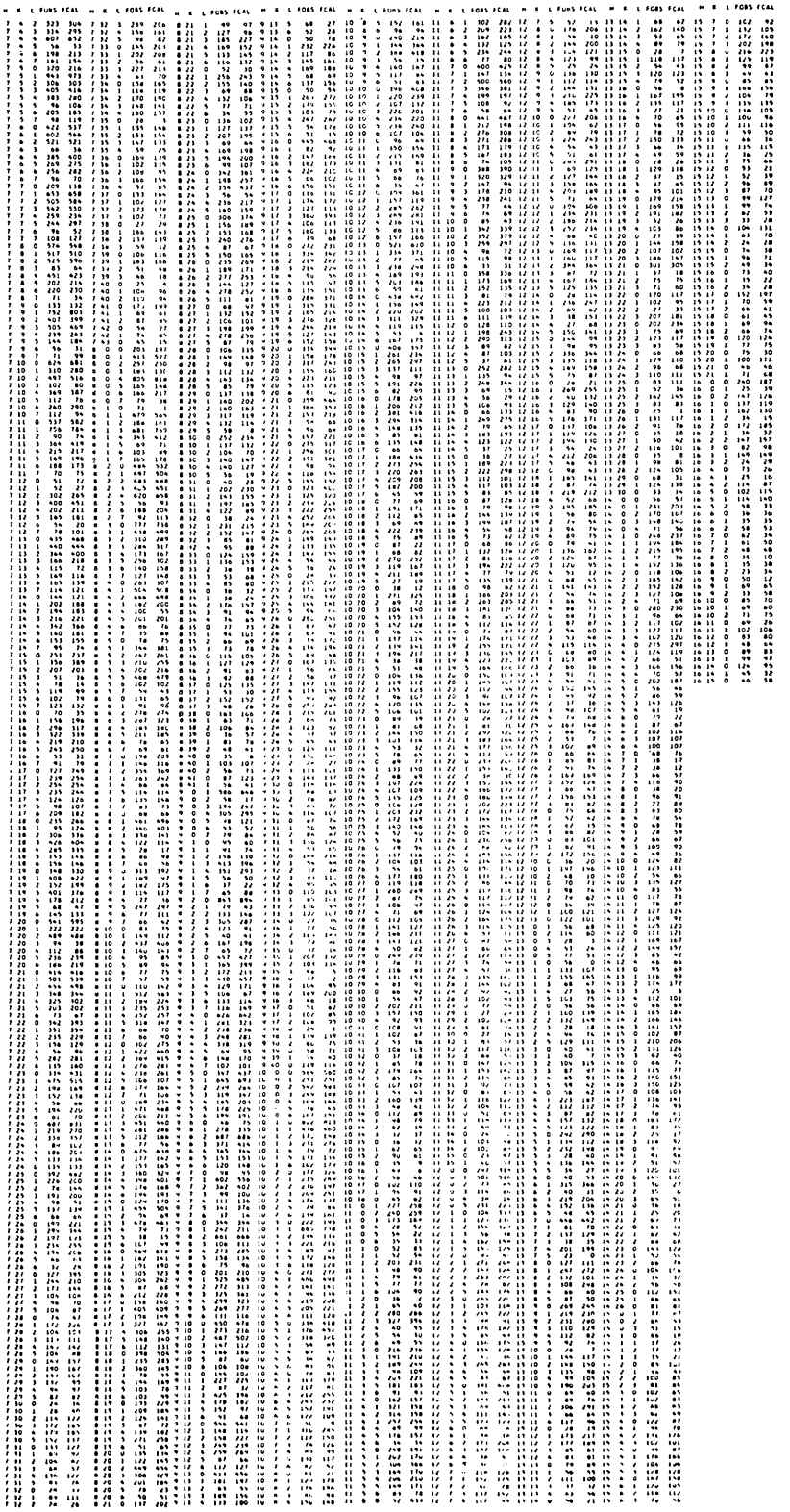


Table 1 (*cont.*)



Structure analysis

The positions of the two bromine atoms in the asymmetric unit were located from a three-dimensional sharpened Patterson map which was computed using the squared unitary structure factor amplitudes.

Calculation of structure factors with the contributions from the two bromine atoms alone gave an R index of 37%, and a three-dimensional Fourier synthesis computed with the phases obtained in this structure factor calculation contained fifty-five additional peaks with heights nearly equal to those to be expected for carbon and oxygen atoms. When carbon atoms were assumed in place of all the above fifty-five peaks, and a difference Fourier synthesis was calculated, ten of the fifty five 'atoms' turned out to be spurious and the map contained five additional peaks. This set of positions gave a model compatible with the presumed stereochemistry of the molecule, in which all the atoms could be identified. The model was refined by least-squares,* with a block-diagonal approximation to the normal equations, with 9×9 blocks for the two bromine atoms, corresponding to the three positional and six anisotropic thermal parameters, and 4×4 blocks for the carbon and oxygen atoms, corresponding to the three positional and one isotropic thermal parameter. The R index after four cycles of refinement was 10·7%. The scattering factors for all atoms were obtained from *International Tables for X-ray Crystallography* (1962).

Thus far in the refinement, $\Delta f''_{Br}$ the imaginary part of the anomalous dispersion factor was omitted and only the real part, $\Delta f'_{Br}$, was taken into account. At this stage, to determine the absolute configuration of the molecule, two sets of structure factors were calculated, one with $\Delta f''_{Br}=+1{\cdot}46$ and another with $\Delta f''_{Br}=-1{\cdot}46$. The former gave an R index of 10·3%, whereas the latter gave 10·7%. This confirmed that the configuration of the molecule hitherto assumed in our model was the correct and absolute one. (According to Hamilton (1965), a difference in R factor of less than 0·1% is sufficient to justify explicit selection when only one variable parameter is concerned, and the data from 4475 reflections are used.)

