

References

- BRINDLEY, G. W., OUGHTON, B. M. & ROBINSON, K. (1950). *Acta Cryst.* **3**, 408.
- BROWN, B. E. & BAILEY, S. W. (1962). *Amer. Min.* **47**, 819.
- BROWN, B. E. & BAILEY, S. W. (1963). *Amer. Min.* **48**, 42.
- DRITS, V. A. & LAZARENKO, E. K. (1967). *Mineralog. Sb. L'vovsk. Geol. Obshchestvo pri L'vovsk. Gos. Univ.* **21**, 40.
- GARRIDO, I. (1949). *Bull. Soc. Franç. Minér. Crist.* **72**, 549.
- McMURCHY, R. C. (1934). *Z. Kristallogr.* **88**, 420.
- PAULING, L. (1930). *Proc. Nat. Acad. Sci. Wash.* **16**, 578.
- SHIROZU, H. & BAILEY, S. W. (1965). *Amer. Min.* **50**, 868.
- SHIROZU, H. & BAILEY, S. W. (1966). *Amer. Min.* **51**, 1124.
- WLASOW, W. W. & DRITS, V. A. (1967). *Rentgenografija mineralnogo syrja*, **6**, 114.
- ZVYAGIN, B. B. (1964). *Elektronografija i strukturnaja kristallografija glinistykh mineralow*. Izd. Nauka.
- ZVYAGIN, B. B. & MISZCZENKO, K. C. (1965). *Kristallografiya*, **10**, 555.

Acta Cryst. (1969). **B25**, 639

Crystal and Molecular Structure of 6 β -Bromoprogesterone

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The steroid 6 β -bromoprogesterone (6 β -bromo- Δ^4 -pregnene-3,20-dione, C₂₁H₂₉O₂Br) crystallizes in the orthorhombic space group $P2_12_12_1$ with unit-cell dimensions $a = 13.431$, $b = 18.288$ and $c = 7.645$ Å and with four steroid molecules per unit cell. The atomic positions of all the atoms, including the hydrogen atoms, have been refined using anisotropic temperature factors for carbon and heavier atoms and isotropic temperature factors for hydrogen atoms, giving an R value of 4.7% for 2208 independent reflections. The A ring is highly distorted because of the Δ^4 -double bond and the ketone oxygen O(3). The rings B and C are chair-shaped. The D ring is a distorted half-chair. The molecules are held together in the crystalline state by van der Waals forces.

Introduction

Progesterone is unique among the steroid hormones (Applezweig, 1962) in that its role is mainly concerned with motherhood. It is produced by the corpus luteum and placenta and is involved initially in stimulating maturation of the uterine mucosa in order to prepare it for reception of a fertilized ovum; this progestational action is withdrawn by degeneration of the corpus luteum if fertilization does not occur, and the excess uterine tissue is removed through menstruation as the progesterone level drops. In the event of fertilization, however, the corpus luteum persists and continues to secrete a high level of progesterone, which now serves to maintain and protect a successful pregnancy by preventing uterine motility or further ovulation and by stimulating milk gland formation in the breasts. Any fault in the cycle of progesterone production or metabolism can give rise to numerous physiologic disorders; amenorrhea, habitual abortion, and premature delivery are all likely sequelae. While the potential usefulness of progesterone in treatment of numerous human

disorders seems obvious, administration of the compound itself has proven to be a disappointment in most cases. First, progesterone differs from other steroid hormones in that a relatively large dosage is required in order to produce a physiologic effect. Secondly, since it is a time-cycle hormone, the where, when and how of its delivery becomes, as it were, a difficult problem in logistics. Since progesterone arises in some endocrine tissues which are seemingly not concerned with gestation, and since large doses are required to produce many of its so-called progestogenic effects, there is some doubt as to whether it is progesterone itself or some of its metabolites which are responsible for the different biological activities ascribed to the hormone.

Under these circumstances, a thorough and detailed investigation of the crystal and molecular structure of some of the derivatives of progesterone will certainly be useful in understanding the biological activity of this hormone and the related steroids. The present paper reports the study of the 6 β -bromo derivative of progesterone (Fig. 1).

Experimental

The sample used in this investigation was prepared by refluxing progesterone with N -bromosuccinimide in

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dry carbon tetrachloride for one hour. This produced a 41% yield of 6 β -bromoprogesterone (Sondheimer, Kaufmann, Romo, Martinez & Rosenkranz, 1953). Small prismatic crystals of the steroid were grown by slow evaporation of a solution of a 1:1 mixture of n-hexane and acetone, and a crystal of dimensions 0.30 \times 0.20 \times 0.22 mm was selected for study. All X-ray measurements were made on a General Electric single-crystal counter diffractometer using Cu K α radiation. The crystal was mounted with its *b* axis parallel to the ϕ axis of the instrument.

The systematic extinctions ($h00, h=2n+1; k=2n+1, 00l, l=2n+1$) showed that the crystal belonged to the orthorhombic space group $P2_12_12_1$. The unit-cell dimensions are $a=13.431 \pm 0.002$, $b=18.288 \pm 0.004$, and $c=7.645 \pm 0.001$ Å (measured at 20°C; Cu K $\alpha=1.5418$ Å). The density calculated on the basis of four molecules per unit cell is 1.391 g.cm $^{-3}$ as compared with the measured value of 1.397 g.cm $^{-3}$, determined by flotation of a crystal in an aqueous potassium iodide solution.

The intensities of 2208 independent reflections with 2θ less than 144° were measured by the stationary-crystal stationary-counter technique using balanced nickel and cobalt filters. Each reflection was measured for 10 seconds with each filter. The crystal did not show any observable decay as based on test measurements of the intensities of 10 standard reflections, made daily through the period of 14 days required to collect the data. The intensities of two planes with $\chi=90.0^\circ$ were studied for variation with respect to ϕ -orientation due to absorption: the intensity of the 040 reflection with $\theta=19.60^\circ$ varied up to a maximum of $\pm 8.7\%$ from its mean value, whereas the intensity of the 0,12,0 reflection with $\theta=60.87^\circ$ varied up to a maximum of 5.7%. The observed intensities were not corrected for this absorption. The intensities were reduced to structure amplitudes after making appropriate corrections for Lorentz and polarization factors. Of the 2208 reflections, 80 were found to have their measured intensities less than twice the estimated standard deviation in their intensity measurement. The observed structure factor amplitudes were placed on the absolute scale by Wilson's (1942) method. The scale factor obtained by Wilson's method was later found to be only 4% higher than that obtained finally in the least squares refinement process.

