The Crystal and Molecular Structures of 4-Bromoestradiol

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The crystal and molecular structures of 4-bromoestradiol have been determined by three-dimensional X-ray crystallographic methods. Crystals of 4-bromoestradiol obtained from a methanol solution belong to the space group $P2_12_12_1$ and have four bromoestradiol molecules per unit cell ($a = 12\cdot672$, $b = 22\cdot474$, $c = 6\cdot325$ Å, all $\pm0\cdot004$ Å). One methanol molecule is associated with each steroid molecule.

Bond lengths and angles have been calculated and are consistent with the currently accepted values for carbon–carbon systems. 'Best' plane equations have been calculated for the entire molecule and for various portions thereof. The root mean square distance of atoms from the 'best' plane of the entire molecule is 0·241 Å. Smaller root mean square distances are obtained by referring the atoms to the 'best' planes of the various subdivisions of the ring system. A hydrogen bond system involving the phenolic oxygen (O3), the hydroxyl oxygen (O17), and the methanol oxygen stabilizes the position of the methanol group and causes the formation of quasi-polymeric 4-bromo-estradiol chains parallel to the x direction. Numerous medium range van der Waals contacts are present.

Introduction

Estradiol ($C_{18}H_{24}O_2$), an estrogenic hormone which is produced in women by the ovaries, controls the development of the female sexual characteristics, and initiates the first phase of the menstrual cycle. Estradiol is important in the study and treatment of cancer. It is used chiefly in replacement therapy in cases of estrogen deficiency, and in the treatment

Fig. 1. 4-Bromoestradiol.

of breast and prostate cancers and their metastases. Estradiol has been found to produce tumors in various test animals, but the relationship between estradiol and cancer is none too clear, and is, in fact paradoxical. In animals, small doses of estradiol stimulate tumor growth, while large doses inhibit growth.

The structural investigation herein reported was undertaken to supply a detailed description of the molecular architecture of the estradiol molecule, in the form of its monobromo derivative (Fig. 1), with the hope that this information will ultimately increase our understanding of the estrogens, and help to elucidate the now seemingly inconsistent relationship between estradiol and cancer.
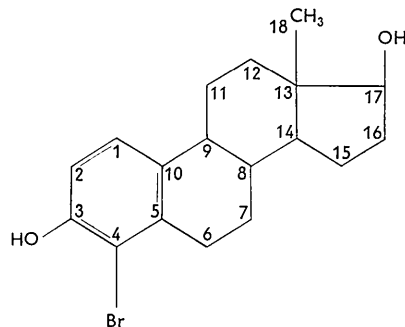
Crystal data

The crystal data for estradiol ($C_{18}H_{24}O_2$), and for 4-bromoestradiol, which has associated with it one methanol molecule per molecule ($C_{18}H_{23}O_2Br \cdot CH_3OH$), are given in Table 1. Systematic absences and optical activity data were used to establish the space groups of estradiol ($P2_12_12$) and 4-bromoestradiol ($P2_12_12_1$).

Table 1. *Crystal data for estradiol and 4-bromoestradiol*

	Space group	a	b	c	V	D_m	D_x	Z
		(in Å $\pm0\cdot004$)						
Estradiol	$P2_12_12$	12·054	19·282	6·634	1541 Å³	1·197 g.cm⁻³	1·173 g.cm⁻³	4
4-Bromoestradiol (with one methanol molecule per molecule of steroid)	$P2_12_12_1$	12·672	22·474	6·325	1801	1·413	1·413	4

Experimental measurements

A small prismatic crystal of 4-bromoestradiol, approximately 0·3 mm in diameter, was selected for the experimental measurements. Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å) was used to measure the intensities of all reflections (2350) with 2θ values less than 164°, the positions of which had been previously calculated on an IBM 650 computer. Measurements were made with a General Electric XRD 5 X-ray diffraction unit by the stationary crystal method and the balanced filter technique. Geometrical corrections were applied, and all the intensities were converted into structure amplitudes of reflections on an IBM 650 computer.

A table of observed and calculated structure factors is available from the authors upon request.