When anisotropic temperature factors were used for all atoms and four cycles of least-squares refinement

* Quantity minimized: $\Sigma w(|F_o|-|F_c|)^2$. Weighting scheme: $\sqrt{w}=1$ if $|F_o|<20$, $\sqrt{w}=20/|F_o|$ otherwise.

Table 2(*a*). *Positional and thermal parameters of the non-hydrogen atoms, at the end of the least-squares refinement.*

The atoms of the two molecules are distinguished by the prefixes 1 and 2 respectively. Thermal parameters are listed in the form $\exp\{-2\pi^2(U_{11}h^2a^{*2}+2U_{12}hka^*b^*+\ldots)\}$.

	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
1C 1	0.29040(74)	0.06744(24)	0.2353 (13)	0.0699(66)	0.0558(56)	0.0378(52)	0.0172(49)	-0.0191(51)	-0.0095(45)
1C 2	0.38565(73)	0.08008(24)	0.1700 (14)	0.0650(61)	0.0578(55)	0.0460(58)	0.0019(50)	-0.0086(57)	0.0084(51)
1C 3	0.39247(79)	0.11784(24)	0.1763 (16)	0.0759(70)	0.0604(56)	0.0509(62)	0.0074(53)	-0.0193(64)	0.0106(55)
1C 4	0.36748(79)	0.13180(25)	0.3785 (14)	0.0845(72)	0.0555(57)	0.0436(55)	-0.0049(54)	-0.0226(57)	0.0183(48)
1C 5	0.27304(78)	0.11932(23)	0.4509 (13)	0.0878(73)	0.0441(50)	0.0377(55)	0.0085(50)	-0.0254(55)	-0.0050(44)
1C 6	0.26003(91)	0.12411(25)	0.6688 (15)	0.1132(90)	0.0540(59)	0.0432(61)	0.0015(61)	-0.0183(68)	-0.0054(53)
1C 7	0.16078(92)	0.11792(23)	0.7370 (15)	0.1126(93)	0.0469(50)	0.0510(65)	0.0089(59)	-0.0106(71)	-0.0121(49)
1C 8	0.13149(77)	0.08057(23)	0.6983 (15)	0.0798(69)	0.0459(51)	0.0467(54)	0.0052(50)	-0.0068(59)	-0.0132(51)
1C 9	0.15690(70)	0.07040(21)	0.4874 (14)	0.0747(64)	0.0431(48)	0.0397(49)	0.0024(47)	-0.0055(59)	-0.0095(46)
1C10	0.25818(72)	0.08033(21)	0.4313 (13)	0.0722(63)	0.0365(48)	0.0406(53)	0.0119(47)	-0.0152(50)	-0.0014(42)
1C11	0.13544(78)	0.03272(23)	0.4556 (15)	0.0784(69)	0.0507(54)	0.0473(64)	-0.0047(50)	-0.0044(58)	-0.0100(49)
1C12	0.03202(71)	0.02300(25)	0.5137 (16)	0.0700(64)	0.0646(61)	0.0505(59)	-0.0007(51)	-0.0001(64)	-0.0114(58)
1C13	0.00906(71)	0.03414(23)	0.7205 (14)	0.0649(60)	0.0556(53)	0.0475(58)	0.0122(48)	-0.0040(56)	-0.0021(50)
1C14	0.03042(77)	0.07292(24)	0.7383 (14)	0.0795(72)	0.0543(56)	0.0446(57)	0.0188(52)	0.0032(56)	-0.0047(48)
1C15	-0.01468(87)	0.08162(27)	0.9378 (15)	0.0959(81)	0.0663(68)	0.0455(61)	0.0245(64)	0.0104(62)	-0.0012(54)
1C16	-0.10107(90)	0.05871(29)	0.9550 (16)	0.0904(82)	0.0867(79)	0.0508(68)	0.0263(67)	0.0001(67)	0.0027(61)
1C17	-0.09625(80)	0.03375(25)	0.7781 (16)	0.0803(74)	0.0619(60)	0.0539(66)	0.0165(56)	-0.0013(64)	0.0072(56)
1C18	0.06578(92)	0.01246(28)	0.8687 (17)	0.0920(83)	0.0706(68)	0.0655(73)	0.0298(67)	-0.0127(72)	0.0073(59)
1C19	0.32796(86)	0.06966(23)	0.5991 (14)	0.0940(79)	0.0488(53)	0.0408(53)	0.0000(58)	-0.0286(63)	-0.0034(46)
1C20	-0.13872(89)	0.00023(32)	0.8227 (21)	0.0829(82)	0.0889(85)	0.0887(92)	0.0286(70)	0.0200(80)	0.0354(80)
1C21	-0.15373(98)	-0.02478(33)	0.6535 (22)	0.1045(98)	0.0942(90)	0.1029(97)	-0.0200(80)	-0.0195(93)	0.0074(85)
10 3	0.48557(58)	0.12962(18)	0.1214 (11)	0.0877(56)	0.0715(45)	0.0603(46)	-0.0030(43)	-0.0078(46)	0.0216(39)