Structure analysis

The position of the bromine atom was located from a three-dimensional Patterson synthesis calculated using $[F(\text{obs}) \cdot Z_{\text{Br}} / (f_{\text{Br}} \exp(-B \sin^2 \theta / \lambda^2))]$ as the sharpened structure amplitude. A value of 4.07 Å 2 for *B*, as obtained from Wilson's method, was used for this purpose. A structure factor calculation made at this stage with the bromine atom alone gave an *R* value of 44% and the remainder of the atoms in the steroid molecule were located by straight forward application of the

heavy atom method. Three cycles of least-squares refinement were carried out on the positional and isotropic temperature parameters using 4 \times 4 matrix blocks (corresponding to *x, y, z*, and *B(iso)* for each atom) whereupon the *R* value was reduced to 9.2%. A weighting scheme of the type $1/\{1 + [(|F_o| - 30)/10]^2\}$, which made the average weighted squares of $(|F_o| - |F_c|)$ at different ranges of $|F_o|$ nearly equal, was used throughout the least-squares refinement process. Eighty reflections, whose intensities were less than twice their estimated standard deviations, were ignored during the refinement.*

Up to this stage, $\Delta f''$, the imaginary part of the anomalous dispersion factor, was assumed to be zero. At this point, two sets of structure factors were calculated, one with $\Delta f'' = +1.46$ and the other with $\Delta f'' = -1.46$. The calculation with $\Delta f'' = +1.46$ gave an *R* value of 8.7%, whereas the calculation with $\Delta f'' = -1.46$ gave an *R* value of 9.5%. This established that the configuration which had been assumed hitherto was the real and absolute configuration. According to the statistical theory discussed by Hamilton (1965, concerning significance tests in crystallographic problems, even a difference of 0.01% in *R* value is significant enough to establish the correct configuration when one variable parameter is involved in the refinement and 2208 reflections are used. In the subsequent calculations, $\Delta f'' = +1.46$ was always taken into account for the bromine scattering factors. Three cycles of least-squares refinement carried out using anisotropic temperature factors with 9 \times 9 matrix blocks for each atom reduced the *R* value to 7.6%.

* The scattering factors used throughout the refinement, were for all atoms, those from *International Tables for X-ray Crystallography* (1962), Table 3.3 1A.

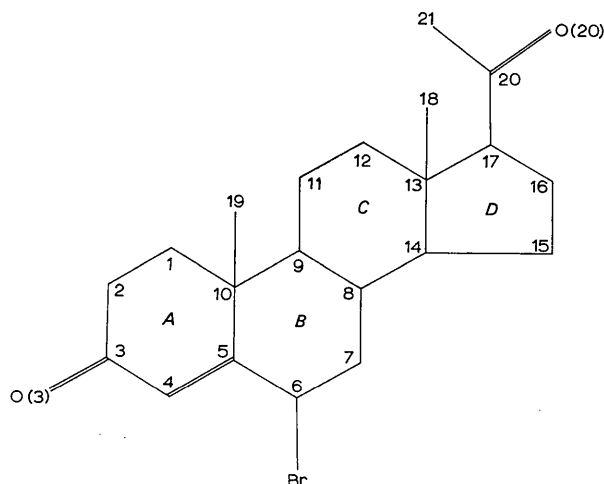


Fig. 1. Schematic representation of the molecule showing the numbering of atoms. Hydrogen atoms are omitted from the diagram, but are given the same number as the carbon atom to which they are attached.

A difference Fourier map subsequently computed revealed 30 peaks of approximately correct heights at the positions expected for hydrogen atoms. Calculation of bond distances and bond angles eliminated ten of them. The next difference Fourier map (including the 20 hydrogen atoms) revealed the other nine hydrogen

Table 1. Comparison of the observed structure amplitudes (F_{obs}) with those calculated (F_{cal}) from the refined parameters

H	K	L	F _{obs}	F _{cal}	H	K	L	F _{obs}	F _{cal}	H	K	L	F _{obs}	F _{cal}	H	K	L	F _{obs}	F _{cal}	H	K	L	F _{obs}	F _{cal}	H	K	L	F _{obs}	F _{cal}	H	K	L	F _{obs}	F _{cal}
0	0	2	1234	1257																														
0	0	4	373	376																														
0	0	6	175	172																														
0	1	7	1796	1821																														
0	1	2	142	139																														
0	1	3	366	360																														
0	1	4	316	317																														
0	1	5	137	135																														
0	1	6	141	131																														
0	1	7	354	367																														
0	1	8	60	30																														
0	1	9	194	206																														
0	2	0	913	916																														
0	2	1	143	138																														
0	2	2	1107	1112																														
0	2	3	350	351																														
0	2	4	90	58																														
0	2	5	105	114																														
0	2	6	191	188																														
0	2	7	235	209																														
0	2	8	180	188																														
0	2	9	30	4																														
0	3	1	1044	1023																														
0	3	2	390	383																														
0	3	3	842	835																														
0	3	4	85	82																														
0	3	5	63	41																														
0	3	6	47	5																														
0	3	7	300	337																														
0	3	8	16	11																														
0	3	9	145	140																														
0	4	0	1326	1343																														
0	4	1	86	87																														
0	4	2	852	846																														
0	4	3	222	215																														
0	4	4	262	247																														
0	4	5	193	200																														
0	4	6	353	363																														
0	4	7	35	37																														
0	4	8	190	193																														
0	4	9	40	32																														
0	5	1	1099	1086																														
0	5	2	123	125																														
0	5	3	105	110																														
0	5	4	152	158																														
0	5	5	36	2																														
0	5	6	1071	1058																														
0	5	7	195	187																														
0	5	8	1159	1136																														
0	5	9	463	437																														
0	6	0	91	67																														
0	6	1	44	24																														
0	6	2	130	119																														
0	6	3	7	15																														
0	6	4	135	130																														
0	6	5	41	46																														
0	6	6	910	898																														
0	6	7	2	483																														
0	6	8	267	260																														
0	6	9	78	92																														
0	7	0	5	38																														
0	7	1	42	12																														
0	7	2	188	192																														
0	7	3	132	154																														
0	7	4	1133	1119																														
0	7	5	147	132																														
0	7	6	292	284																														
0	7	7	27	10																														
0	7	8	111	103																														
0	7	9	23	107																														
0	8	0	357	365																														
0	8	1	42	14																														
0	8	2	144	129																														
0	8	3	382	386																														
0	8	4	74	70																														
0	8	5	292	288																														
0	8	6	103	112																														
0	8	7	115	131																														
0	8	8	61	65																														
0	8	9	127	132																														
0	8	10	44	29																														
0	9	0	136	136																														
0	9	1	85	101																														
0	9	2	432	434																														
0	9	3	68	89																														
0	9	4	38	19																														
0	9	5	174	161																														
0	9	6	90	82																														
0	9	7	35	27																														
0	9	8	104	109																														
0	9	9	58	59																														
0	10	0	585	592																														
0	10	1	226	230																														
0	10	2	166	165																														
0	10	3	166	165																														
0	10	4	181	189																														
0	10	5	66	66																														
0	10	6	35	13																														
0	10	7	112	113																														
0	10	8	30	11																														
0	10	9	713	747																														
0	11	0	100	102																														
0	11	1	437	427																														
0	11	2	183	183																														
0	11	3	42	23																														
0	11	4	25	37																														
0	11	5	105	110																														
0	11	6	10	12																														
0	11	7	10	12																														
0	11	8	61	72																														
0	11	9	304	312																														
0	11	10	135	142																														
0	11	11	53	47																														
0	11	12	49	39																														
0	11	13	43	2																														
0	11	14	106	107																														
0	11	15	106	107																														
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0	11	190	106	107																														
0	1																																	