Structure determination

The structure amplitudes were used in preparing a sharpened three-dimensional Patterson synthesis with an IBM 704 computer. This synthesis gave the bromine coordinates, $x = 0\cdot205$, $y = 0\cdot190$, $z = 0\cdot233$, referred to the conventional origin given in the *International Tables for X-Ray Crystallography* (1952), namely, midway between the three non-intersecting screw axes.

The bromine phases were calculated for all the reflections. With these phases a three-dimensional electron density projection was made, involving all reflections for which the bromine contribution was not near zero, *i.e.* using about 95% of the data within the copper sphere. The resulting Fourier synthesis showed far too many peaks. This was due to the

bromine Z coordinate being very near to $\frac{1}{4}$, causing all the bromine atoms to lie at either $\frac{1}{4}$ or $\frac{3}{4}$, the result being that the phase angle distribution of the bromine contributions was concentrated near $n\pi/2$, where n is an integer. The effect of this was to create an adventitious pseudo-reflection plane in the Fourier synthesis, almost doubling all peaks. However, it was possible to locate the major portion (16 atoms out of 21) of the 4-bromoestradiol molecules with atoms located at some of these peaks from stereochemical considerations. It was difficult, however, to arrive at a definite decision regarding the remaining atoms. One cycle of structure factor calculation, based on the part of the molecule that had been located, followed by a three-dimensional Fourier synthesis cleared up most of the uncertainties regarding the remaining atoms in the molecule. Another cycle of structure factor calculation followed by another Fourier synthesis located all the atoms of the molecule without ambiguity, but gave an unsatisfactory R index of approximately 20%. The Fourier synthesis also showed two peaks close to each other, but well separated from the steroid molecule. These peaks did not disappear, as did the other extra peaks which were due to the doubling effect mentioned above. A three-dimensional difference Fourier synthesis also confirmed the reality of these two peaks. It was assumed at this point, therefore, that these peaks represented a molecule of solvent of crystallization, the solvent having two light non-hydrogen atoms with a covalent bond distance of about 1·4 Å. Since the only possibility was a methanol molecule, it was assumed that one of the peaks corresponded to an oxygen atom and the other to a carbon atom.

Table 2. *Progress made in the final stages of least-squares refinement (Å) of 4-bromoestradiol*