10 6	0.32294(59)	0.09761(16)	0.7382 (9)	0.1063(57)	0.0639(40)	0.0409(38)	-0.0085(43)	-0.0212(44)	-0.0035(32)
1020	-0.15084(78)	-0.01035(23)	0.9834 (16)	0.1605(89)	0.0918(60)	0.1016(71)	0.0203(62)	0.0347(83)	0.0253(62)
1BR	0.17642(10)	0.14583(2)	0.3036 (1)	0.1008(8)	0.0542(5)	0.0538(5)	0.0183(6)	-0.0125(7)	0.0062(5)
2C 1	0.33288(77)	0.24857(23)	-0.0821 (13)	0.0663(66)	0.0534(53)	0.0411(51)	-0.0109(53)	0.0006(54)	-0.0015(45)
2C 2	0.36331(71)	0.21298(23)	-0.1459 (15)	0.0699(61)	0.0486(52)	0.0537(65)	0.0006(49)	0.0174(56)	-0.0003(52)
2C 3	0.46845(78)	0.20861(26)	-0.1325 (14)	0.0748(71)	0.0688(64)	0.0476(59)	0.0095(56)	0.0080(56)	0.0136(53)
2C 4	0.50693(75)	0.21583(27)	0.0687 (14)	0.0686(65)	0.0772(68)	0.0453(57)	0.0172(60)	0.0031(53)	0.0178(56)
2C 5	0.47718(74)	0.25164(25)	0.1346 (14)	0.0626(64)	0.0656(60)	0.0406(56)	-0.0085(52)	-0.0017(52)	0.0197(49)
2C 6	0.48959(76)	0.25578(29)	0.3559 (15)	0.0588(63)	0.0875(76)	0.0420(61)	0.0058(59)	-0.0026(55)	0.0132(58)
2C 7	0.47591(73)	0.29263(27)	0.4239 (14)	0.0585(61)	0.0870(72)	0.0415(57)	0.0023(56)	-0.0143(52)	0.0043(54)
2C 8	0.37443(68)	0.30436(25)	0.3792 (13)	0.0539(55)	0.0683(60)	0.0313(48)	-0.0123(48)	-0.0043(47)	0.0054(47)
2C 9	0.34995(64)	0.29715(23)	0.1639 (13)	0.0456(54)	0.0606(54)	0.0383(51)	-0.0131(44)	-0.0038(47)	0.0089(45)
2C10	0.37154(64)	0.25930(22)	0.1162 (12)	0.0483(52)	0.0462(49)	0.0348(49)	-0.0073(43)	0.0066(45)	0.0044(43)
2C11	0.24848(70)	0.30779(22)	0.1161 (14)	0.0572(58)	0.0509(51)	0.0421(55)	-0.0004(47)	-0.0096(51)	0.0027(46)
2C12	0.22724(72)	0.34509(22)	0.1681 (13)	0.0687(62)	0.0533(56)	0.0352(53)	-0.0071(48)	-0.0093(51)	-0.0015(46)
2C13	0.25077(70)	0.35078(24)	0.3876 (13)	0.0606(59)	0.0550(56)	0.0364(50)	-0.0155(51)	0.0038(48)	-0.0051(49)
2C14	0.35336(68)	0.34144(25)	0.4208 (13)	0.0570(59)	0.0643(59)	0.0407(53)	-0.0126(48)	-0.0070(49)	-0.0003(47)
2C15	0.37506(83)	0.35527(30)	0.6216 (13)	0.0787(76)	0.0908(76)	0.0299(49)	-0.0160(68)	-0.0008(55)	-0.0067(57)
2C16	0.31319(91)	0.38766(29)	0.6377 (16)	0.0903(84)	0.0823(74)	0.0551(67)	-0.0255(69)	0.0089(70)	-0.0132(60)
2C17	0.24983(68)	0.38834(23)	0.4513 (14)	0.0571(54)	0.0584(57)	0.0441(58)	-0.0124(47)	0.0061(50)	-0.0068(48)
2C18	0.18048(80)	0.33061(26)	0.5124 (15)	0.0803(70)	0.0740(66)	0.0438(56)	-0.0132(61)	0.0152(71)	0.0143(56)
2C19	0.33476(76)	0.23593(25)	0.2792 (14)	0.0642(65)	0.0685(60)	0.0469(57)	-0.0010(55)	0.0056(60)	0.0201(52)
2C20	0.15444(90)	0.40356(26)	0.4740 (19)	0.0926(87)	0.0653(64)	0.0849(86)	-0.0165(62)	0.0262(84)	-0.0195(67)
2C21	0.10568(98)	0.41711(34)	0.2908 (22)	0.1019(97)	0.0913(90)	0.0973(96)	0.0146(81)	-0.0196(95)	-0.0196(88)
20 3	0.49378(56)	0.17400(17)	-0.1885 (11)	0.1008(55)	0.0705(45)	0.0545(45)	0.0250(42)	0.0223(49)	0.0061(42)
20 6	0.41166(55)	0.23546(18)	0.4204 (9)	0.0860(54)	0.0788(47)	0.0375(37)	0.0053(41)	0.0094(38)	0.0215(35)
2020	0.11076(68)	0.40315(20)	0.6238 (13)	0.1144(68)	0.0839(53)	0.0850(61)	-0.0122(50)	0.0476(58)	-0.0149(49)
2BR	0.56018(7)	0.28416(3)	-0.0090 (1)	0.0541(5)	0.0917(7)	0.0594(6)	-0.0113(6)	0.0047(6)	0.0232(7)