atoms needed to complete the molecule. Three cycles of least-squares refinement, using 4×4 matrix blocks for each of the hydrogen atoms, for which isotropic temperature factors were used, and 9×9 matrix blocks

for carbon and heavier atoms, for which anisotropic temperature factors were used, brought the R value down to 4.5%. When the 80 weak reflections previously omitted from calculations were also included in the

Table 1 (cont.)

H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL						
5	6	0	402	374	6	0	6	215	217	6	14	5	63	44	7	9	4	259	255	8	5	4	42	23	9	2	3	270	276	10	0	5	17	12	11	0	3	56	54	
5	6	1	222	215	6	0	7	24	20	6	15	6	63	66	7	9	5	123	123	8	5	5	56	37	9	2	4	120	126	10	0	6	53	31	11	0	4	370	378	
5	6	2	350	340	6	0	8	157	153	6	16	6	142	140	7	9	6	187	187	8	5	6	102	102	9	2	5	228	231	10	0	7	123	122	11	0	5	35	30	
5	6	3	359	360	6	1	0	294	285	6	15	7	173	180	7	9	7	61	56	8	5	7	61	56	9	2	6	101	115	10	0	8	217	223	11	0	6	122	128	
5	6	4	442	447	6	1	1	761	784	6	15	8	215	217	7	10	0	50	53	8	6	8	125	134	9	2	7	116	102	10	1	106	105	11	0	7	140	142		
5	6	5	48	48	6	1	2	238	230	6	15	9	289	290	7	10	1	68	47	8	6	0	20	8	9	2	8	40	43	10	1	2	240	240	11	0	8	59	89	
5	6	6	250	260	6	1	3	292	288	6	15	10	344	340	7	10	2	181	177	8	6	1	338	350	9	3	0	167	166	10	1	3	187	187	11	1	1	87	89	
5	6	7	85	84	6	1	4	129	122	6	15	11	415	410	7	10	3	175	174	8	6	2	175	174	9	3	1	116	116	10	1	4	96	97	11	1	2	92	93	
5	6	8	82	67	6	1	5	145	133	6	15	12	519	500	7	10	4	280	275	8	6	3	128	142	9	3	2	355	361	10	1	5	66	61	11	1	3	293	290	
5	7	0	221	214	6	1	6	94	101	6	16	0	177	182	7	10	5	199	199	8	6	4	88	91	9	3	3	94	85	10	1	6	156	150	11	1	4	56	43	
5	7	1	325	324	6	1	7	191	199	6	16	1	241	240	7	10	6	117	118	8	6	5	137	146	9	3	4	319	318	10	1	7	121	124	11	1	5	274	292	
5	7	2	60	54	6	1	8	5	23	6	16	2	96	83	7	10	7	123	122	8	6	6	146	140	9	3	5	146	146	10	2	0	668	664	11	1	6	92	93	
5	7	3	392	395	6	2	0	862	865	6	16	3	106	106	7	11	0	97	99	8	6	7	146	140	9	3	6	73	61	10	2	1	240	244	11	1	7	79	74	
5	7	4	228	222	6	2	1	118	96	6	16	4	46	42	7	11	1	195	98	8	6	8	40	39	9	3	7	60	56	10	2	2	167	161	11	2	0	90	76	
5	7	5	221	208	6	2	2	669	676	6	16	5	42	33	7	11	2	361	367	8	6	9	557	548	9	4	0	91	86	10	2	3	127	134	11	2	1	179	194	
5	7	6	115	114	6	2	3	88	75	6	17	0	42	46	7	11	3	268	259	8	7	1	130	123	9	4	1	133	142	10	2	4	35	22	11	2	352	360		
5	7	7	131	121	6	2	4	64	48	6	17	1	127	130	7	11	4	331	328	8	7	2	175	175	9	4	2	117	117	10	2	5	82	73	11	2	3	61	48	
5	7	8	37	30	6	2	5	67	71	6	17	2	68	75	7	11	5	123	121	8	7	3	175	175	9	4	3	279	273	10	2	6	79	75	11	2	4	309	317	
5	8	0	401	401	6	2	6	97	100	6	17	3	71	72	7	11	6	115	117	8	7	4	129	124	9	4	4	141	147	10	2	7	104	85	11	2	5	28	33	
5	8	1	285	276	6	2	7	61	73	6	17	4	132	132	7	11	7	11	34	26	8	7	5	56	59	9	4	5	234	237	10	3	0	593	610	11	2	6	125	126
5	8	2	499	476	6	2	8	172	173	6	17	5	49	45	7	12	0	162	174	8	7	6	97	85	9	4	6	60	57	10	3	1	292	295	11	2	7	39	38	
5	8	3	304	290	6	3	0	413	414	6	18	0	196	194	7	12	1	162	174	8	7	7	103	98	9	5	0	214	210	10	3	2	177	181	11	3	1	177	172	
5	8	4	355	351	6	3	1	463	466	6	18	1	47	35	7	12	2	136	136	8	7	8	468	468	9	5	1	229	221	10	3	3	71	73	11	3	2	203	210	
5	8	5	239	239	6	3	2	157	148	6	18	2	85	91	7	12	3	218	210	8	7	9	125	118	9	5	2	208	205	10	3	4	35	34	11	3	3	95	83	
5	8	6	240	237	6	3	3	285	282	6	18	3	85	87	7	12	4	125	118	8	7	10	238	239	9	5	3	53	56	10	3	5	63	63	11	3	4	295	294	
5	8	7	53	51	6	3	4	108	102	6	18	4	28	19	7	12	5	131	123	8	7	11	468	468	9	5	4	329	325	10	3	6	107	111	11	3	5	233	232	
5	8	8	40	39	6	3	5	104	85	6	19	0	45	52	7	12	6	104	100	8	7	12	221	229	9	5	5	82	91	10	4	0	226	227	11	3	6	71	67	
5	8	9	378	372	6	3	6	112	610	6	19	1	67	61	7	13	0	139	136	8	7	13	224	227	9	5	6	149	148	10	4	1	130	129	11	3	7	109	99	
5	9	0	241	237	6	3	7	164	159	6	19	2	99	99	7	13	1	171	170	8	7	14	413	413	9	5	7	90	92	10	4	2	313	320	11	4	0	54	38	
5	9	1	222	217	6	3	8	64	42	6	19	3	53	54	7	13	2	133	133	8	7	15	113	113	9	5	8	109	418	10	4	3	55	40	11	4	1	60	66	
5	9	2	369	369	6	3	9	67	61	6	19	4	67	61	7	13	3	149	158	8	7	16	419	418	9	5	9	116	122	10	4	4	25	156	152	11	4	2	312	312
5	9	3	101	88	6	4	0	447	455	6	20	0	97	108	7	13	4	135	136	8	7	17	177	185	9	5	10	216	217	10	4	5	17	24	11	4	3	35	18	
5	9	4	201	190	6	4	1	115	121	6	20	1	50	44	7	13	5	114	103	8	7	18	3	99	101	9	5	11	243	248	10	4	6	89	93	11	4	4	219	224
5	9	5	111	110	6	4	2	88	69	6	20	2	95	98	7	13	6	116	105	8	7	19	107	107	9	5	12	248	248	10	4	7	105	101	11	4	5	59	49	
5	9	6	126	126	6	4	3	184	174	6	21	0	4	16	6	13	116	102	8	7	20	108	104	9	5	13	317	316	10	4	8	116	112	11	4	6	152	151		
5	9	7	42	27	6	4	4	285	281	6	21	1	17	25	7	14	0	90	80	8	7	21	108	104	9	5	14	108	104	10	4	9	316	322	11	4	7	33	31	
5	9	8	73	40	6	4	5	73	69	6	22	1	17	21	7	14	1	140	137	8	7	22	112	126	9	5	15	124	124	10	4	10	221	229	11	4	8	209	217	
5	9	9	119	119	6	4	6	164	179	6	22	2	129	126	7	15	2	119	128	8	7	23	112	126	9	5	16	124	124	10	4	11	212	219	11	4	9	144	145	
5	10	0	125	127	6	5	0	197	199	7	0	2	383	375	7	15	3	131	141	8	7	24	116	120	9	5	17	101	107	10	4	12	101	107	11	4	10	217	215	
5	10	1	280	282	6	5	1	793	781	7	0	3	337	344	7	15	4	145	145	8	7	25	116	120	9	5	18	111	111	10	4	13	222	229	11	4	11	209	217	
5	10	2	432	439	6	5	2	157	148	7	0	4	335	338	7	15	5	131	132	8	7	26	116	120	9	5	19	112	112	10	4	14	214	221	11	4	12	191	191	
5	10	3	50	49	6	5	3	212	214	7	0	5	179	176	7	15	6	131	132	8	7	27	116	120	9	5	20	113	113	10	4	15	214	221	11	4	13	189	191	
5	10	4	144	141	6	5	4	149	158	7	0	6	179	176	7	15	7	131	132	8	7	28	116	120	9	5														

