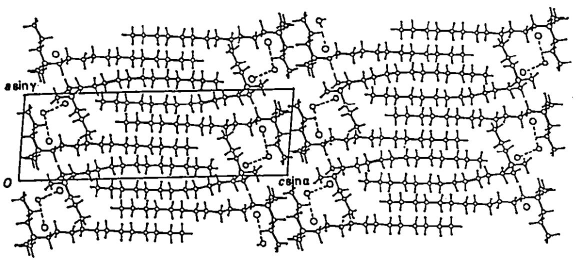

Fig. 2. Packing diagram projected along the *b* axis.

different from that of the monohydrate with thickness 17·1 Å. This difference is caused by the absence of a water molecule in the ionic region of the hemihydrate bilayer. The one water molecule links the two Br ions with Br···H—O hydrogen bonds, while in the monohydrate form the two water molecules bridge the two Br ions. The Br···O distances of 3·361 (5) and 3·332 (5) Å are comparable with those of the monohydrate, but the Br···O···Br angle of 119·4 (5)° is larger than 108·0 (1)° of the monohydrate. The Br ions are arranged in a distorted trigonal bipyramidal form about the ammonium group; N(1) is surrounded by five Br ions with N···Br distances 4·332 (5)–5·318 (5) Å, while N(1′) is surrounded by four Br ions with N···Br distances 4·284 (5)–4·899 (6) Å [one Br ion missing at one apex of the trigonal bipyramid about the central N(1′) atom]. Such ionic interactions between the Br ions and the terminal groups of long-chain molecules probably have a large influence on the chain packing. The long hydrocarbon chains are efficiently packed at the central region of the bilayer, while they are loosely packed at the boundary region. The comparatively regular-packing portions of the hydrocarbon chains at the central region are arranged in an approximate orthorhombic packing $O^{\parallel}$ ($B22_12$) (Abrahamsson, Dahlén, Löfgren & Pascher, 1978) with the dimensions $a_s = 8{\cdot}36$, $b_s = 8{\cdot}93$ and $c_s = 2{\cdot}54$ Å (c_s corresponds to the translation in the chain direction and the a_s axis is parallel to the *a* axis); the cell dimensions are comparable with those of (−)-2-ethyl-2-methylicosanoic acid, the first molecule found with $O^{\parallel}$ packing (von Sydow, 1958). According to Segerman (1965), the $O^{\parallel}$ packing has a slightly higher attractive van der Waals energy in comparison with the other types of packings. There are no short C···C intermolecular contacts less than 4·0 Å between adjacent dodecyl chains, and the shortest C···C contact between dodecyl and propyl chains is 3·74 (1) Å at C(3′)···C(15′) $(-1+x,+y,+z)$. Thus the chain packing in this bilayer structure is loose, and is different from that of the monohydrate in which the fully extended dodecyl chains are tightly packed in the $T^{\parallel}$ arrangement.

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Structure of 17α-Ethynylestra-1,3,5(10)-trien-3,17β-diol Hemihydrate (Ethynyl Estradiol)

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Abstract. $C_{20}H_{24}O_2.\frac{1}{2}H_2O$, $M_r = 305{\cdot}42$, monoclinic, $C2$, $a = 20{\cdot}99$ (1), $b = 6{\cdot}647$ (7), $c = 12{\cdot}124$ (2) Å, $\beta = 90{\cdot}51°$, $V = 1692$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}199$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 660$, room temperature, $R = 0{\cdot}053$ for 1491 unique reflections with $I \geq 2{\cdot}5\sigma(I)$. The molecular conformation is similar to the conformations found for estradiol. In the crystal, bilayers are formed of

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hydrogen-bonded steroid and water molecules, which are identical to those found in estradiol hemihydrate, but are staggered instead of being stacked.

Introduction. Ethynyl estradiol (EE) is employed in estrogenic hormone therapy. It is the most widely used estrogenic component in low-dose oral contraceptives and is at least twenty times as potent in oral doses as the natural estradiol hormone.