Table 2(*b*). *Positional and isotropic thermal parameters for the hydrogen atoms*

	Molecule 1				Molecule 2			
	x/a	*y/b*	*z/c*	*B*	*x/a*	*y/b*	*z/c*	*B*
H(1*A*)	0·239	0·070	0·155	3·5	0·344	0·264	−0·200	5·3
H(1*B*)	0·295	0·042	0·258	2·3	0·257	0·249	−0·089	0·2
H(2*A*)	0·391	0·067	0·038	4·4	0·337	0·205	−0·259	5·3
H(2*B*)	0·440	0·073	0·236	5·1	0·323	0·198	−0·066	3·5
H(3*A*)	0·344	0·125	0·106	3·5	0·501	0·222	−0·239	3·7
H(4*A*)	0·374	0·161	0·368	3·5	0·587	0·212	0·097	3·5
H(4*B*)	0·415	0·125	0·454	4·1	0·468	0·199	0·145	2·1
H(6*A*)	0·292	0·150	0·706	3·5	0·559	0·249	0·400	3·0
H(7*A*)	0·100	0·130	0·658	3·5	0·529	0·309	0·381	3·5
H(7*B*)	0·159	0·119	0·879	3·5	0·483	0·293	0·559	3·5
H(8*B*)	0·173	0·065	0·800	3·5	0·332	0·286	0·468	3·7
H(9*A*)	0·120	0·083	0·400	3·5	0·391	0·313	0·070	2·0
H(11*A*)	0·156	0·027	0·316	8·0	0·238	0·308	−0·010	3·5
H(11*B*)	0·188	0·019	0·514	9·6	0·195	0·293	0·190	4·9
H(12*A*)	−0·022	0·033	0·420	3·5	0·273	0·362	0·104	2·6
H(12*B*)	0·022	−0·004	0·522	3·5	0·155	0·352	0·150	3·0
H(14*A*)	−0·010	0·083	0·650	3·5	0·391	0·353	0·325	3·0
H(15*A*)	−0·033	0·103	0·953	5·2	0·447	0·361	0·619	3·5
H(15*B*)	0·039	0·078	1·037	3·5	0·357	0·338	0·719	2·7
H(16*A*)	−0·168	0·071	0·945	3·5	0·357	0·410	0·639	5·8
H(16*B*)	−0·097	0·045	1·083	4·5	0·265	0·389	0·743	5·5
H(17*A*)	−0·144	0·036	0·706	6·8	0·276	0·404	0·376	4·2
H(18*A*)	0·137	0·015	0·855	5·9	0·193	0·336	0·637	3·5
H(18*B*)	0·053	−0·012	0·846	2·8	0·123	0·341	0·479	3·6
H(18*C*)	0·037	0·017	1·014	3·5	0·189	0·303	0·470	5·5
H(19*A*)	0·302	0·044	0·670	3·5	0·323	0·212	0·225	3·0
H(19*B*)	0·398	0·068	0·525	3·5	0·273	0·246	0·350	3·0
H(21*A*)	−0·211	−0·037	0·704	3·5	0·151	0·431	0·222	6·2
H(21*B*)	−0·099	−0·040	0·620	3·5	0·045	0·432	0·326	3·5
H(21*C*)	−0·173	−0·014	0·553	6·0	0·080	0·400	0·222	3·5
H(22)	0·554	0·125	0·227	7·7	0·481	0·156	−0·104	5·3

Table 3. *Torsional angles in the rings*

$\theta(A–B)$ 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	$\theta(A–B)$*	Bond	$\theta(A–B)$*	Bond	$\theta(A–B)$*	Bond	$\theta(A–B)$*
C(1)–C(2)	−53·1†	C(5)–C(6)	−68·0	C(8)—C(9)	−57·3	C(13)–C(14)	46·9
	−51·8		−67·3		−53·9		46·9
C(2)–C(3)	54·7	C(6)–C(7)	62·6	C(9)—C(11)	52·8	C(14)–C(15)	−33·8
	56·2		62·2		54·4		−32·9
C(3)–C(4)	−53·0	C(7)–C(8)	−47·9	C(11)–C(12)	−53·3	C(15)–C(16)	7·5
	−55·4		−51·1		−55·4		6·3
C(4)–C(5)	48·2	C(8)–C(9)	47·9	C(12)–C(13)	54·3	C(16)–C(17)	22·1
	51·2		52·1		57·5		21·6
C(5)–C(10)	−44·4	C(9)–C(10)	−59·1	C(13)–C(14)	−60·5	C(13)–C(17)	−42·3
	−47·0		−64·2		−62·5		−41·5
C(1)–C(10)	46·6	C(5)–C(10)	64·3	C(8)—C(14)	62·0		
	46·8		67·6		59·9		

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

† These values are given with those for molecule 1 above those for molecule 2.

were carried out, the *R* index dropped to 8·5%. Two successive difference Fourier syntheses located all sixty-two hydrogen atoms. Because of the limited core-storage of the computer used in the refinement (an IBM 7040, with 32K core), further refinement was carried out alternately for the positions and temperature factors of sixty hydrogen atoms in one cycle, and for the positions and temperature factors of the remaining fifty-two atoms in the next cycle. The final *R* index obtained after four cycles of refinement was 6·5%, at which time the calculated shifts were less than one third of their respective estimated standard deviations. Table 1 lists the observed and calculated structure amplitudes. The final atomic parameters are listed in Table 2(*a*) and (*b*).

Description of the molecular structure

Bond lengths and bond angles

Bond lengths and angles not involving hydrogen atoms are shown in Fig. 2(*a*) and (*b*), respectively. The average deviations of individual bond lengths and an-

gles from the mean values calculated for equivalent bonds and angles in the two molecules are 0·011 Å and 0·7°, respectively.* The C–O and C–Br bond lengths agree well with those found in similar structures (Gopalakrishna, Cooper & Norton, 1969; *International Tables for X-ray Crystallography*, 1962; Bartell & Bonham, 1960). The C(sp^3)–(sp^3) bonds have lengths varying between 1·50 and 1·61 Å with an average of 1·55 Å. The differences between the corresponding bond lengths in the two molecules give an evaluation of the accuracy of the bond lengths determined. These differences in some cases are as large as 0·08 Å. The C-H bond length varies between 0·84 and 1·16 Å with an average value of 1·01 Å.

Bond angles agree with those found in similar steroids (Cooper & Norton, 1968; Gopalakrishna *et al.*, 1969). The average value for bond angles of the type C–C–C in the five membered oxido ring comprised of atoms C(6), O(6), C(19), C(10) and C(5) is 102·5°. Owing to the distortion introduced by the oxido bond, bond angle C(10)–C(5)–C(6) is reduced from its expected value of 109·5° to 100°.

Also as a result of the oxido bridging between C(6) and C(19), the two torsional angles θ(10,1) and θ(5,10), in the *A* ring, with values of +47° and −47° respectively, deviate from those observed in the normal staggered conformation. The oxido bridge also causes *B* ring deformation, and the extent of distortion is indicated by the torsional angles θ(5,10) and θ(5,6), which have values of +68° and −68° respectively. The torsional angles in the *C* ring approximately conform to the staggered conformation. The torsional angles in the *D* ring indicate that this ring has a slightly distorted β-envelope conformation. The angle θ[O(6),19], which is nearly 0° (0° in molecule 1 and −2° in mloecule 2), shows that atoms C(10), C(19), O(6) and C(6) are coplanar, and that atom C(5) does not lie in this plane. Consequently, the five-membered ring comprised of these five atoms is almost an ideal envelope. Other torsional angles in the steroid nucleus are given in Table 3.