	Cycle 2			Cycle 3			Cycle 4 (Final)		
	Δx (Å)	Δy (Å)	Δz (Å)	Δx (Å)	Δy (Å)	Δz (Å)	Δx (Å)	Δy (Å)	Δz (Å)
Br	0·0001	0·0000	$\overline{0\cdot0002}$	0·0000	0·0000	$\overline{0\cdot0001}$	0·0000	0·0000	$\overline{0\cdot0002}$
C(1)	0·0002	$\overline{0\cdot0001}$	0·0017	0·0000	0·0000	0·0013	$\overline{0\cdot0001}$	$\overline{0\cdot0001}$	$\overline{0\cdot0022}$
C(2)	$\overline{0\cdot0015}$	0·0002	0·0016	$\overline{0\cdot0008}$	0·0000	$\overline{0\cdot0001}$	0·0005	$\overline{0\cdot0001}$	0·0010
C(3)	$\overline{0\cdot0002}$	$\overline{0\cdot0002}$	$\overline{0\cdot0032}$	$\overline{0\cdot0002}$	$\overline{0\cdot0001}$	$\overline{0\cdot0003}$	0·0001	0·0001	0·0001
C(4)	0·0001	0·0000	0·0001	0·0000	$\overline{0\cdot0002}$	0·0002	0·0004	0·0001	0·0014
C(5)	$\overline{0\cdot0001}$	$\overline{0\cdot0005}$	0·0001	$\overline{0\cdot0001}$	$\overline{0\cdot0005}$	0·0006	0·0000	$\overline{0\cdot0003}$	0·0010
C(6)	$\overline{0\cdot0001}$	$\overline{0\cdot0002}$	$\overline{0\cdot0049}$	$\overline{0\cdot0002}$	$\overline{0\cdot0004}$	$\overline{0\cdot0018}$	$\overline{0\cdot0009}$	0·0003	0·0029
C(7)	0·0005	$\overline{0\cdot0006}$	$\overline{0\cdot0020}$	0·0005	$\overline{0\cdot0005}$	0·0003	0·0002	0·0009	0·0015
C(8)	$\overline{0\cdot0007}$	$\overline{0\cdot0004}$	$\overline{0\cdot0033}$	$\overline{0\cdot0003}$	0·0002	$\overline{0\cdot0004}$	0·0001	$\overline{0\cdot0006}$	0·0009
C(9)	0·0003	$\overline{0\cdot0001}$	0·0036	0·0001	$\overline{0\cdot0001}$	0·0012	0·0003	0·0002	$\overline{0\cdot0010}$
C(10)	$\overline{0\cdot0001}$	0·0003	0·0027	$\overline{0\cdot0001}$	0·0003	0·0000	$\overline{0\cdot0001}$	0·0002	$\overline{0\cdot0018}$
C(11)	0·0001	0·0010	0·0058	0·0000	0·0007	0·0017	$\overline{0\cdot0002}$	$\overline{0\cdot0003}$	0·0000
C(12)	0·0001	0·0003	0·0039	0·0000	0·0000	0·0002	0·0006	0·0007	0·0022
C(13)	0·0002	0·0003	$\overline{0\cdot0039}$	0·0001	0·0003	$\overline{0\cdot0015}$	$\overline{0\cdot0003}$	0·0000	0·0010
C(14)	0·0004	$\overline{0\cdot0007}$	$\overline{0\cdot0055}$	0·0003	$\overline{0\cdot0003}$	$\overline{0\cdot0013}$	0·0002	0·0003	$\overline{0\cdot0006}$
C(15)	0·0010	0·0000	0·0038	0·0002	$\overline{0\cdot0001}$	0·0009	$\overline{0\cdot0009}$	0·0008	0·0068
C(16)	$\overline{0\cdot0008}$	0·0005	$\overline{0\cdot0028}$	$\overline{0\cdot0002}$	0·0002	$\overline{0\cdot0004}$	0·0009	$\overline{0\cdot0002}$	$\overline{0\cdot0048}$
C(17)	$\overline{0\cdot0008}$	0·0006	0·0063	$\overline{0\cdot0003}$	0·0005	0·0025	0·0000	$\overline{0\cdot0004}$	0·0032
C(18)	$\overline{0\cdot0004}$	0·0001	0·0009	$\overline{0\cdot0001}$	0·0002	$\overline{0\cdot0003}$	$\overline{0\cdot0001}$	0·0005	0·0012
O(3)	0·0006	0·0004	$\overline{0\cdot0029}$	0·0003	0·0003	$\overline{0\cdot0006}$	$\overline{0\cdot0005}$	0·0004	$\overline{0\cdot0010}$
O(17)	$\overline{0\cdot0006}$	$\overline{0\cdot0003}$	0·0020	$\overline{0\cdot0002}$	$\overline{0\cdot0002}$	0·0010	$\overline{0\cdot0008}$	0·0002	0·0011
C(MeOH)	$\overline{0\cdot0002}$	$\overline{0\cdot0008}$	0·0083	$\overline{0\cdot0002}$	$\overline{0\cdot0004}$	0·0036	0·0002	0·0009	$\overline{0\cdot0005}$
O(MeOH)	0·0003	0·0010	0·0026	0·0004	0·0008	0·0013	$\overline{0\cdot0011}$	0·0003	0·0020
Mean $\Delta x, y, z$	0·0004 Å	0·0004 Å	0·0031 Å	0·0002 Å	0·0003 Å	0·0009 Å	0·0004 Å	0·0003 Å	0·0017 Å

Table 3. *Final fractional atomic coordinates, standard deviations, and temperature factors of* 4-*bromoestradiol*

