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Structural Comparison of 1-Bromo- and 1-Fluoroestradiol with D-Estradiol

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Abstract. 1-Bromoestra-1,3,5(10)-trien-3,17β-diol, $C_{18}H_{23}BrO_2$, $M_r = 351{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}3864$ (12), $b = 12{\cdot}927$ (2), $c = 12{\cdot}948$ (2) Å, $V = 1571{\cdot}1$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}484$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 259$ mm^{-1}, $F(000) = 728$, $T = 298$ K, $R = 0{\cdot}0514$ for 2083 observed reflections. 1-Fluoroestra-1,3,5(10)-trien-3,17β-diol.0·5H_2O, $C_{18}H_{23}FO_2.0{\cdot}5H_2O$, $M_r = 299{\cdot}4$, orthorhombic, $P2_12_12$, $a = 12{\cdot}046$ (4), $b = 19{\cdot}358$ (5), $c = 6{\cdot}656$ (2) Å, $V = 1552{\cdot}1$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}28$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 86$ mm^{-1}, $F(000) = 644$, $T = 293$ K, $R = 0{\cdot}0776$ for 2781 observed reflections. Except for the carbon–halogen bond, bond angles and bond lengths of 1-bromoestradiol are within 7 e.s.d.'s of estradiol. Bond angles and bond lengths of 1-fluoroestradiol are within 11 and 7 e.s.d.'s of estradiol, respectively. The molecular conformations are nearly identical to that of estradiol. Like estradiol, 1-fluoroestradiol is present as a hemihydrate and extensive hydrogen bonding is observed. 1-Bromoestradiol is not hydrated and hydrogen bonding is limited to hydroxyl groups along the *c* axis.

Introduction. The radiohalogenated analogs of 1-bromo- and 1-fluoroestradiol, (1) and (2), respectively, were being considered by our group as receptor-mediated radiopharmaceuticals for potential use in nuclear medicine for breast cancer studies. Their observed *in vitro* binding affinities to estrogen receptors, however, were substantially lower than that of estradiol. The structural characteristics of these compounds relative to estradiol became important for elucidation of the relationship between molecular conformations and the observed *in vitro* binding affinities. This paper describes the molecular and crystal structures of the 1-halogenated compounds and their structural similarities to estradiol.

Experimental. The title compounds were prepared in our laboratory (Hylarides, Leon, Mettler & Wilbur, 1984; Hylarides, Leon & Mettler, unpublished) as colorless transparent prisms by slow crystallization from ethanol/H_2O. Cell dimensions were determined from 25 diffractometer-measured reflections in the 2θ range 10 to 40° for (1) and 7 to 28° for (2) (Syntex

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$P3/F$, Mo $K\alpha$, graphite monochromator). For (1), intensities of 4596 independent reflections with $(\sin\theta)/\lambda < 0.703$ Å^{-1}, $h < 14$, $k < 19$, $l < 19$; empirical absorption correction applied; max. and min. transmissions are 0·144 and 0·110; Friedel-related reflections collected from a crystal of dimensions 0·30 × 0·31 × 0·34 mm, ω–2θ scan technique; 2083 reflections had $|F_o| > 5\sigma(F)$; three standard reflections (400, 060 and 006) monitored every 141 reflections showed random intensity fluctuations of 4%. For (2), intensities of 5641 independent reflections with $(\sin\theta)/\lambda < 0.76$ Å^{-1}, $h < 19$, $k < 30$, $l < 11$; empirical absorption correction applied; max. and min. transmissions are 0·201 and 0·176; Friedel-related reflections obtained from a crystal 0·20 × 0·34 × 0·53 mm, ω–2θ scan technique; 2781 observed reflections had $|F_o| > 4\sigma(F)$; three standard reflections (600, 060, 003) measured every 141 reflections showed 3% intensity fluctuation

Table 1. *Atom coordinates and equivalent isotropic thermal parameters* (*Willis & Pryor*, 1975)