The methylene group attached to C(10) is rotated approximately 30° to facilitate the oxido bridging between C(19) and C(6), and consequently, the related torsional angles are nearly midway between the staggered and eclipsed configurations. The methyl group attached to C(13) has an approximately staggered conformation. The methyl group attached to C(20) is oriented with respect to C(17), as well as to O(20), nearly halfway between the eclipsed and staggered conformation.

With the exception of the orientations of the side chains, the molecular structures of the two molecules not related by crystal symmetry are identical within the observed standard deviations. Fig. 3(*a*) and (*b*) are identical perspective views of these two molecules. Equations of the least-squares planes for different portions of the molecule are given in Table 4(*a*).

* Standard deviations for interatomic distances and angles average 0·02 Å and 1·3° respectively.

Because the oxido oxygen atom forms a five-membered ring with atoms C(19), C(10), C(5) and C(16), atoms C(10) and C(8) have been pulled closer together, causing atoms C(10), C(5) and C(6) to move away from the mean plane of the *B* ring (by about 0·1 Å), and atom C(8) to move closer to the plane (by 0·07 Å). The oxido bridge, in addition to giving rise to a distortion in the *B* ring, has apparently caused a rotation of the *A* ring as a whole, by about 5° with respect to the *B* ring. This relative rotation can easily be seen in the perspective view given in Fig. 3. The *D* rings have slightly distorted β-envelope conformations. The three atoms in the side chain, C(20), C(21) and O(20), along with C(17), are coplanar within ±0·02 Å. The oxido oxygen atom, together with atoms C(6), C(5), C(10) and C(19), forms a five-membered ring having the conformation of an ideal envelope with C(6), O(6), C(19) and C(10) lying in a plane and C(5) out of this plane. The four atoms

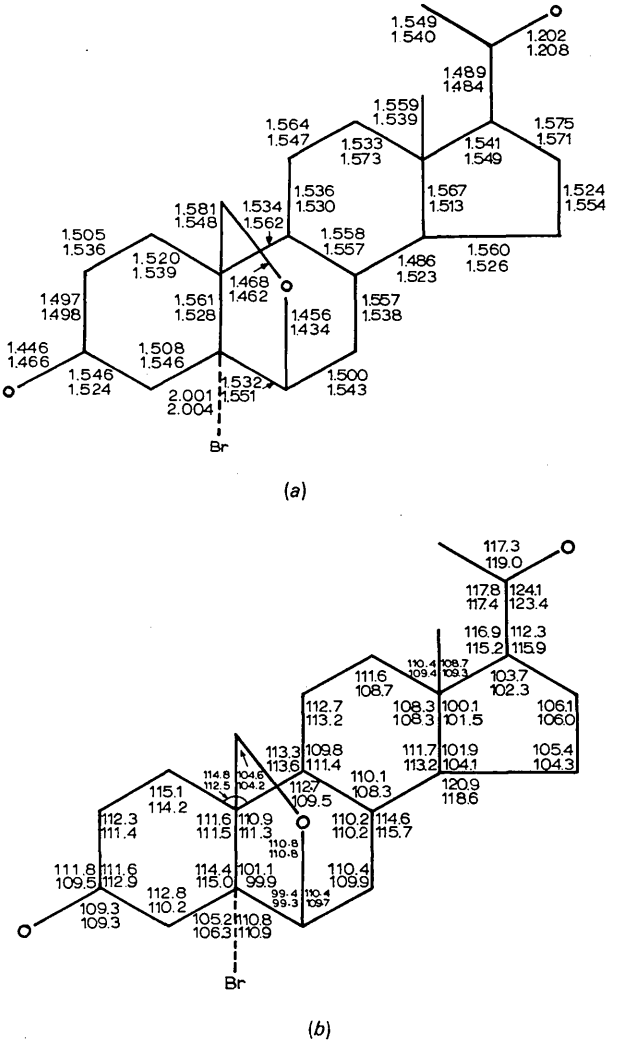


Fig. 2. Interatomic distances (*a*) and angles (*b*) in the molecule. The figures for molecule 1 of the asymmetric unit are given above those for molecule 2.

Table 4(*a*). *Least-squares planes through the atoms of the steroid nucleus*

The equations are of the form $lX+mY+nZ=p$ where X, Y, Z are expressed in Å units relative to the crystal axes.

Plane	Atom	*l*	*m*	*n*	*p*
*A*1	C(2), C(3), C(4)	0·965	−0·0698	0·2695	5·328*
		0·1272	0·9608	−0·2464	8·989
*A*2	C(1), C(2), C(4), C(5)	0·4473	−0·4845	0·7518	1·779
		0·5284	0·3980	−0·7500	6·820
*A*3*B*1	C(1), C(5), C(6), C(10)	0·9648	−0·1267	0·2305	3·908
		0·1827	0·9580	−0·2212	10·487
*B*2	C(6), C(7), C(9), C(10)	0·3515	−0·6435	0·6800	1·277
		0·6904	0·2957	−0·6602	6·128
*B*3*C*1	C(7), C(8), C(9), C(11)	0·9151	−0·2705	0·2991	2·314
		0·3365	0·9074	−0·2519	12·024
*C*2	C(8), C(11), C(12), C(14)	0·3169	−0·6053	0·7302	2·159
		0·6897	0·2869	−0·6648	5·365
*C*3*D*1	C(12), C(13), C(14), C(15)	0·8996	−0·2203	0·3771	1·620
		0·2885	0·9067	−0·3077	12·852
*D*2	C(13), C(15), C(16), C(17)	0·3418	−0·6049	0·7192	2·733
		0·6690	0·3453	−0·6582	5·473
*D*3	C(14), C(15), C(16), C(17)	0·5954	−0·6388	0·4873	0·935
		0·6999	0·5739	−0·4252	9·973
A	C(1), C(2), C(3), C(4), C(5), C(10)	0·6733	−0·3750	0·6373	2·999
		0·4350	0·6340	−0·6394	8·445
B	C(5), C(6), C(7), C(8), C(9), C(10)	0·6148	−0·5291	0·5551	2·034
		0·5933	0·6021	−0·5342	9·162
C	C(8), C(9), C(11), C(12), C(13), C(14)	0·6010	−0·5066	0·6182	2·232
		0·6049	0·5751	−0·5508	8·903
D	C(13), C(14), C(15), C(16), C(17)	0·5285	−0·5299	0·6632	2·358
		0·6071	0·5165	−0·6039	7·981
C1–C17		0·6007	−0·5118	0·6142	2·140
		0·5855	0·5665	−0·5799	8·680