| | B | X | Y | Z | Standard deviations (Å) | | |
					$\sigma(ax)$	$\sigma(by)$	$\sigma(cz)$
Br	3·677	$0·204_2$	$0·188_3$	$0·242_9$	0·001	0·001	0·001
C(1)	3·491	$0·477_1$	$0·389_9$	$0·256_1$	0·008	0·008	0·007
C(2)	3·989	$0·085_0$	$0·103_3$	$0·713_2$	0·009	0·009	0·008
C(3)	3·511	$0·153_5$	$0·129_7$	$0·859_6$	0·008	0·008	0·007
C(4)	3·245	$0·108_1$	$0·159_7$	$0·028_8$	0·007	0·007	0·006
C(5)	2·765	$0·002_1$	$0·169_1$	$0·056_4$	0·007	0·006	0·006
C(6)	3·647	$0·463_5$	$0·293_7$	$0·758_8$	0·009	0·008	0·007
C(7)	3·300	$0·344_3$	$0·278_6$	$0·782_9$	0·008	0·007	0·007
C(8)	3·276	$0·281_9$	$0·335_2$	$0·836_7$	0·008	0·007	0·007
C(9)	3·283	$0·312_6$	$0·353_8$	$0·066_0$	0·008	0·007	0·006
C(10)	3·499	$0·433_4$	$0·359_6$	$0·089_2$	0·008	0·008	0·007
C(11)	4·040	$0·254_7$	$0·412_7$	$0·124_5$	0·009	0·009	0·008
C(12)	3·777	$0·131_7$	$0·407_2$	$0·102_3$	0·009	0·008	0·007
C(13)	3·154	$0·103_5$	$0·385_0$	$0·879_6$	0·007	0·007	0·006
C(14)	3·387	$0·162_3$	$0·326_4$	$0·839_1$	0·008	0·008	0·007
C(15)	4·190	$0·110_4$	$0·300_5$	$0·633_8$	0·010	0·009	0·008
C(16)	4·735	$0·491_5$	$0·179_2$	$0·340_0$	0·011	0·010	0·009
C(17)	3·749	$0·489_9$	$0·138_4$	$0·139_0$	0·009	0·008	0·008
C(18)	3·937	$0·123_9$	$0·434_1$	$0·712_7$	0·009	0·009	0·008
O(3)	4·007	$0·260_0$	$0·122_6$	$0·849_4$	0·007	0·006	0·006
O(17)	3·749	$0·489_9$	$0·138_4$	$0·139_0$	0·009	0·008	0·008
C(MeOH)	6·116	$0·379_5$	$0·004_0$	$0·640_9$	0·015	0·014	0·013
O(MeOH)	6·274	$0·334_4$	$0·055_5$	$0·548_7$	0·010	0·010	0·010

This assumption also introduced the possibility of a stabilizing hydrogen bond system, which was later verified.

The addition of the two atoms of the methanol group to the twenty-one main atoms of the 4-bromoestradiol molecule gave a final R value of 0·13 after four cycles of IBM 7090 diagonal least-squares refinement (Van den Hende, 1961) using all of the 2350 reflections. There were no accidentally absent reflections, hence all of the reflections measured (2350), weak or strong, were treated the same in the least squares refinement. Table 2 shows the progress made in the final stages of the refinement of the structure of 4-bromoestradiol. An electron density projection down the c axis gives the molecule with most of the atoms well resolved (Fig. 2). Table 3 lists the final fractional atomic coordinates, standard deviations, and temperature factors.
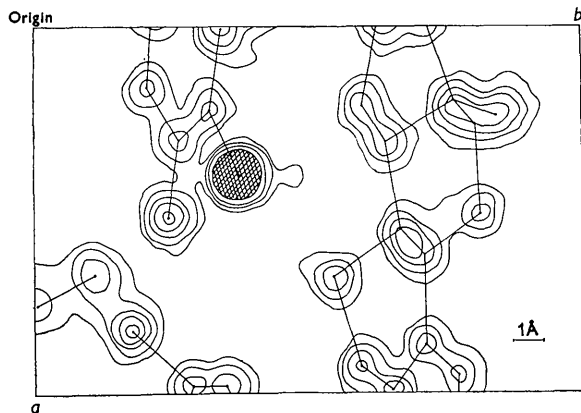

Fig. 2. Projection of the electron density of 4-bromoestradiol down the c axis.