	1-Bromoestradiol				1-Fluoroestradiol				
	x	y	z	U(Å^2)		x	y	z	U(Å^2)
Br	0·93576 (9)	0·96142 (5)	−0·08276 (5)	0·0562 (2)	F	0·0587 (2)	0·0798 (1)	−0·4286 (3)	0·059 (1)
C(1)	0·8716 (6)	0·8254 (5)	−0·1173 (4)	0·034 (2)	C(1)	0·1286 (3)	0·0999 (2)	−0·2761 (4)	0·042 (1)
C(2)	0·8426 (6)	0·8099 (5)	−0·2211 (4)	0·039 (2)	C(2)	0·2386 (3)	0·0860 (2)	−0·3083 (5)	0·043 (1)
C(3)	0·8159 (7)	0·7099 (5)	−0·2549 (5)	0·042 (2)	C(3)	0·3136 (3)	0·1050 (2)	−0·1596 (5)	0·045 (1)
C(4)	0·8265 (7)	0·6302 (5)	−0·1870 (4)	0·038 (2)	C(4)	0·2751 (3)	0·1405 (2)	0·0054 (5)	0·042 (1)
C(5)	0·8538 (6)	0·6456 (4)	−0·0827 (5)	0·038 (2)	C(5)	0·1632 (3)	0·1547 (2)	0·0322 (4)	0·036 (1)
C(6)	0·8795 (8)	0·5520 (5)	−0·0143 (4)	0·047 (2)	C(6)	0·1306 (3)	0·1960 (2)	0·2147 (5)	0·046 (1)
C(7)	0·9657 (7)	0·5812 (4)	0·0823 (4)	0·040 (2)	C(7)	0·0090 (3)	0·2188 (2)	0·2136 (5)	0·046 (1)
C(8)	0·8870 (6)	0·6678 (4)	0·1357 (4)	0·032 (2)	C(8)	−0·0634 (3)	0·1587 (2)	0·1505 (4)	0·037 (1)
C(9)	0·8887 (6)	0·7672 (4)	0·0722 (4)	0·032 (2)	C(9)	−0·0405 (2)	0·1403 (2)	−0·0713 (4)	0·035 (1)
C(10)	0·8673 (6)	0·7472 (5)	−0·0433 (4)	0·033 (2)	C(10)	0·0840 (3)	0·1306 (2)	−0·1076 (4)	0·034 (1)
C(11)	0·7811 (8)	0·8423 (5)	0·1193 (5)	0·043 (2)	C(11)	−0·1119 (2)	0·0777 (2)	−0·1356 (5)	0·047 (1)
C(12)	0·8207 (7)	0·8681 (4)	0·2314 (4)	0·039 (2)	C(12)	−0·2370 (2)	0·0891 (2)	−0·0940 (4)	0·043 (1)
C(13)	0·8354 (6)	0·7719 (4)	0·2974 (4)	0·031 (2)	C(13)	−0·2578 (2)	0·1083 (2)	0·1251 (4)	0·035 (1)
C(14)	0·9366 (7)	0·6961 (4)	0·2437 (4)	0·027 (1)	C(14)	−0·1876 (3)	0·1717 (2)	0·1753 (5)	0·037 (1)
C(15)	0·9673 (7)	0·6137 (4)	0·3257 (4)	0·041 (2)	C(15)	−0·2331 (3)	0·1975 (2)	0·3764 (5)	0·051 (1)
C(16)	0·9622 (7)	0·6749 (4)	0·4285 (4)	0·041 (2)	C(16)	−0·3575 (3)	0·1802 (2)	0·3645 (6)	0·057 (1)
C(17)	0·9141 (7)	0·7848 (4)	0·3993 (4)	0·034 (2)	C(17)	−0·3731 (3)	0·1381 (2)	0·1699 (5)	0·045 (1)
C(18)	0·6870 (7)	0·7244 (5)	0·3193 (5)	0·051 (2)	C(18)	−0·2359 (3)	0·0465 (2)	0·2626 (5)	0·049 (1)
O(3)	0·7846 (6)	0·6885 (4)	−0·3555 (3)	0·054 (2)	O(3)	0·4243 (2)	0·0890 (1)	−0·1808 (4)	0·059 (1)
O(17)	0·8359 (6)	0·8282 (4)	0·4852 (4)	0·049 (2)	O(17)	−0·4624 (2)	0·0894 (1)	0·1832 (4)	0·059 (1)
					O(21)	−0·5000	0·0000	0·5189 (5)	0·065 (1)