* These values are given with those for molecule 1 above those for molecule 2.

Table 4(*b*). *Interplanar angles*

Plane 1	Plane 2	Angle
*A*1	*A*2	131·8
		129·4
*A*3*B*1	*A*2	131·8
		130·1
*A*3*B*1	*B*2	125·3
		123·7
*B*3*C*1	*B*2	134·4
		131·8
*B*3*C*1	*C*2	132·2
		131·3
*C*3*D*1	*C*2	133·9
		131·6
*C*3*D*1	*D*2	135·4
		135·1
*C*3*D*1	*D*3	149·3
		148·5
A	*B*	169·8
		168·9
B	*C*	175·5
		178·1
C	*D*	174·9
		175·5
C(1)–C(17)	(100)	53·1
		54·2
C(1)–C(17)	(010)	120·8
		124·5
C(1)–C(17)	(001)	52·1
		54·6

* Angles are given with the values for molecule 1 above those for molecule 2.

Table 5. *Intermolecular distances less than* 3·9 Å *between non-hydrogen atoms*

Molecule 1–Molecule 1		
1O(6)—1O(3)	1/001*	3·731 Å
–1C(1)	1/001	3·673
–1C(2)	1/001	3·195
–1C(3)	1/001	3·287
1O(20)–1C(20)	3/$\bar{1}$00	3·810
–1C(21)	3/$\bar{1}$00	3·307
1C(18)–1C(1)	3/000	3·867
1C(20)–1C(21)	3/$\bar{1}$00	3·845
Molecule 2–Molecule 1		
2 Br–1Br	4/000	3·810
2O(3)–1O(3)	1/100	2·778
–1O(6)	1/00$\bar{1}$	3·898
–1C(3)	1/000	3·656
–1C(4)	1/00$\bar{1}$	3·867
2O(20)–1O(3)	4/$\bar{1}$01	2·814
–1O(20)	2/001	3·543
–1C(2)	4/$\bar{1}$01	3·548
–1C(3)	4/$\bar{1}$01	3·480
–1C(4)	4/$\bar{1}$01	3·704
–1C(20)	2/001	3·875
–1C(21)	2/001	3·295
2C(3)—1O(3)	1/000	3·592
2C(4)—1O(3)	1/000	3·440
2C(20)–1O(20)	2/001	3·415
–1C(21)	2/001	3·831
Molecule 2–Molecule 2		
2O(3)—2O(6)	1/00$\bar{1}$	3·813
–2C(11)	4/000	3·703

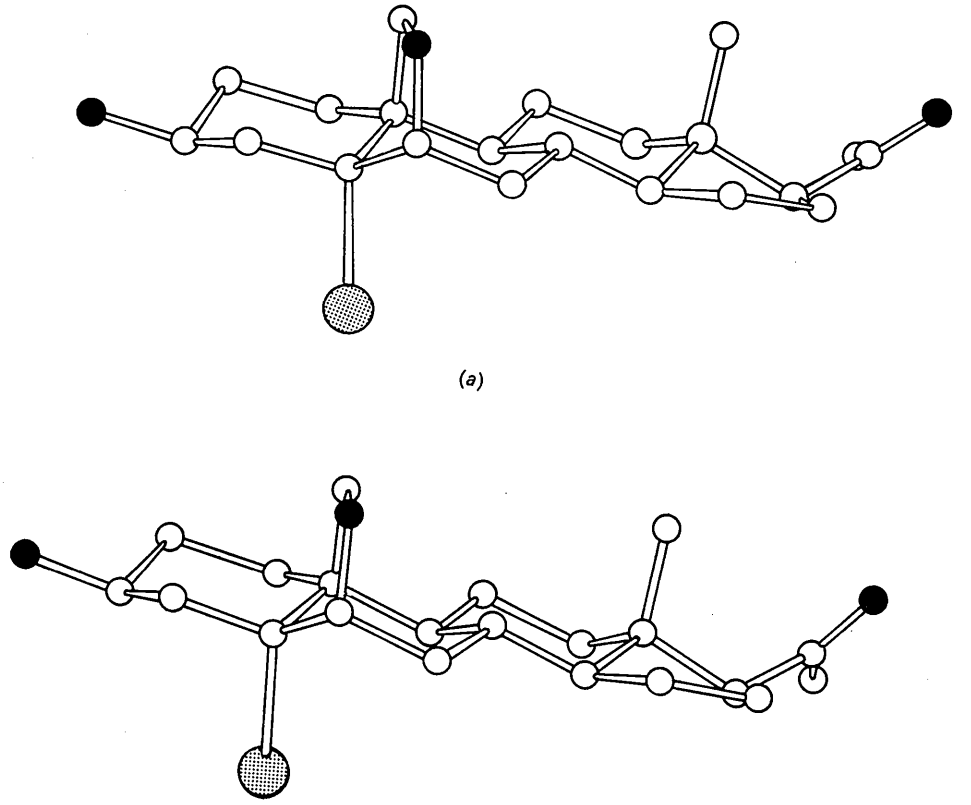


Fig. 3. Identical views of (*a*) molecule 1 and (*b*) molecule 2, of the asymmetric unit. Large shaded circles are bromine atoms, smaller shaded circles are oxygen atoms.