Discussion

Table 4 lists the bond lengths and bond angles of 4-bromoestradiol. Routine statistical treatment of carbon–carbon single-bond lengths and of the carbon–carbon bond lengths in the A-ring (aromatic) gave standard deviations of 0·032 and 0·017 Å respectively. The weighted bond length standard deviation is 0·028 Å. Since less than one-third of the bond values obtained for each of the two types of carbon–carbon bonds lie outside of the appropriate σ range, no unusually long or short carbon bonds are proved to be present in the molecule. As in the case of 4-bromoestrone (Norton, Kartha & Lu, 1962), the standard deviation (σ) obtained herein by statistical treatment $(\sigma = (\overline{X^2} - \overline{X}^2)^{\frac{1}{2}})$ is greater than that arrived at using the Cruickshank formula (Cruickshank, 1949), being approximately four times as large for 4-bromoestradiol. The estimated standard deviation for the bond angles is 1·20 degrees.

Table 5 gives the coefficients in the equations of the mean planes of 4-bromoestradiol calculated by the method of Schomaker, Waser, Marsh & Bergman (1959). The planarity of the entire molecule is described by a root mean square distance of 0·241 Å of all the carbon atoms (excluding C18) from the best plane of the molecule

$$(0·150x + 0·733y - 0·635z - 2·543 = 0) \ .$$

The root mean square distances of atoms from rings A, B, C, D are 0·025, 0·228, 0·257, and 0·219 Å respectively. Shorter root mean square distances are obtained by further dividing the ring system (with the exception of ring A) as shown in Table 6. The perpendicular distances of each atom from the one

Table 4. *Bond lengths and bond angles in 4-bromoestradiol*

Bond lengths

C(1)–C(2)	1·389 Å
C(2)–C(3)	1·400
C(3)–C(4)	1·390
C(3)–O(3)	1·362
C(4)–C(5)	1·371
C(4)–Br	1·931
C(5)–C(10)	1·423
C(10)–C(1)	1·373
C(5)–C(6)	1·518
C(6)–C(7)	1·556
C(7)–C(8)	1·536
C(8)–C(9)	1·559
C(9)–C(10)	1·544
C(9)–C(11)	1·557
C(11)–C(12)	1·570
C(12)–C(13)	1·536
C(13)–C(14)	1·534
C(14)–C(8)	1·528
C(14)–C(15)	1·566
C(15)–C(16)	1·584
C(16)–C(17)	1·568
C(17)–C(13)	1·537
C(17)–O(17)	1·479
C(13)–C(18)	1·594

Methanol molecule

C–O	1·415

Bond angles

C(1)–C(2)–C(3)	118·9°
C(2)–C(3)–C(4)	118·6
C(3)–C(4)–C(5)	123·0
C(4)–C(5)–C(10)	119·1
C(5)–C(10)–C(1)	118·6
C(10)–C(1)–C(2)	123·0
C(3)–C(4)–Br	116·9
Br–C(4)–C(5)	118·5
C(2)–C(3)–O(3)	122·7
C(4)–C(3)–O(3)	120·8
C(10)–C(5)–C(6)	123·6
C(5)–C(6)–C(7)	110·1
C(6)–C(7)–C(8)	109·1
C(7)–C(8)–C(9)	107·6
C(8)–C(9)–C(10)	110·0
C(9)–C(10)–C(5)	120·5
C(8)–C(14)–C(13)	111·1
C(14)–C(13)–C(12)	113·8
C(13)–C(12)–C(11)	109·2
C(12)–C(11)–C(9)	112·7
C(11)–C(9)–C(8)	109·6
C(9)–C(8)–C(14)	105·2
C(12)–C(13)–C(18)	109·9
C(14)–C(15)–C(16)	101·1
C(15)–C(16)–C(17)	105·6
C(16)–C(17)–C(13)	104·5
C(17)–C(13)–C(18)	110·4
C(17)–C(13)–C(14)	98·5
C(13)–C(14)–C(15)	104·2
C(16)–C(17)–O(17)	110·3
C(13)–C(17)–O(17)	111·9
C(7)–C(8)–C(14)	113·3
C(8)–C(14)–C(15)	117·9
C(12)–C(13)–C(17)	113·7
C(1)–C(10)–C(9)	120·0
C(4)–C(5)–C(6)	119·1
C(10)–C(9)–C(11)	111·2
C(18)–C(13)–C(14)	116·6