Table 1 (cont.)

H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	
12	1	4	73	65	12	13	0	71	55	13	10	0	57	45	14	10	1	142	133	
12	1	5	67	62	12	13	1	184	175	13	10	1	57	56	14	10	2	52	53	
12	1	6	50	42	12	13	2	108	101	13	10	2	64	75	14	10	3	48	57	
12	2	0	208	197	13	0	0	0	0	13	10	3	95	97	14	10	4	48	129	
12	2	1	160	158	12	14	0	127	132	13	10	4	57	52	14	11	1	43	93	
12	2	2	189	185	12	14	1	84	95	13	11	0	56	65	14	11	2	83	93	
12	2	3	35	4	12	14	2	12	13	13	11	1	48	49	14	11	3	41	37	
12	2	4	81	72	12	14	3	72	79	13	11	2	117	120	14	12	1	91	104	
12	2	5	33	39	12	15	0	71	75	13	11	3	39	31	15	0	0	16	0	
12	2	6	89	94	12	15	1	103	114	13	12	0	48	49	15	0	1	40	49	
12	3	0	43	82	12	15	2	80	92	13	12	1	47	44	15	0	2	60	65	
12	3	1	208	213	13	0	0	25	0	13	12	2	49	55	15	0	3	119	122	
12	3	2	83	81	13	0	1	234	240	13	12	3	43	52	15	0	4	71	65	
12	3	3	156	149	13	0	2	175	181	13	13	0	71	67	15	1	0	46	41	
12	3	4	72	72	13	0	3	149	145	13	13	1	38	21	15	1	1	46	35	
12	3	5	74	66	13	0	4	126	126	13	13	2	81	95	15	1	2	93	89	
12	3	6	39	15	13	0	5	102	108	13	14	0	81	75	15	1	3	40	29	
12	3	7	210	200	13	0	6	78	82	13	14	1	57	66	15	1	4	100	104	
12	4	1	165	157	13	1	0	66	62	14	0	0	149	148	15	2	0	16	25	
12	4	2	149	150	13	1	1	86	79	14	0	1	253	250	15	2	1	125	123	
12	4	3	24	45	13	1	2	165	162	14	0	2	68	44	15	2	2	44	41	
12	4	4	35	47	13	1	3	142	141	14	0	3	120	112	15	2	3	104	104	
12	4	5	39	45	13	1	4	116	111	14	0	4	31	24	15	2	4	49	53	
12	4	6	112	120	13	1	5	102	99	14	0	5	31	19	15	3	0	73	68	
12	4	7	175	166	13	1	6	103	127	14	1	0	220	212	15	3	1	45	41	
12	5	1	175	172	13	2	0	25	38	14	1	1	68	71	15	3	2	115	112	
12	5	2	43	28	13	2	1	114	115	14	1	2	221	227	15	3	3	53	51	
12	5	3	121	114	13	2	2	134	128	14	1	3	46	36	15	4	4	56	61	
12	5	4	24	47	13	2	3	167	174	14	1	4	43	38	15	4	0	75	79	
12	5	5	94	89	13	2	4	175	180	14	1	5	64	70	15	4	1	60	50	
12	5	6	128	114	13	2	5	105	102	14	1	6	46	40	15	4	2	44	40	
12	6	0	295	290	13	3	0	35	20	14	2	1	189	188	15	4	3	110	108	
12	6	1	97	93	13	3	1	66	71	14	2	2	53	47	15	5	0	55	57	
12	6	2	185	187	13	3	2	113	119	14	2	3	97	95	15	5	1	44	37	
12	6	3	65	62	13	3	3	111	114	14	2	4	53	45	15	5	2	76	73	
12	6	4	48	43	13	3	4	210	207	14	2	5	64	64	15	5	3	64	60	
12	6	5	44	39	13	3	5	110	112	14	3	0	207	195	15	6	0	43	40	
12	6	6	68	76	13	3	6	135	135	14	3	1	35	15	15	6	1	59	59	
12	7	0	135	136	13	4	1	74	73	14	3	2	170	172	15	6	2	84	85	
12	7	1	199	190	13	4	2	140	142	14	3	3	80	82	15	6	3	76	84	
12	7	2	116	115	13	4	3	162	153	14	3	4	42	49	15	7	0	21	9	
12	7	3	62	31	13	4	4	126	124	14	3	5	30	34	15	7	1	66	62	
12	7	4	63	49	13	4	5	138	148	14	4	0	35	34	15	7	2	58	63	
12	7	5	37	34	13	5	0	82	83	14	4	1	227	222	15	7	3	29	22	
12	8	0	261	218	13	5	1	55	52	14	4	2	75	69	15	8	0	67	53	
12	8	1	127	133	13	5	2	95	97	14	4	3	61	54	15	8	1	20	30	
12	8	2	167	169	13	5	3	142	134	14	4	4	75	72	15	8	2	51	35	
12	8	3	68	54	13	5	4	185	196	14	4	5	40	240	232	15	8	3	27	23
12	8	4	66	64	13	5	5	87	87	14	5	1	64	55	15	9	1	51	45	