Synthetic estrogenic compounds (Sneader, 1985) have a phenolic ring in common and superimposing the aromatic rings of different molecular structures shows a significant difference in the *D*-ring region of the molecule (Duax, Griffin, Rohrer, Swenson & Weeks, 1981). The binding to the receptor is believed to be limited to the *A*- and *B*-ring region of the molecule (Duax, 1986).

Three different crystal forms of estradiol have been reported in the literature: the hemihydrate (Busetta & Hospital, 1972), a propanol complex (Busetta, Courseille, Geoffre & Hospital, 1972) and a urea complex (Duax, 1972).

Experimental. Data were measured on a crystal of approximate dimensions 0·08 × 0·04 × 0·02 cm on an Enraf–Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation; lattice parameters refined by least-squares fitting of 2θ values of 18 reflections in the range of $18 < 2\theta < 32°$; ω–2θ scan mode, $\Delta\omega = (0{\cdot}40 + 0{\cdot}35\tan\theta)°$, 1633 independent reflections measured up to $\theta = 25°$, $h,k,\pm l$ (max. range 24, 7, 14), 1491 of these considered observed $[I \geq 2{\cdot}5\sigma(I)]$ and used for structure refinement. Three periodically measured standard reflections ($\bar{2}20$, $00\bar{2}$, 400) showed a variation in intensity less than 2%; Lp corrections, no correction for absorption.

Structure solved by direct methods using *SHELXS*86 (Sheldrick, 1986); best *E* map gave all non-H atoms, including the water O atom. H atoms were included in the refinement at calculated positions riding on their bonded atoms, except the hydroxyl group, the ethynyl group and the water H atoms, which were located on a difference map. In the final cycles of two-block full-matrix refinement, using *SHELX*76 (Sheldrick, 1976), 105 and 113 parameters were varied respectively, including an overall scale factor, positional and individual anisotropic parameters for C and O atoms, positional parameters for H[O(3)], H[O(17)], H[C(21)] and H[O(aq)] and overall thermal parameters for all H atoms. The refinement on F converged at $R = 0{\cdot}053$ and $wR = 0{\cdot}047$, where $w = 1/\sigma^2(F)$. The mean-square amplitude of vibration for H atoms refined to 0·100 (4) Å^2, $\Delta/\sigma = 0{\cdot}02$ (3) (av.) and 0·2 (max.) for non-H atom parameters. $\Delta/\sigma = 0{\cdot}08$ (5) (av.) and 0·3 (max.) for H-atom parameters; final electron density $-0{\cdot}2 < \Delta\rho < 0{\cdot}3$ e Å^{-3}. Scattering factors were taken from Cromer & Mann (1968) for C and O atoms and from Stewart, Davidson & Simpson (1965) for H atoms.

Discussion. The final atomic parameters are given in Table 1.* The conformation of the steroid molecule and atom numbering is shown in Fig. 1, and the bond distances and bond angles involving the non-H atoms are given in Table 2.

Table 1. *Positional and equivalent isotropic thermal parameters* (Å^2) *for non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3\sin^2\beta.$$