Table 5. *Coefficients a, b, c, d, in the equations*
$$(ax + by + cz + d = 0)$$
of the best planes of 4-bromoestradiol

	a	b	c	d
Entire molecule	0·150	0·733	−0·635	−2·543
A	−0·009	0·857	−0·516	−3·325
B*	0·066	0·783	−0·618	−2·482
B1	−0·009	0·815	−0·579	−2·549
B2	−0·119	0·758	−0·641	−1·138
B3	0·756	0·560	−0·362	−4·970
C	0·286	0·702	−0·652	−2·570
C1	0·770	0·527	−0·358	−4·822
C2	−0·044	0·695	−0·717	−1·243
C3	0·773	0·511	−0·377	−3·339
D	0·178	0·686	−0·704	−1·932
D1	0·670	0·488	−0·559	−1·994
D2	−0·026	0·689	−0·725	−1·798
B3–C1	0·777	0·532	−0·335	−5·049
C3–D1	0·715	0·510	−0·479	−2·602

* B designates the entire ring B, C the entire C ring, D the entire D ring.

Table 6. *The root mean square distance* $(\sqrt{\lambda})$ *of the atoms from the best planes of 4-bromoestradiol*

	$\sqrt{\lambda}$
Entire molecule	0·241 Å
A	0·025
B	0·228
B1	0·000
B2	0·081
B3	0·000
C	0·257
C1	0·000
C2	0·040
C3	0·000
D	0·219
D1	0·000
D2	0·122
B3–C1	0·055
C3–D1	0·076

Table 7. *The perpendicular distances* (Å) *of individual atoms from one more of the mean planes*

	A	B	B1	B2	B3	C	C1	C2	C3	D	D1	D2	Entire molecule
C(1)	+0·031	—	—	—	—	—	—	—	—	—	—	—	−0·266
C(2)	+0·047	—	—	—	—	—	—	—	—	—	—	—	−0·072
C(3)	+0·010	—	—	—	—	—	—	—	—	—	—	—	+0·211
C(4)	−0·011	—	—	—	—	—	—	—	—	—	—	—	+0·311
C(5)	−0·087	+0·073	0·000	—	—	—	—	—	—	—	—	—	+0·066
C(6)	—	+0·108	0·000	+0·091	—	—	—	—	—	—	—	—	+0·125
C(7)	—	−0·352	—	−0·085	0·000	—	—	—	—	—	—	—	−0·450
C(8)	—	+0·382	—	—	0·000	+0·289	+0·003	+0·041	—	—	—	—	+0·149
C(9)	—	−0·162	—	+0·096	0·000	−0·252	+0·003	—	—	—	—	—	−0·410
C(10)	−0·003	−0·049	0·000	−0·082	—	—	—	—	—	—	—	—	−0·176
C(11)	—	—	—	—	—	+0·227	+0·004	−0·039	—	—	—	—	+0·216
C(12)	—	—	—	—	—	−0·214	—	+0·045	+0·001	—	—	—	−0·034
C(13)	—	—	—	—	—	+0·252	—	+0·001	+0·001	+0·315	0·000	+0·096	+0·458
C(14)	—	—	—	—	—	−0·292	—	+0·040	+0·001	−0·275	0·000	—	−0·232
C(15)	—	—	—	—	—	—	—	—	—	+0·123	0·000	−0·088	+0·067
C(16)	—	—	—	—	—	—	—	—	—	+0·052	—	+0·146	+0·071
C(17)	—	—	—	—	—	—	—	—	—	−0·219	—	−0·143	−0·069
C(18)	—	—	—	—	—	—	—	—	—	+1·894	+1·212	+1·658	+1·977
Br	+0·127	—	—	—	—	—	—	—	—	—	—	—	+0·885
O(3)	+0·102	—	—	—	—	—	—	—	—	—	—	—	+0·491
O(17)	—	—	—	—	—	—	—	—	—	−0·351	—	−1·298	+0·687
Methanol group													
C	—	—	—	—	—	—	—	—	—	—	—	—	+1·833
O	—	—	—	—	—	—	—	—	—	—	—	—	+0·528

or more best planes which contain it are listed in Table 7.

The geometry of the side groups of the 4-bromo-estradiol molecule may be described as follows:

(a) The bromine atom, which is attached to carbon four, lies at a distance of 0·127 Å from the best plane of ring A. The Br–C(4) bond makes an angle of 4·1° with the line of intersection of (1) the plane which is perpendicular to ring A and contains the Br–C(4) bond and (2) the plane of ring A. The bromine atom, therefore, has an equatorial configuration.