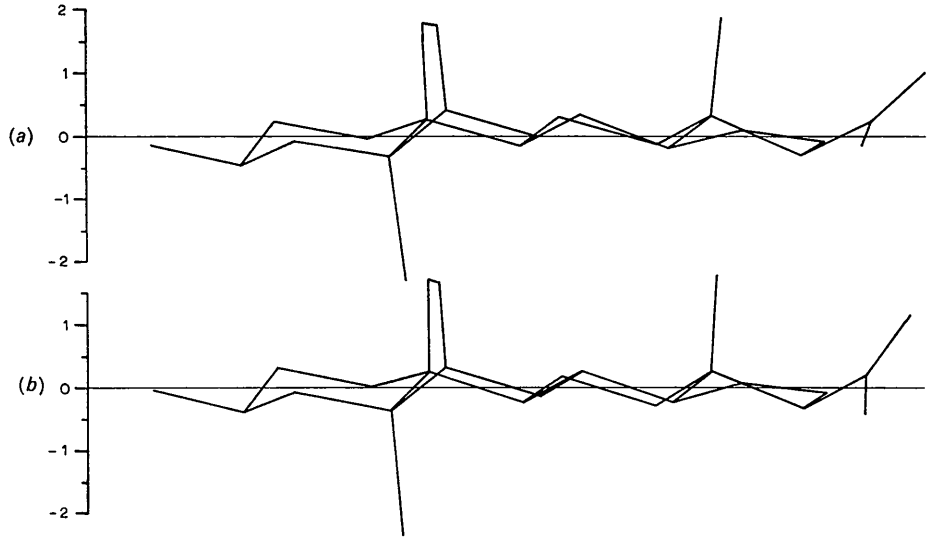


Fig. 4. Projections parallel to the least-squares planes through atoms C(1) to C(17) of (*a*) molecule 1, and (*b*) molecule 2. The scales give distances in Å units of atoms from the plane.

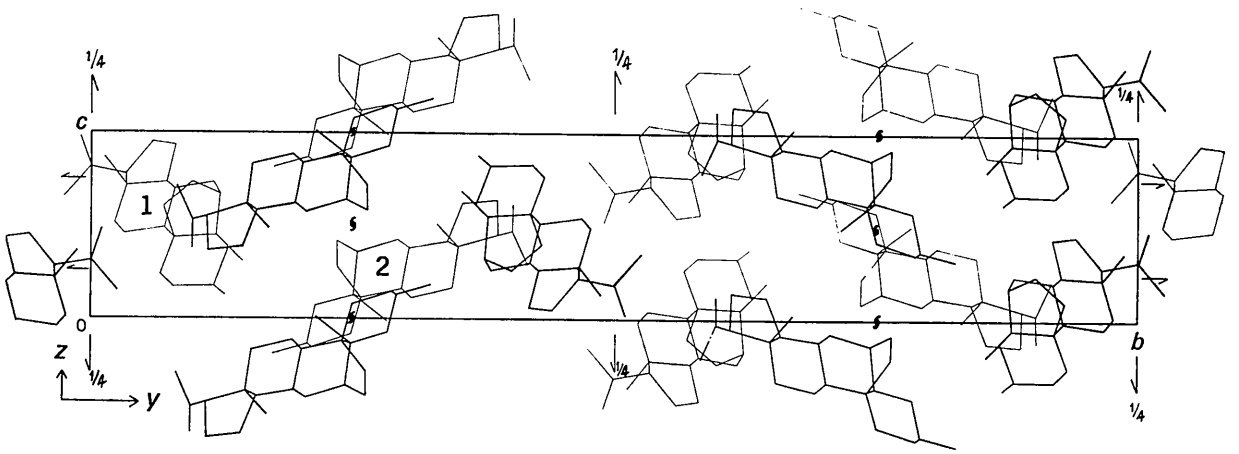
Table 5 (*cont.*)

–2C(12)	4/000	3·386
–2C(18)	4/000	3·466
2O(6)—2C(1)	1/001	3·657
–2C(2)	1/001	3·205
–2C(3)	1/001	3·369
2C(4)—2C(11)	4/000	3·762

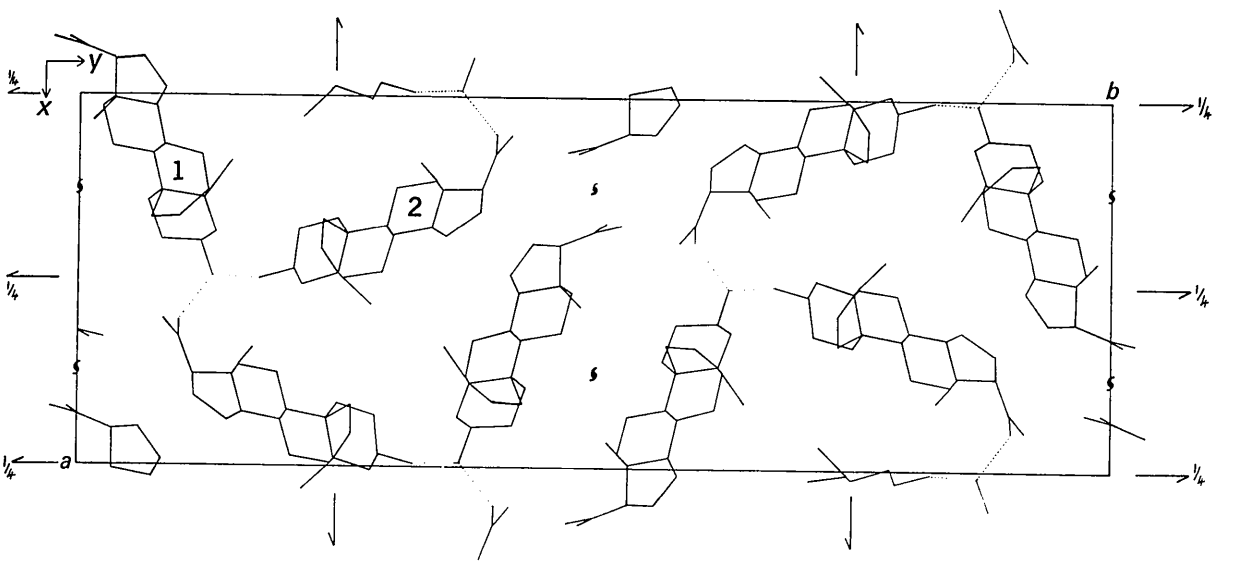
* Equivalent position nomenclature: 2O(20)–1O(3) 4/$\bar{1}$01 means that the second atom named, *viz.* 1O(3), is at equivalent position 4, and translated −1, 0, and 1 unit cells in the **a**, **b**, and **c** directions respectively. The equivalent positions are: $1=x,y,z$; $2=-x,\frac{1}{2}+y,\frac{1}{2}-z$; $3=\frac{1}{2}-x,\frac{1}{2}-y,-z$.