	x	y	z	U_{eq}
O(3)	0·4267 (2)	0·0130 (5)	0·0627 (2)	0·067 (1)
O(17)	0·4076 (1)	0·3863 (5)	0·9386 (2)	0·063 (1)
C(1)	0·4154 (2)	−0·0705 (6)	0·3583 (3)	0·041 (1)
C(2)	0·4290 (2)	−0·1044 (4)	0·2505 (2)	0·045 (1)
C(3)	0·4119 (2)	0·0320 (6)	0·1702 (2)	0·045 (1)
C(4)	0·3789 (2)	0·2040 (6)	0·2038 (3)	0·046 (1)
C(5)	0·3645 (2)	0·2378 (6)	0·3119 (3)	0·040 (1)
C(6)	0·3294 (2)	0·4308 (6)	0·3411 (3)	0·047 (1)
C(7)	0·3070 (2)	0·4391 (6)	0·4586 (2)	0·045 (1)
C(8)	0·3572 (2)	0·3646 (6)	0·5383 (2)	0·038 (1)
C(9)	0·3705 (2)	0·1374 (5)	0·5150 (3)	0·036 (1)
C(10)	0·3839 (1)	0·1019 (6)	0·3947 (2)	0·034 (1)
C(11)	0·4216 (2)	0·0541 (6)	0·5942 (2)	0·045 (1)
C(12)	0·4062 (2)	0·0916 (6)	0·7161 (3)	0·047 (1)
C(13)	0·3929 (2)	0·3159 (6)	0·7376 (3)	0·040 (1)
C(14)	0·3396 (2)	0·3844 (6)	0·6588 (2)	0·039 (1)
C(15)	0·3193 (2)	0·5902 (6)	0·7045 (3)	0·054 (1)
C(16)	0·3328 (2)	0·5806 (6)	0·8273 (3)	0·062 (1)
C(17)	0·3633 (2)	0·3694 (6)	0·8500 (3)	0·050 (1)
C(18)	0·4545 (2)	0·4384 (7)	0·7241 (3)	0·057 (1)
C(20)	0·3128 (2)	0·2238 (7)	0·8822 (3)	0·056 (2)
C(21)	0·2738 (3)	0·1127 (9)	0·9110 (4)	0·089 (2)
O(aq)	0·5(*)	0·6731(*)	0·(*)	0·061 (2)

* Kept fixed during refinement.

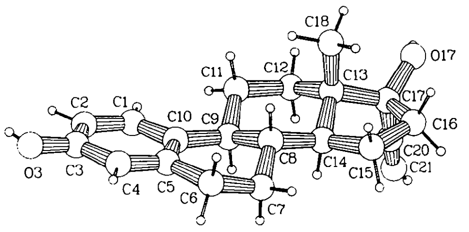

Fig. 1. Molecular structure with atom numbering of ethynyl estradiol.

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* Lists of structure factors, torsion angles, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43753 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for non*-H *atoms with e.s.d.'s in parentheses*

O(3)—C(3)	1·348 (4)	C(9)—C(10)	1·506 (4)
O(17)—C(17)	1·419 (5)	C(9)—C(11)	1·536 (5)
C(1)—C(2)	1·359 (4)	C(11)—C(12)	1·536 (4)
C(1)—C(10)	1·397 (5)	C(12)—C(13)	1·539 (6)
C(2)—C(3)	1·376 (5)	C(13)—C(14)	1·534 (5)
C(3)—C(4)	1·399 (6)	C(13)—C(17)	1·544 (5)
C(4)—C(5)	1·366 (5)	C(13)—C(18)	1·538 (6)
C(5)—C(6)	1·523 (6)	C(14)—C(15)	1·538 (6)
C(5)—C(10)	1·408 (5)	C(15)—C(16)	1·514 (5)
C(6)—C(7)	1·505 (5)	C(16)—C(17)	1·566 (6)
C(7)—C(8)	1·507 (5)	C(17)—C(20)	1·490 (6)
C(8)—C(14)	1·516 (4)	C(20)—C(21)	1·159 (7)
C(8)—C(9)	1·562 (5)		