(b) The phenol oxygen atom, which is attached to C(3), is at a distance of 0·102 Å from the best plane of ring A. The O(3)–C(3) bond makes an angle of 3·4° with the line of intersection of (1) the plane perpendicular to ring A containing the O(3)–C(3) bond and (2) the plane of ring A. The phenolic oxygen, therefore, has an equatorial configuration.

(c) The hydroxyl oxygen atom (attached to C17) is 0·351 Å from the best plane of ring D. The O(17)–C(17) bond makes an angle of 27·7° with the line of intersection of (1) the plane perpendicular to ring D containing the O(17)–C(17) bond and (2) the plane of ring D. The hydroxyl oxygen atom, therefore, has an equatorial configuration.

(d) The methyl carbon atom (attached to C13) is 1·894 Å from the best plane of ring D. This distance approximately represents the sum of the C(13)–C(18) bond length (1·594 Å) and the perpendicular distance of C(13) (0·315 Å) to the best plane of ring D. A similar relationship exists between the methyl

carbon and the best plane of the entire molecule. The C(18)–C(13) bond makes an angle of 85·9° with the line of intersection of (1) the plane containing the C(18)–C(13) bond and perpendicular to ring D and (2) the plane of ring D. The methyl carbon atom, therefore, has an axial configuration.

The angles between the various portions of the intramolecular chair–chair configuration have been calculated and are listed in Table 8. It can be seen

Table 8. *The dihedral angles between best planes of 4-bromoestradiol*

Planes	Angle
A–B	171·6°
A–B1	175·2
B1–B2	171·1
B2–B3	124·4
B3–C	147·7
B3–C1	177·6
B–C	166·3
C1–C2	126·9
C2–C3	126·8
C3–D	138·2
C3–D1	167·7
C–D	172·8
D1–D2	136·6

that the chair of ring B is unsymmetrical, having intra-chair angles of 171·1 and 124·4 degrees. The ring C chair, on the other hand, is symmetrical with intra-chair angles of 126·9 and 126·8 degrees. B3 and C1 are almost the same plane, as is shown by an interplane angle of 178°. This is further illustrated
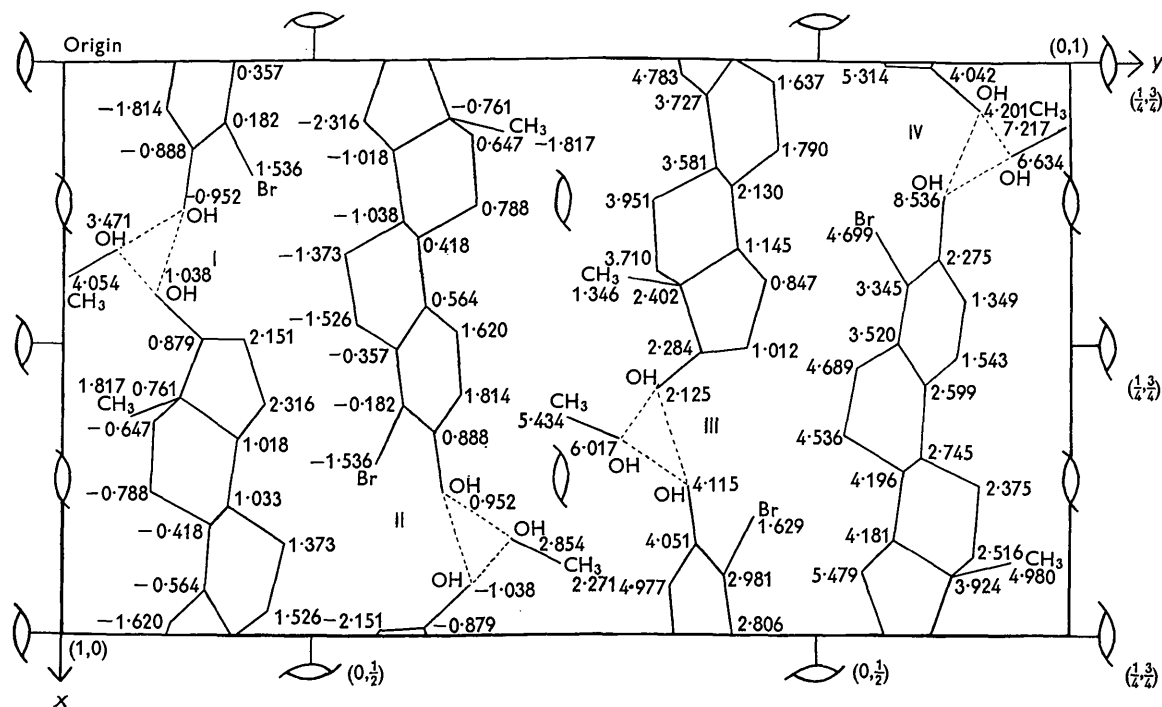