12	8	5	29	34	13	6	0	74	71	14	5	2	177	167	15	10	0	82	90	
12	9	0	136	131	13	6	1	42	25	14	5	3	50	51	16	0	1	138	138	
12	9	1	42	49	13	6	2	59	114	14	5	4	33	14	16	1	2	49	45	
12	9	2	72	62	13	6	3	133	129	14	6	0	34	13	16	2	3	119	125	
12	9	3	98	90	13	6	4	93	87	14	6	1	223	219	16	1	0	84	85	
12	9	4	71	75	13	6	5	67	77	14	6	2	40	38	16	1	1	105	111	
12	9	5	11	39	13	7	0	54	58	14	6	3	66	60	16	1	2	75	79	
12	10	0	150	157	13	7	1	114	112	14	6	4	47	54	16	2	0	216	225	
12	10	1	108	115	13	7	2	123	122	14	7	0	271	257	16	2	1	94	97	
12	10	2	171	172	13	7	3	108	96	14	7	1	57	54	16	2	2	78	81	
12	10	3	62	62	13	7	4	139	139	14	7	2	91	83	16	3	0	63	61	
12	10	4	31	14	13	7	5	54	53	14	7	3	47	46	16	3	1	151	150	
12	10	5	42	49	13	8	0	59	114	14	7	4	33	14	16	3	2	70	73	
12	11	0	120	106	13	8	1	64	67	14	8	0	23	4	16	4	0	123	133	
12	11	1	149	140	13	8	2	68	68	14	8	1	154	151	16	4	1	68	75	
12	11	2	97	99	13	8	3	155	157	14	8	2	31	35	16	4	2	97	110	
12	11	3	50	47	13	8	4	89	91	14	8	3	57	56	16	5	0	70	68	
12	11	4	53	55	13	8	5	96	118	14	8	4	40	36	16	5	1	74	79	
12	12	0	200	202	13	9	0	24	42	14	9	0	175	160	16	6	0	114	120	
12	12	1	6	53	13	9	1	53	64	14	9	1	49	35	16	6	1	29	41	
12	12	2	138	141	13	9	2	100	95	14	9	2	87	82						
12	12	3	119	116	13	9	3	71	76	14	9	3	27	20						
12	12	4	36	34	13	9	4	127	138	14	10	0	47	47						

Table 2(b) Positional parameters for the hydrogen atoms at the end of the least-squares refinement

	X/a	Y/b	Z/c
H(1A)	0.8776	0.1709	0.5007
H(1B)	0.7928	0.2159	0.3708
H(2A)	0.7635	0.0837	0.3440
H(2B)	0.6811	0.1295	0.4157
H(4)	0.7516	0.0926	0.8641
H(6A)	0.8119	0.1743	1.0614
H(7A)	0.9242	0.2582	0.9259
H(7B)	0.8747	0.2955	1.0845
H(8B)	0.7878	0.3517	0.8323
H(9A)	0.9070	0.2749	0.6380
H(11A)	0.8576	0.3413	0.3996
H(11B)	0.7701	0.3700	0.4989
H(12A)	0.9844	0.3989	0.5005
H(12B)	0.8906	0.4466	0.4376
H(14A)	0.9890	0.3654	0.8063
H(15A)	0.9792	0.4045	1.0855
H(15B)	0.8835	0.4465	1.0440
H(16A)	1.0758	0.4949	0.9583
H(16B)	0.9818	0.5284	0.9632
H(17A)	1.0534	0.4869	0.6976
H(18A)	0.8027	0.5346	0.6169
H(18B)	0.7542	0.4665	0.7080
H(18C)	0.8155	0.5105	0.8208
H(19A)	0.6498	0.2813	0.4748
H(19B)	0.6504	0.3008	0.6688
H(19C)	0.6058	0.2172	0.6233
H(21A)	1.0027	0.6431	0.4443
H(21B)	0.9270	0.5713	0.3992
H(21C)	1.0317	0.5679	0.4633

Description of the structure

Bond lengths and angles

Bond lengths and bond angles between all atoms, excluding the hydrogen atoms, are shown schematically in Fig. 2(a) and (b); the estimated standard deviations are 0.004 to 0.009 Å and 0.4 to 0.5°, respectively. Bond lengths involving hydrogen atoms have standard devi-

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

	x/a	y/b	z/c	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	0.7985	0.1868	0.4611	0.0680	0.0371	0.0450	-0.0067	-0.0032	-0.0053
C(2)	0.7353	0							

ations lying between 0.03 and 0.07 Å and bond angles of the types H-C-C and H-C-H, have standard deviations of 2.0 to 4.0° and 4.0 to 7.0°, respectively.