Table 2. *Bond lengths* (Å)

1-Bromoestradiol				1-Fluoroestradiol			
Br–C(1)	1·911 (6)	C(1)–C(2)	1·385 (8)	F–C(1)	1·376 (4)	C(1)–C(2)	1·370 (4)
C(1)–C(10)	1·394 (8)	C(2)–C(3)	1·388 (9)	C(1)–C(10)	1·377 (4)	C(2)–C(3)	1·390 (5)
C(3)–C(4)	1·358 (9)	C(3)–O(3)	1·364 (7)	C(3)–C(4)	1·376 (5)	C(3)–O(3)	1·377 (4)
C(4)–C(5)	1·389 (9)	C(5)–C(6)	1·519 (8)	C(4)–C(5)	1·387 (4)	C(5)–C(6)	1·507 (4)
C(5)–C(10)	1·414 (8)	C(6)–C(7)	1·537 (8)	C(5)–C(10)	1·412 (4)	C(6)–C(7)	1·529 (5)
C(7)–C(8)	1·509 (8)	C(8)–C(9)	1·525 (8)	C(7)–C(8)	1·512 (5)	C(8)–C(9)	1·544 (4)
C(8)–C(14)	1·518 (7)	C(9)–C(10)	1·531 (8)	C(8)–C(14)	1·526 (4)	C(9)–C(10)	1·530 (4)
C(9)–C(11)	1·528 (8)	C(11)–C(12)	1·535 (8)	C(9)–C(11)	1·546 (4)	C(11)–C(12)	1·549 (4)
C(12)–C(13)	1·515 (8)	C(13)–C(14)	1·532 (8)	C(12)–C(13)	1·526 (4)	C(13)–C(14)	1·528 (4)
C(13)–C(17)	1·521 (7)	C(13)–C(18)	1·549 (9)	C(13)–C(17)	1·533 (4)	C(13)–C(18)	1·529 (4)
C(14)–C(15)	1·531 (7)	C(15)–C(16)	1·548 (8)	C(14)–C(15)	1·530 (5)	C(15)–C(16)	1·538 (5)
C(16)–C(17)	1·538 (8)	C(17)–O(17)	1·445 (7)	C(16)–C(17)	1·542 (5)	C(17)–O(17)	1·433 (4)

Table 3. *Bond angles* (°)