C(2)—C(1)—C(10)	123·0 (3)	C(9)—C(11)—C(12)	113·0 (3)
C(1)—C(2)—C(3)	121·0 (4)	C(11)—C(12)—C(13)	111·1 (3)
C(2)—C(3)—C(4)	117·3 (3)	C(12)—C(13)—C(14)	108·3 (3)
O(3)—C(3)—C(2)	124·2 (4)	C(14)—C(13)—C(17)	100·6 (3)
O(3)—C(3)—C(4)	118·5 (3)	C(12)—C(13)—C(17)	116·6 (3)
C(3)—C(4)—C(5)	121·9 (3)	C(12)—C(13)—C(18)	109·9 (3)
C(4)—C(5)—C(6)	118·2 (3)	C(17)—C(13)—C(18)	108·5 (3)
C(4)—C(5)—C(10)	120·9 (4)	C(14)—C(13)—C(18)	112·7 (3)
C(6)—C(5)—C(10)	120·8 (3)	C(8)—C(14)—C(13)	113·1 (3)
C(5)—C(6)—C(7)	114·0 (3)	C(13)—C(14)—C(15)	104·0 (3)
C(6)—C(7)—C(8)	111·9 (3)	C(8)—C(14)—C(15)	119·7 (3)
C(7)—C(8)—C(14)	114·5 (3)	C(14)—C(15)—C(16)	105·5 (3)
C(9)—C(8)—C(14)	107·7 (3)	C(15)—C(16)—C(17)	106·4 (3)
C(7)—C(8)—C(9)	109·1 (3)	O(17)—C(17)—C(20)	108·4 (3)
C(8)—C(9)—C(11)	111·1 (3)	O(17)—C(17)—C(16)	109·0 (3)
C(8)—C(9)—C(10)	111·2 (3)	O(17)—C(17)—C(13)	114·8 (3)
C(10)—C(9)—C(11)	114·4 (3)	C(13)—C(17)—C(20)	112·0 (3)
C(5)—C(10)—C(9)	122·3 (3)	C(16)—C(17)—C(20)	109·7 (3)
C(1)—C(10)—C(9)	121·8 (3)	C(13)—C(17)—C(16)	102·6 (3)
C(1)—C(10)—C(5)	115·8 (3)	C(17)—C(20)—C(21)	177·6 (4)

The conformation of the steroid molecule of EE and the three complexes of estradiol show almost no variation, as is illustrated in Fig. 2, which shows a least-squares fit of the *A* rings. The conformation found in the urea complex shows the most prominent deviation. The six C atoms in the planar *A* ring have a root-mean-square deviation from the least-squares plane of 0·01 Å. The *B* ring has a distorted 7α,8β half-chair conformation and this was observed for the estradiol structures as well and is illustrated by the asymmetry parameter ΔC_2[C(7)—C(8)] = 8·7 (5)° (Duax & Norton, 1975). The half-chair conformation for the *B* ring was observed for 35 out of 45 estra-1,3,5(10)-triene steroids in the Cambridge Crystallographic Database (Allen *et al.*, 1979). The *C* ring is in an ideal chair conformation and the *D* ring of EE has a 13β-envelope conformation {ΔC_s[C(13)] = 2·9 (4)°}. For the estradiol structures intermediate conformations between a 13β-envelope and a 13β,14α-half chair have been observed and the difference with EE can be due to packing forces involving the 17α-ethynyl group.

The molecular packing is illustrated in Fig. 3, which shows a stereoview down **b**. Steroid molecules are hydrogen bonded head to tail: O(17)→O(3)($x,y,z+1$) with O···O = 2·928 (4) Å and O—H···O = 167 (4)°, and form infinite chains parallel to **c**. Adjacent chains are related by twofold rotation and held together by hydrogen-bonded water molecules, which in turn further bind adjacent double strands into infinite bilayers perpendicular to **a**; O(3)→O(aq)($x,y-1,z$) and O(aq)→O(17)($-x+1,y,-z+1$) with O···O distances of 2·841 (4) and 2·815 (3) Å and O—H···O angles of 155 (6) and 143 (3)° respectively. These two-dimensional networks are identical to those found in estradiol hemihydrate, but here adjacent bilayers are stacked, whereas in EE they are staggered and related by the *C* centering (see Fig. 4). There are no intermolecular H···H contact distances less than 2·2 Å.

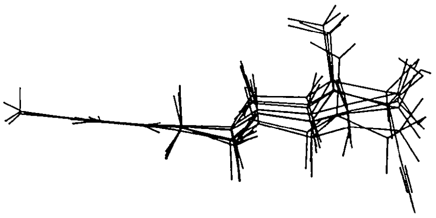


Fig. 2. Least-squares fit of the *A* rings of ethynyl estradiol and estradiol (water, propanol and urea complex).