Taking the average estimated standard deviation (0.007 Å) into account, it is apparent that all the single bonds of the type $C(sp^3)-(sp^3)$ in the 6 β -bromo progesterone molecule are not equivalent and that five out of sixteen of them [C(6)-C(7)=1.495 Å, C(9)-C(10)=1.571 Å, C(10)-C(1)=1.560 Å, C(10)-C(19)=1.553 Å, and C(11)-C(12)=1.557 Å] deviate by more than three standard deviations from the expected value of 1.533 ± 0.003 Å (Bonham & Bartell, 1959). In particular, the bond C(6)-C(7) is shorter and C(9)-C(10) is longer, each by as much as six times the estimated standard deviation. The bond between C(6) and Br with a length of 1.990 Å appears to be normal*. All other bond distances appear to be normal.

Torsional angles

Important torsional angles calculated for this molecule are listed in Table 3. The Δ^4 bond causes the torsional angle $\theta(4,5)$ to assume practically an eclipsed configuration; $\theta(4,5)$ is $+0.7^\circ$ (estimated standard deviation is 0.6°). The torsional angle $\theta(3,4)$ with a value of $+3.7^\circ$ is also influenced by the Δ^4 bond in addition to the double bond between C(3) and O(3). These two double bonds also affect the two torsional angles $\theta(2,3)$ and $\theta(5,10)$ in the A ring, whose values are $+21.9^\circ$ and -28.7° respectively, less than half the value for the symmetrically staggered configuration. Angles $\theta(5,10)$ and $\theta(5,6)$ reveal the transmitted distortion in the B ring caused primarily by the bromine atom. These two angles, with values of $+33.8^\circ$ and -36.9° respectively, are just about midway between the values for the eclipsed and the symmetrically staggered configurations. The torsional angles in the C ring are those expected for the symmetrically staggered configuration, indicating that the C ring is virtually strain-free. In the D ring $\theta(15,16)$ is $+9.2^\circ$ and $\theta(16,17)$ is $+18.8^\circ$, whereas in the ideal half-chair conformation of cyclopentane, $\theta(15,16)$ is equal to $\theta(16,17)$, and is approximately $+16^\circ$ (Brutcher & Leopold, 1966).

* Though a value of 1.937 ± 0.003 is listed in *International Tables* (1962), values between 1.990 and 2.005 Å have been obtained in nine out of twelve instances in our work on the structures of brominated steroids. In only three instances is the length smaller than 1.995 Å.

When viewed from the top, as in Fig. 3(a), the methyl group attached to C(10) is rotated anti-clockwise by about 18° from the symmetrically staggered configuration. This rotation keeps the non-bonded atoms Br and H(19B) at a reasonable distance from one another, namely, 3.10 Å or just about the normal van der Waals distance. The methyl group attached to C(13) is almost in the symmetrically staggered configuration, as shown

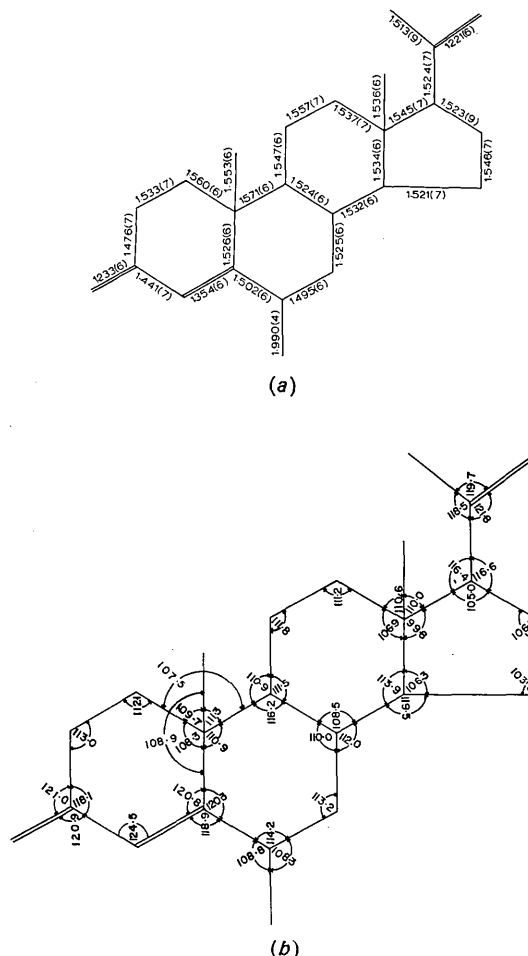


Fig. 2. Interatomic distances (a), and angles (b), in the steroid molecule. Standard deviations are given in parentheses for the distances, and are the range 0.4–0.5° for angles.

Table 3. Torsion angles in the steroid nucleus

$\theta(A-B)$ is the torsion 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)	-50.7	C(5)-C(6)	-36.9	C(8)-C(9)	-54.5	C(13)-C(14)	45.2
C(2)-C(3)	21.9	C(6)-C(7)	47.6	C(9)-C(11)	54.0	C(14)-C(15)	-34.2
C(3)-C(4)	3.7	C(7)-C(8)	-57.7	C(11)-C(12)	55.5	C(15)-C(16)	9.2
C(4)-C(5)	0.7	C(8)-C(9)	56.0	C(12)-C(13)	56.7	C(16)-C(17)	18.8
C(5)-C(10)	-28.7	C(9)-C(10)	-43.4	C(13)-C(14)	-60.9	C(13)-C(17)	-38.9
C(1)-C(10)	52.6	C(5)-C(10)	33.8	C(8)-C(14)	60.2		

in Fig.3(b). In this case, four of the torsional angles conform closely to the 60° value of the symmetrically staggered configuration. The other two angles [$\theta[17, 13, 18, H(18A)]$ and $\theta[17, 13, 18, H(18C)]$], however, with values of $+71.7^\circ$ and -52.0 , deviate from that which is expected for the symmetrically staggered configuration. This has been caused by C(17), which, being a part of a five membered ring, is pulled further toward C(14), resulting in an increase of $\theta[17, 13, 18, H(18A)]$ and a decrease of $\theta[17, 13, 18, H(18C)]$. The methyl group attached to C(20) has an approximately symmetrically staggered configuration with respect to C(17) (rotated

by approximately 10° from the symmetrically staggered configuration, apparently due to the interaction between the methyl group attached to C(20) and the one attached to C(13)].