1-Bromoestradiol				1-Fluoroestradiol			
Br–C(1)–C(2)	115·0 (4)	Br–C(1)–C(10)	121·0 (4)	F–C(1)–C(2)	114·9 (3)	F–C(1)–C(10)	119·0 (3)
C(2)–C(1)–C(10)	123·8 (6)	C(1)–C(2)–C(3)	118·5 (6)	C(2)–C(1)–C(10)	126·1 (3)	C(1)–C(2)–C(3)	117·7 (3)
C(2)–C(3)–C(4)	119·3 (6)	C(2)–C(3)–O(3)	122·0 (6)	C(2)–C(3)–C(4)	118·8 (3)	C(2)–C(3)–O(3)	119·8 (3)
C(4)–C(3)–O(3)	118·7 (6)	C(3)–C(4)–C(5)	122·3 (6)	C(4)–C(3)–O(3)	121·4 (3)	C(3)–C(4)–C(5)	121·9 (3)
C(4)–C(5)–C(6)	118·9 (5)	C(4)–C(5)–C(10)	120·0 (5)	C(4)–C(5)–C(6)	117·5 (3)	C(4)–C(5)–C(10)	120·5 (3)
C(6)–C(5)–C(10)	121·0 (5)	C(5)–C(6)–C(7)	111·2 (5)	C(6)–C(5)–C(10)	122·0 (3)	C(5)–C(6)–C(7)	113·5 (3)
C(6)–C(7)–C(8)	107·3 (5)	C(7)–C(8)–C(9)	111·9 (4)	C(6)–C(7)–C(8)	109·4 (3)	C(7)–C(8)–C(9)	109·9 (2)
C(7)–C(8)–C(14)	116·8 (5)	C(9)–C(8)–C(14)	106·9 (4)	C(7)–C(8)–C(14)	114·1 (3)	C(9)–C(8)–C(14)	108·5 (2)
C(8)–C(9)–C(10)	112·5 (4)	C(8)–C(9)–C(11)	108·2 (4)	C(8)–C(9)–C(10)	110·8 (2)	C(8)–C(9)–C(11)	110·3 (2)
C(10)–C(9)–C(11)	114·3 (5)	C(1)–C(10)–C(5)	115·3 (5)	C(10)–C(9)–C(11)	113·9 (2)	C(1)–C(10)–C(5)	114·5 (3)
C(1)–C(10)–C(9)	123·0 (5)	C(5)–C(10)–C(9)	121·4 (5)	C(1)–C(10)–C(9)	124·3 (3)	C(5)–C(10)–C(9)	121·2 (3)
C(9)–C(11)–C(12)	110·8 (5)	C(11)–C(12)–C(13)	112·2 (5)	C(9)–C(11)–C(12)	112·4 (3)	C(11)–C(12)–C(13)	111·4 (2)
C(12)–C(13)–C(14)	109·0 (4)	C(12)–C(13)–C(17)	116·3 (5)	C(12)–C(13)–C(14)	108·3 (2)	C(12)–C(13)–C(17)	115·2 (2)
C(14)–C(13)–C(17)	99·4 (4)	C(12)–C(13)–C(18)	110·3 (5)	C(14)–C(13)–C(17)	99·0 (2)	C(12)–C(13)–C(18)	110·7 (3)
C(14)–C(13)–C(18)	112·7 (5)	C(17)–C(13)–C(18)	108·8 (5)	C(14)–C(13)–C(18)	113·7 (2)	C(17)–C(13)–C(18)	109·5 (3)
C(8)–C(14)–C(13)	112·5 (5)	C(8)–C(14)–C(15)	122·0 (4)	C(8)–C(14)–C(13)	112·8 (2)	C(8)–C(14)–C(15)	120·0 (3)
C(13)–C(14)–C(15)	104·3 (4)	C(14)–C(15)–C(16)	103·6 (4)	C(13)–C(14)–C(15)	104·8 (2)	C(14)–C(15)–C(16)	103·5 (3)
C(15)–C(16)–C(17)	105·7 (4)	C(13)–C(17)–C(16)	104·7 (4)	C(15)–C(16)–C(17)	106·1 (3)	C(13)–C(17)–C(16)	104·6 (3)
C(13)–C(17)–O(17)	117·6 (5)	C(16)–C(17)–O(17)	108·6 (4)	C(13)–C(17)–O(17)	116·4 (3)	C(16)–C(17)–O(17)	112·8 (3)

throughout data collection (no decrease observed); Lorentz, polarization and absorption corrections based on an ellipsoidal fit to azimuthal scan data were made. Structure solution by direct methods of *SHELXTL* (Sheldrick, 1983); block-cascade least-squares refinements on F; atomic scattering factors for neutral atoms taken from the analytical expressions given in *International Tables for X-ray Crystallography* (1974); weights used are defined as $1/[\sigma^2(F)+gF^2]$, $g=0{\cdot}0091$ for (1) and $g=0{\cdot}00019$ for (2). H atoms attached to the carbon skeleton were fixed in their ideal positions with fixed isotropic temperature factors; x,y,z for the hydroxyl H atoms in (1) were refined; for (2), the H-atom position of the water molecule and half of the hydroxyl H-atom positions found in difference maps were included and were positionally fixed; isotropic U's of the hydroxyl H atoms were allowed to vary; final agreement factors of (1) with 196 parameters: $R=5{\cdot}14$, $wR=4{\cdot}73\%$, $S=1{\cdot}097$; max. Δ/σ after refinement 0·011; (2) with 197 parameters: $R=7{\cdot}76$, $wR=6{\cdot}37\%$, $S=1{\cdot}721$; max./min. heights in the difference maps 0·57/−0·56 for (1), and 0·46/−0·52 e Å^{-3} for (2) with a max. Δ/σ 0·083.* The high R value for (2) is due to poor crystal quality.