Fig. 3. 4-Bromoestradiol: stacking diagram.

by a root mean square distance of 0·055 Å of atoms C(7), C(8), C(9), and C(11) from the mean plane $B3-C1$ $(0·777x+0·532y-0·335z-5·049=0)$. Planes $C3$ and $D1$, however, are less similar in this respect, since they have an interplane angle of 167°, and since atoms C(12), C(13), C(14), and C(15) have a root mean square distance of 0·076 Å from the mean plane of $C3-D1$ $(0·715x+0·510y-0·479z-2·602=0)$.

The stacking diagram for 4-bromoestradiol parallel to the x-y plane is shown in Fig. 3. The numbers beside each atom represent the height of the atom along z. The molecules are joined together in quasi-polymeric chains parallel to the x axis by hydrogen bonds between O(3) and O(17) which are 2·87 Å long. The position of the methanol group is stabilized by

Table 9. *Distances of closest approach less than* 4·000 Å

x direction		z direction	
O(3)–O(17)	2·869	C(1)–C(6)	3·848
O(3)–O(methanol)	2·604	C(3)–O(methanol)	3·450
O(17)–O(methanol)	2·736	C(4)–C(14)	3·993
C(2)–C(methanol)	3·652	C(7)–Br	3·966
C(3)–O(17)	3·908	C(18)–C(12)	3·921
C(3)–C(methanol)	3·517	C(18)–C(11)	3·755
C(4)–C(methanol)	3·750	O(3)–C(methanol)	3·337
C(16)–Br	3·698	O(3)–C(7)	3·689
C(17)–Br	3·847	Br–C(2)	3·845
C(17)–O(methanol)	3·751	C(methanol)–O(17)	3·851
O(3)–C(17)	3·459		
O(3)–C(methanol)	3·823		

y direction	
C(6)–C(15)	3·756
C(6)–C(16)	3·709
C(7)–O(3)	3·689
C(12)–C(18)	3·921
Br–C(15)	3·727

two hydrogen bonds. One of these is 2·60 Å in length and joins the methanol oxygen atom to the phenolic oxygen atom, O(3). The other is 2·74 Å long and bonds the methanol oxygen atom to the hydroxyl oxygen atom, O(17). Numerous van der Waals interactions hold the molecules together in the x-, y-, and z-directions. Table 9 shows the various distances of closest approach less than 4·000 Å.

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Atomic Coordinates of AlPO₄

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The X-ray powder diffraction data on AlPO₄ have been obtained on a diffractometer. The system is found to be trigonal with cell constants $a = 4·941$ Å, $c = 10·95$ Å and space group $P3_121$. From the known similarity between AlPO₄ and α-quartz, the atomic coordinates have been determined to be

$$O(1): \quad x = 0·275, \quad y = 0·406, \quad z = 0·118$$
$$O(2): \quad x = 0·275, \quad y = 0·406, \quad z = 0·600$$
$$Al: \quad x = 0·500$$
$$P: \quad x = 0·500$$

The reliability index is 0·16.

Introduction

The study of compounds similar to quartz is a subject of considerable interest; Buerger (1948, 1954) has dis-

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cussed the physico-chemical basis of the structure of such compounds in detail. The structure of aluminum phosphate which is iso-electronic with quartz is of still greater interest. According to Buerger (1948), AlPO₄ is a half-breed derivative of quartz in which half of the Si positions are occupied by trivalent