Least squares planes

Tables 4, 5 and 6 show respectively the equations of the least-squares planes through various portions of the molecule, the perpendicular distances of atoms from these planes, and the dihedral angles. The A ring is highly distorted because of the double bond between C(4) and C(5). The six atoms C(3), C(4), C(5), C(6), (10), and H(4) are coplanar to within 0.004 \AA compared to the estimated standard deviation in their positions of about 0.006 \AA for carbon atoms and larger for hydrogen atoms. Rings B and C are chair shaped. The A⁴ bond has transmitted a certain amount of distortion to the B-ring as well. The atom C(5) is pulled closer to the mean plane of the B ring and is at a distance of 0.097 \AA compared to the value of 0.256 \AA in a strain free cyclohexane ring. As a result of C(5) coming nearer to the mean plane of the B ring, the atom C(8), situated on the opposite side of the B ring, is slightly pushed away from that plane and is at a distance of 0.283 \AA from it. The rings C and D appear to be normal and are little affected by the distortions in rings A and B. The D ring is a distorted half-chair. As compared with the conformation of the D ring in $2\beta,3\alpha$ -dichloro- 5α -cholestane (Brutcher & Leopold, 1966), $11\beta,12\alpha$ -dibromo- $3\alpha,9$ -epoxy cholanolic acid methyl ester (Gopalakrishna, Cooper & Norton, 1969) and $11\beta,12\beta$ -dibromo- $3\alpha,9$ -epoxycholanolic acid methyl ester (Gopalakrishna, *et al.* 1969), where it is also a distorted half-chair, the D-ring in the present steroid is more distorted. The four atoms C(17), C(20), C(21), and O(20) in the side chain of the molecule, lie exactly in a plane. All the ring system junctions are *trans* fused. The two methyl group bonds, C(10)–C(19) and C(13)–C(18), are not parallel, but are inclined at an angle of 17.8° to each other.

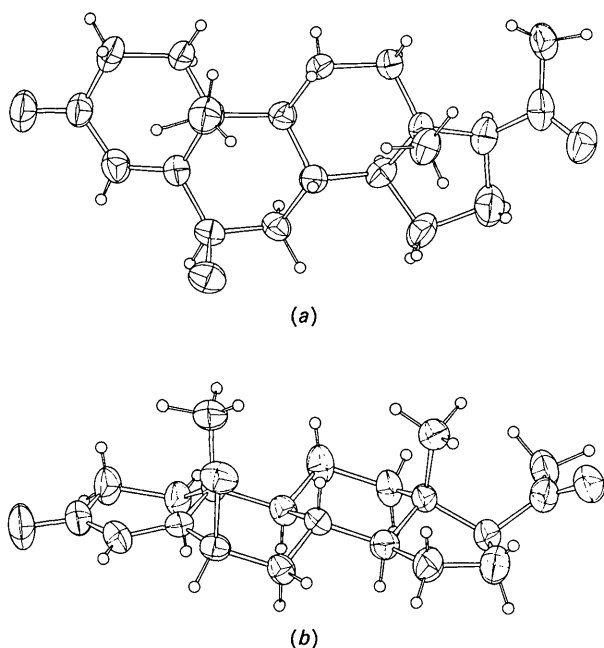


Fig.3. Two perspective views of the molecule, including the 50% probability thermal ellipsoids of the non-hydrogen atoms.

Table 4. Least-squares planes through the atoms

The planes are of the form $lX + mY + nZ = p$, where X , Y , Z and p are in \AA units relative to the crystal axes.

Plane	Atoms included	l	m	n	p
A1	C(2), C(3), C(4)	0.9706	-0.2262	-0.0324	8.8202
A2	C(1), C(2), C(4), C(5)	0.9141	-0.4044	0.0297	8.3635
A3B1	C(1), C(5), C(6), C(10)	0.9856	0.1671	0.0244	11.0848
B2	C(6), C(7), C(9), C(10)	0.7310	-0.6608	-0.1704	3.8899
B3C1	C(7), C(8), C(9), C(11)	0.9907	0.1204	-0.0635	11.6086
C2	C(8), C(11), C(12), C(14)	0.7108	-0.6828	-0.1691	2.8793
C3D1	C(12), C(13), C(14), C(15)	0.9894	0.0587	-0.1331	11.9750
D2	C(13), C(15), C(16), C(17)	0.7199	-0.6643	-0.2013	2.3203
D3	C(14), C(15), C(16), C(17)	0.8860	-0.4637	-0.0023	7.6597
A	C(1), C(2), C(3), C(4), C(5), C(10)	0.9691	-0.2441	0.0359	9.3573
B	C(5), C(6), C(7), C(8), C(9), C(10)	0.8726	-0.4628	-0.1562	6.4047
C	C(8), C(9), C(11), C(12), C(13), C(14)	0.8941	-0.4264	-0.1372	6.9462
D	C(13), C(14), C(15), C(16), C(17)	0.8362	-0.5103	-0.2008	5.2277
E	C(17), C(20), C(21), O(20)	0.9961	0.0772	0.0419	14.3213
F	C(10), C(13), C(18), C(19)	-0.0692	-0.1431	0.9873	3.2801
G	C(3), C(4), C(5), C(6), C(10)	0.9785	-0.1668	-0.1218	8.7929
C(1)–C(17)		0.9096	-0.4051	-0.0923	7.6474

Table 5. Perpendicular distances of atoms (\AA) from the least squares planes

Atom	A2	A3B1	B2	B3C1	C2	C3D1	D2	D3	A	B	C	D	E	F	G	C(1)-C(17)
C(1)	0.134	0.143							0.329						0.099	0.399
C(2)	-0.135								-0.190						-0.099	0.152
C(3)	0.150								-0.029						0.003	0.285
C(4)	0.154								0.106						-0.004	0.136
C(5)	-0.154	-0.219	0.401						0.025	0.097					0.001	-0.188
C(6)		0.173	-0.012						-0.147	-0.147					0.002	-0.302
C(7)			0.013						0.239	0.239						0.186
C(8)			-0.670						-0.283	-0.283	-0.239					-0.352
C(9)			-0.012	0.658					0.225	0.225	0.219					0.030
C(10)	-0.557	-0.098	0.012						-0.241	-0.131				0.098	-0.001	-0.442
C(11)				0.016							-0.223					-0.443
C(12)				-0.013							0.239					0.065
C(13)				-0.721	0.083						-0.259	-0.277		-0.099		-0.357
C(14)				0.013	-0.087	-0.069	-0.666				0.264	0.260				0.192
C(15)					-0.078	0.614	0.035					-0.135				0.037
C(16)					0.082	0.069	-0.054					0.032				0.278
C(17)						-0.111	0.054					0.183	-0.000			0.324
C(18)						0.110	-0.036							0.093		-1.882
C(19)														-0.092		-1.952
C(20)													0.001			-0.258
C(21)													-0.000			-0.129
O(20)													-0.000			-0.824
H(4)															-0.003	-0.239

Table 6. Dihedral angles

Plane 1	Plane 2	Angle
A1	A2	12.5°
A2	A3B1	33.5
A3B1	B2	52.7
B2	B3C1	49.1
B3C1	C2	50.8
C2	C3D1	46.7
C3D1	D2	45.6
C3D1	D3	31.8
A	B	17.6
B	C	2.7
C	D	6.9
D	E	38.3
A	C(1)-C(17)	28.2
B	C(1)-C(17)	2.5
C	C(1)-C(17)	6.2
D	C(1)-C(17)	3.6
E	C(1)-C(17)	29.4
F	C(1)-C(17)	95.5

Dihedral angles

The mean plane of the *A* ring makes an angle of 17.6° with that of the *B* ring. The mean planes of the *B* and *C* rings have a dihedral angle of only 2.7°, and the dihedral angle between *C* and *D* is 6.9°. The plane containing the three atoms of the side chain and C(17) is inclined to the mean plane of the nucleus at an angle of 29.4°. The inclination of the *A* ring to the mean plane of the main nucleus is 28.2°, that of the *B* ring 2.5°, that of the *C*-ring 6.2°, and that of the *D* ring is 3.6°. These angular relationships show that the three ring systems *B*, *C*, and *D* are almost parallel to each other, whereas the *A* ring is inclined by about 20° to the rest of the nucleus.