C(10), C(13), C(18) and C(19) are coplanar within ±0·12 Å.

Table 4(*b*) gives all the important interplanar angles between the various least-squares planes. The mean planes of rings *A* and *B* are inclined to each other by about 10°, whereas the inclinations between the mean planes of rings *B* and *C* and of rings *C* and *D* are less than 5°. The inclinations of the mean planes of rings *A*, *B*, *C* and *D* to the mean plane C(1)–C(17) are 10°, 5°, 2° and 4°, respectively. As mentioned earlier, the larger inclination of the *A* ring to the rest of the nucleus of the molecule is due to the oxido bridge between C(6) and C(19). The least-squares plane of atoms C(17), C(20), C(21) and O(20) is inclined to the mean plane of the steroid nucleus, C(1)–C(17), at an angle of 39° in molecule 1, and at 53° in molecule 2. The mean plane of the four atoms C(10), C(13), C(18) and C(19) is inclined to the plane C(1)–C(17 at an angle of 98°. The five membered ring of the envelope comprised of atoms C(5), C(6), O(6), C(19) and C(10) is inclined to the *A* ring at an angle of 73°, to the *B* ring at an angle



(*a*)



(*b*)

Fig. 5. Projections of one unit cell (*a*) along the *a* axis and (*b*) along the *c* axis. Hydrogen bonding is shown by dotted lines in (*b*).

of 76° and to the mean plane, C(1)–C(17), at an angle of 79°. Views of the molecules, as projected parallel to their respective least-squares planes through atoms C(1)–C(17), are given in Fig. 4.

The length of the nucleus of the steroid molecule, calculated as the distance between atoms C(3) and C(16) is 9·13 Å in molecule 1 and 9·16 Å in molecule 2.

Molecular packing

The hydroxyl oxygen atom, 1O(3), of molecule 1 is hydrogen-bonded to the ketone oxygen atom 2O(20) of another molecule, not related to the former by symmetry, as well as to the hydroxyl oxygen atom 2O(3) of a third molecule related to the second by the *a*-screw axis, but not related to the first one by symmetry. These hydrogen bonds are indicated by dotted lines in the axial projections given in Fig. 5(*a*) and (*b*). The distance between the hydrogen-bonded atoms 1O(3) and 2O(20) is 2·81 Å, and the hydrogen-bond distance between 1O(3) of one molecule and 2O(3) of another molecule is 2·76 Å.

Table 5 lists the forty-one intermolecular contacts shorter than 4·0 Å (ignoring hydrogen atoms). The two bromine atoms not related by crystal symmetry are in van der Waals contact, being separated by a distance of 3·81 Å. Apart from this contact, the bromine atoms do not have intermolecular contacts shorter than 4·0 Å. Of the forty-one contacts less than 4·0 Å, the side chain atoms carry eighteen contacts, and, therefore, play a major part in the molecular packing.

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The Crystal and Molecular Structure of Bis-π-cyclopentadienyl(2-aminoethanethiolato)-molybdenum Iodide

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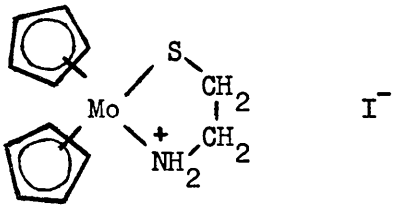
$(\pi\text{-}C_5H_5)_2MoS(CH_2)_2NH_2^+I^-$ crystallizes in space group *Pbcn* with $a=11{\cdot}86\pm0{\cdot}01$, $b=14{\cdot}97\pm0{\cdot}01$, $c=15{\cdot}46\pm0{\cdot}01$ Å and $Z=8$. Full-matrix least-squares refinement with anisotropic temperature factors for molybdenum and iodide gave an R index of 0·087 for 1746 absorption-corrected photographic data. The Mo–S and Mo–NH_2 bonds are $2{\cdot}438\pm0{\cdot}005$ and $2{\cdot}211\pm0{\cdot}015$ Å respectively, and lie in a plane between staggered cyclopentadienyl rings. The angle between ring normals is 130·9°. There are intermolecular hydrogen bonds from the amino group to the sulphur atom (3·3 Å) and to the iodide ion (3·6 Å).

Introduction

In $(\pi\text{-}C_5H_5)_2MoH_2$ (Gerloch & Mason, 1965) and $(\pi\text{-}C_5H_5)_2MoS_2C_6H_3CH_3$ (Knox & Prout, 1967) the cyclopentadienyl rings have the non-parallel arrangement predicted by Ballhausen & Dahl (1961). The rings are eclipsed in the former compound and are staggered in the latter. To see what effect ligand atoms of different size have on ring configuration and molecular geometry, we have determined the structure of bis-π-cyclopentadienyl(2-aminoethanethiolato)molybdenum iodide:



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