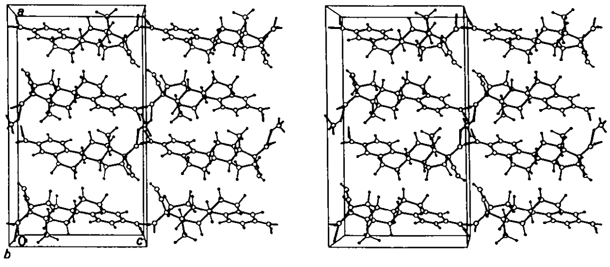
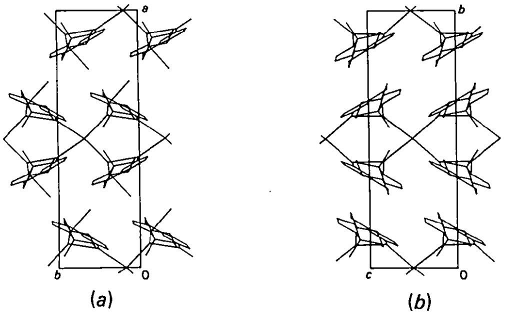


Fig. 3. Stereo packing diagram viewed down **b**.



(*a*) (*b*)

Fig. 4. (*a*) Bilayer packing of ethynyl estradiol hemihydrate ($C2$, viewed down **c**) and (*b*) estradiol hemihydrate ($P2_12_12$, viewed down **a**).

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Acta Cryst. (1987). C**43**, 1209–1211

Structure of *trans*-Dicyanobis(ethylenediamine)cobalt(III) Perchlorate

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Abstract. *trans*-$[\mathrm{Co(CN)_2(C_2H_8N_2)_2}]^+.\mathrm{ClO_4^-}$, $M_r = 330{\cdot}6$, monoclinic, $C2/c$, $a = 17{\cdot}556\,(3)$, $b = 6{\cdot}930\,(1)$, $c = 10{\cdot}604\,(2)$ Å, $\beta = 93{\cdot}07\,(1)°$, $V = 1288{\cdot}3\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}706$, $D_x = 1{\cdot}705$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}61$ mm^{-1}, $F(000) = 680$, room temperature, $R = 0{\cdot}037$ for 2433 observed reflections and 116 refined parameters. The cation reveals the point symmetry $\bar{1}$ (C_i) with the Co atom in the special position. The coordination of the Co atom is slightly distorted from an ideal octahedron; the axis formed by the two cyano groups is almost parallel to the c axis. The anion is located on a twofold axis (C_2) and one O atom shows a tendency to disorder while the other one forms a weak N—H···O hydrogen bridge.

Experimental. Spectroscopic investigations and the preparation of the compound under study have been reported by Hakamata, Urushiyama, Degen, Kupka & Schmidtke (1983). Well shaped yellow crystals have been crystallized by the same authors. Photographs around directions [011] (Weissenberg) and [100] (Buerger–precession) showed monoclinic symmetry and systematic absences of the space group Cc or $C2/c$ [fully reduced mesh, cell choice 1, *International Tables for Crystallography* (1983)]; the latter has been confirmed by the structure determination. Density, determined by flotation, yielded $Z = 4$ formula units per cell. A crystal shaped as a parallelogram of approx. $0{\cdot}5 \times 0{\cdot}4 \times 0{\cdot}2$ mm has been used for the determination of the lattice constants (15 reflections, $56 < 2\theta < 60°$, Mo $K\alpha$, Syntex $P2_1$, crystal monochromator) as well as for the data collection. The intensities of all 2840 symmetry-independent reflections up to $(\sin\theta)/\lambda = 0{\cdot}704$ Å^{-1} have been measured with an ω scan of 0·7° and variable speeds between 0·7 and 29·3° min^{-1}. The indices ranged from 0 to $h = 28$, $k = 11$ and from $l = -17$ to 16. Three standard reflections ($3\bar{3}7$, $5\bar{5}3$, 337) measured every 100 reflections varied only within experimental errors. Six reflections with too high intensities and at a later stage five weak reflections with $F_o \gg F_c$ showing asymmetric

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