The length of the nucleus of the steroid molecule, calculated as the distance between C(3) and C(16), is 8.998 Å, and is similar to the lengths of the nuclei of other steroids considered thus far (Norton, 1965).

Molecular packing

Fig. 4(a) and (b) show two axial projections of the crystal structure. There are only thirteen inter-molecular contacts shorter than 4.0 Å when hydrogen atoms are ignored. These are listed in Table 7. Out of these, three are between the bromine atom of one molecule and the atoms of the side chain of the neighboring molecule, and another six contacts are between O(3) of one molecule and the atoms C(2), C(4), C(17), C(19), C(20), and C(21) of the neighbouring molecules. The contact between the bromine atom and O(20) has an unusually short distance of 3.191 Å and is the shortest contact in this structure when hydrogen atoms are ignored. The molecules are packed such that their mean planes are nearly perpendicular to the (001) plane and, as a result, molecules related by the *c*-screw axis are parallel to each other.

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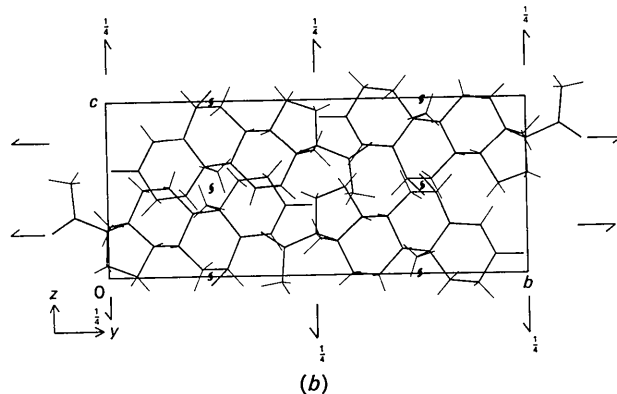
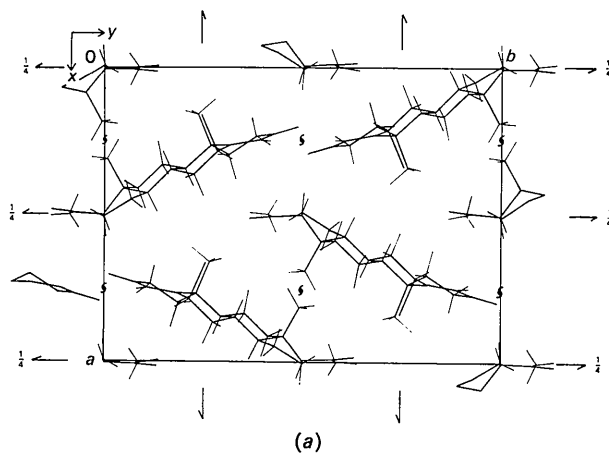


Fig. 4. Projection of one unit cell (a) onto the (001) plane and (b) onto the (100) plane.

Table 7. Intermolecular contacts less than 4.0 Å between carbon and heavier atoms

Atom 1	Atom 2	Position*	Distance
Br	C(1)	1/001	3.805 (5) Å
Br	C(2)	1/001	3.993 (5)
Br	C(20)	2/110	3.763 (5)
Br	C(21)	2/110	3.679 (5)
Br	O(20)	2/110	3.191 (4)
O(3)	C(2)	2/100	3.576 (6)
O(3)	C(4)	2/10 $\bar{1}$	3.439 (6)
O(3)	C(17)	3/ $\bar{1}$ 01	3.787 (8)
O(3)	C(20)	3/ $\bar{1}$ 01	3.820 (6)
O(3)	C(21)	3/ $\bar{1}$ 01	3.326 (6)
O(20)	C(19)	2/110	3.803 (6)
C(1)	C(6)	1/00 $\bar{1}$	3.856 (7)
C(12)	C(15)	1/00 $\bar{1}$	3.975 (7)

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

References

- APPLEZWEIG, N. (1962). *Steroid Drugs*. New York: McGraw Hill.
- BONHAM, R. A. & BARTELL, L. S. (1959). *J. Amer. Chem. Soc.* **81**, 3491.
- BRUTCHER, V. & LEOPOLD, E. J. (1966). *J. Amer. Chem. Soc.* **88**, 3156.
- GOPALAKRISHNA, E. M., COOPER, A. & NORTON, D. A. (1969). To be published.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- NORTON, D. A. (1965). *Biophys. J.* **5**, 425.
- SONDHEIMER, F., KAUFMANN, S., ROMO, J., MARTINEZ, H. & ROSENKRANZ, G. (1953). *J. Amer. Chem. Soc.* **75**, 4712, 4715.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.

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The Crystal Structure of Potassium Mercuric Tribromide Monohydrate, $\text{KHgBr}_3 \cdot \text{H}_2\text{O}$

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The crystal structure of potassium mercuric tribromide monohydrate has been determined by X-ray diffraction techniques. The structure consists of four molecules linked by hydrogen bonds and van der Waals forces, in a unit cell of $Cmc2_1$ symmetry, and of dimensions $a = 4.37$, $b = 16.87$ and $c = 10.14$ Å. The mercury atom is surrounded by four bromine atoms in an irregular tetrahedron. The bromine atoms at $x = \frac{1}{2}$ and $-\frac{1}{2}$ are shared, resulting in a zigzag chain of Br-Hg-Br-Hg atoms along the a axis. The other bromine atoms are held by hydrogen bonds of the water molecule.

Introduction

While making a survey of the literature for structures having hydrogen bonded bromine atoms, the authors

became interested in the crystal structure of potassium mercuric tribromide monohydrate. Unit-cell dimensions were determined by Herak, Manojilic & Malcis (1963) but no complete structure analysis has yet been