Discussion. The atomic parameters with their e.s.d.'s are listed in Table 1. Bond distances and angles are listed in Tables 2 and 3. The crystal structure of previously reported estradiol hemihydrate (Busetta & Hospital, 1972) is isostructural with that of 1-fluoroestradiol which is presented here. The general features of (2) are similar to the reported structure of 4-fluoroestradiol (Go, Kartha & Neeman, 1982). 1-Bromoestradiol (1) did not crystallize as a hemihydrate and does not have atomic coordinates similar to those of estradiol, 1-fluoroestradiol or the previously reported 4-bromoestradiol (Norton, Kartha & Lu, 1964). The bond angles and bond lengths of (1), (2) and estradiol are similar with the exception of the carbon–halogen bond lengths [1·911 Å for (1) and 1·375 Å for (2)]. The nearly identical conformations of the three compounds are typified by 1-fluoroestradiol in Fig. 1.

In regard to favorable biological binding affinity to estrogen receptors, the intramolecular distance between O(3) and O(17) has been reported to be critical (Chernayaev *et al.*, 1975). The intramolecular distances between O(3) and O(17) are very similar in all cases: 1-fluoroestradiol 10·95 Å, 1-bromoestradiol 11·05 Å and estradiol 10·93 Å. This intramolecular distance for 4-bromoestradiol was not reported. A trend of size of substituent at the 1-position *versus* distance may be implied; however, the significance of these subtle differences is not understood.

1-Bromoestradiol (1) does not have any close intramolecular interactions; however, there is a hydrogen bond, O(3)—H(3)···O(17), connecting individual molecules along the c axis. In the crystal structure, the H atom on O(17) does not appear to be involved in any hydrogen bonding (Fig. 2). Unlike (1), (2) shows extensive hydrogen bonding within the crystal in which both hydroxyl groups in the molecule and a water molecule are involved. There is a close approach between O(17) of one molecule and O(3) of another molecule (2·78 Å). This direction and intermolecular distance are within the range for hydrogen bonding between these hydroxyl groups (Fig. 3). This head-to-tail bonding between neighbouring molecules was

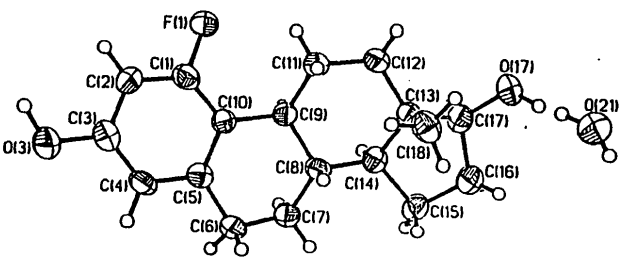

Fig. 1. Molecular conformation of 1-fluoroestradiol with atom numbering.

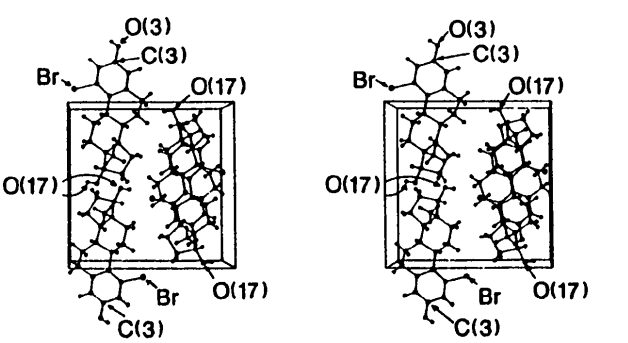

Fig. 2. Crystal structure of 1-bromoestradiol. No hydrogen bonding observed with O(17).

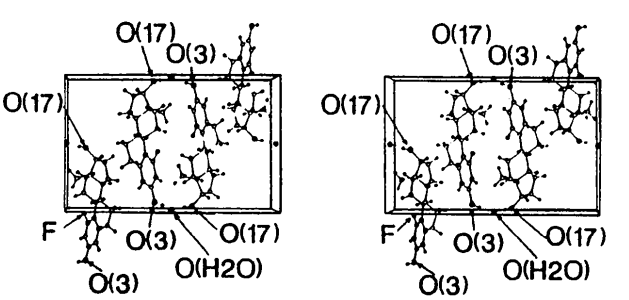

Fig. 3. Crystal structure of 1-fluoroestradiol. Extensive hydrogen bonding observed.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44540 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

observed for estradiol hemihydrate (Busetta & Hospital, 1972) and 4-fluoroestradiol (Go, Kartha & Neeman, 1982). The O(3)···O(17) distances were 2·774 and 2·77 Å in these structures. In this study, however, no H atoms corresponding to this link could be found.

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The Structure of N^1,N^2-Diphenylbenzamidine and a Comparison with its Transition-Metal Complexes

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Abstract. N^1,N^2-Diphenylbenzenecarboximidamide, $C_{19}H_{16}N_2$, $M_r = 272{\cdot}4$, monoclinic, $P2_1/a$, $a = 31{\cdot}340$ (8), $b = 10{\cdot}259$ (3), $c = 9{\cdot}527$ (3) Å, $\beta = 92{\cdot}34$ (3)°, $U = 3060{\cdot}5$ (2) Å^3, $Z = 8$, $D_x = 1{\cdot}18$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}65$ cm^{-1}, $F(000) = 1151{\cdot}79$, $T = 298$ K, $R = 0{\cdot}055$ for 1490 unique observed $[I/\sigma(I) \geq 3{\cdot}0]$ reflections. The two molecules of the asymmetric unit are linked by a single hydrogen bond [N(4)–H···N(1) (x, y, $1+z$) 2·46 (5) Å]. The C–N bonds show distinct amine [1·360 (8) Å average] and imine [1·302 (7) Å average] characteristics, which on complexation become near-equivalent C···N bonds with a high degree of delocalization. The change in the N–C–N 'bite' angle on complexation is determined by the bonding mode adopted; the angle changes by a mean value of 3·9° where the ligand bridges two metals, and by a mean value of 13·1° for bidentate bonding to a single metal.

Introduction. Recently, a number of structural papers concerning the structures of amidines have appeared (Tykarska, Jaskólski & Kosturkiewicz, 1986*a*; Thailambal, Pattabhi & Guru Row, 1986; Tykarska, Jaskólski & Kosturkiewicz, 1986*b*; Barker, Gould & Kilner, 1987; Barker, Cameron, Mahmoud, Kilner & Wallwork, 1986), reflecting the widespread interest in such compounds because of their pharmaceutical, bonding and ligand properties, and their biological importance. This structural investigation was undertaken to investigate the effect of diaryl substitution on the central benzamidine fragment, the possibility of hydrogen bonding, and to examine the structural changes which occur to an amidine upon complexation with a transition metal to form an important pseudo-allyl group (Fig. 1).

Experimental. N^1,N^2-Diphenylbenzamidine was prepared by the method of Kroehnke (Kroehnke & Steuernagel, 1963) and crystals were obtained by slow recrystallization from acetone in darkness. A large colourless elongated plate 1·7 × 0·14 × 0·26 mm was used. (Despite the unusual length of the crystal, it appeared to be satisfactorily located within the beam and refinement encountered no problems.) Syntex $P2_1$

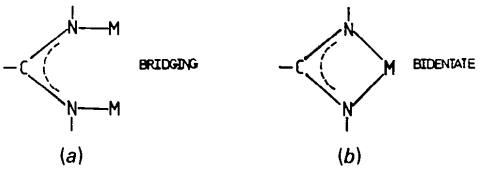

Fig. 1. Amidino bonding modes.

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