

## 18-Methyloestradiol

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**Abstract.**  $C_{19}H_{27}O_2 \cdot C_4H_8O_2$ , orthorhombic,  $P2_12_12_1$ ,  $a=12.320$  (7),  $b=22.737$  (10),  $c=7.561$  (4) Å,  $Z=4$ . The molecular conformation and crystal structure are close to those found for the oestradiol-propanol complex.

**Introduction.** This compound is derived from the oestradiol molecule, the angular methyl group of the oestran framework being replaced by an ethyl group. It is described in a Roussel Uclaf French patent (No. 1476509). Methyloestradiol was crystallized from ethyl acetate with one solvent molecule per molecule of the diol. Cell parameters and 1832 independent reflexions, 1404 of which were observed, were measured on an automatic Siemens diffractometer with Cu  $K\alpha$  radiation. The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by least squares. The H atoms were located either at their theoretical positions, or from a difference synthesis. The final  $R$  was 0.049. The positional and

anisotropic thermal parameters of the heavy atoms are listed in Table 1, the H coordinates and their isotropic thermal parameters in Table 2.\*

**Discussion.** Bond lengths and valence and dihedral angles are given in Fig. 1. The conformation is very close to that of the natural oestradiol hormone (Busetta & Hospital, 1972; Busetta, Courseille, Geoffre & Hospital, 1972). The added ethyl group is turned towards the outside of the molecule (Fig. 2). Allowing for the different close contacts between the terminal methyl group C(19) and the H atoms of C(12), as well as with O(20), we may consider the added ethyl group as fixed in position. The apparent shortening of C(18)–C(19) (1.51<sub>6</sub> Å) may be related to the large

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31582 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and thermal parameters for non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	3075 (3)	2949 (2)	-1471 (6)	58 (3)	25 (1)	158 (8)	-8 (3)	-43 (9)	25 (5)
C(2)	1978 (3)	2956 (2)	-1012 (6)	64 (3)	26 (1)	159 (8)	-13 (3)	17 (9)	14 (5)
C(3)	1224 (3)	3149 (2)	-2223 (6)	58 (3)	22 (1)	187 (9)	-8 (3)	13 (9)	-2 (5)
C(4)	1557 (3)	3336 (2)	-3847 (6)	57 (3)	20 (1)	179 (9)	4 (3)	-29 (9)	6 (5)
C(5)	2653 (3)	3329 (2)	-4332 (5)	61 (3)	18 (1)	143 (7)	-6 (3)	-18 (9)	10 (4)
C(6)	2961 (3)	3534 (2)	-6167 (5)	60 (3)	29 (1)	149 (8)	-5 (3)	-35 (9)	23 (5)
C(7)	4088 (3)	3348 (2)	-6716 (5)	65 (3)	28 (1)	125 (7)	-6 (3)	-27 (9)	14 (5)
C(8)	4886 (3)	3484 (2)	-5228 (5)	52 (3)	19 (1)	105 (7)	0 (2)	-24 (7)	9 (4)
C(9)	4623 (3)	3090 (2)	-3624 (5)	52 (3)	17 (1)	138 (7)	-5 (2)	-29 (8)	4 (4)
C(10)	3434 (3)	3132 (2)	-3121 (5)	58 (3)	18 (1)	140 (8)	-7 (3)	-24 (8)	7 (4)
C(11)	5427 (3)	3206 (2)	-2101 (5)	63 (3)	23 (1)	131 (7)	-2 (3)	-37 (9)	24 (5)
C(12)	6609 (3)	3146 (2)	-2688 (5)	56 (3)	22 (1)	149 (8)	-2 (3)	-28 (8)	20 (5)
C(13)	6873 (3)	3550 (2)	-4257 (5)	50 (3)	17 (1)	152 (7)	0 (2)	4 (8)	10 (4)
C(14)	6075 (3)	3391 (2)	-5740 (5)	56 (3)	18 (1)	129 (7)	0 (3)	-19 (8)	-3 (4)
C(15)	6534 (4)	3703 (2)	-7366 (6)	59 (3)	37 (1)	144 (8)	-12 (3)	10 (9)	11 (6)
C(16)	7775 (4)	3650 (2)	-7118 (6)	65 (3)	36 (1)	164 (8)	3 (4)	26 (10)	-2 (6)
C(17)	7934 (3)	3404 (2)	-5240 (6)	52 (3)	24 (1)	198 (9)	2 (3)	3 (9)	-4 (5)
C(18)	6821 (3)	4202 (2)	-3744 (6)	70 (3)	20 (1)	183 (9)	-9 (3)	-25 (10)	0 (5)
C(19)	7373 (5)	4392 (2)	-2046 (8)	108 (5)	28 (1)	320 (14)	2 (4)	-135 (15)	-55 (7)
O(20)	150 (2)	3135 (2)	-1720 (4)	50 (2)	37 (1)	235 (7)	-4 (2)	17 (7)	27 (4)
O(23)	8915 (2)	3598 (1)	-4411 (5)	47 (2)	36 (1)	259 (7)	-6 (2)	-25 (7)	43 (5)
O(24)	5023 (4)	5397 (2)	-898 (6)	153 (4)	60 (2)	387 (12)	-72 (4)	6 (14)	-74 (8)
C(25)	3693 (6)	4671 (3)	-445 (10)	139 (6)	44 (2)	380 (18)	-19 (6)	58 (20)	-22 (10)
C(26)	4299 (4)	5118 (2)	-1491 (9)	89 (4)	29 (1)	359 (15)	-1 (4)	48 (14)	-29 (8)
O(27)	3983 (4)	5134 (2)	-3103 (6)	166 (5)	45 (1)	361 (11)	-70 (4)	-128 (13)	79 (6)
C(28)	4555 (7)	5543 (4)	-4324 (12)	224 (10)	51 (2)	437 (21)	-75 (8)	-110 (27)	114 (13)
C(29)	4483 (7)	5323 (4)	-6096 (12)	184 (9)	61 (3)	519 (26)	35 (8)	207 (26)	156 (15)

thermal motion of the terminal C(19). The same reason may be given for the very short bond lengths observed for the included ethyl acetate.

The  $c$  projection of the crystal structure is shown in Fig. 3. The crystal packing is very similar to that in the oestradiol-propanol complex (Busetta *et al.*, 1972). The molecules are all disposed in sheets parallel to the  $(a, c)$

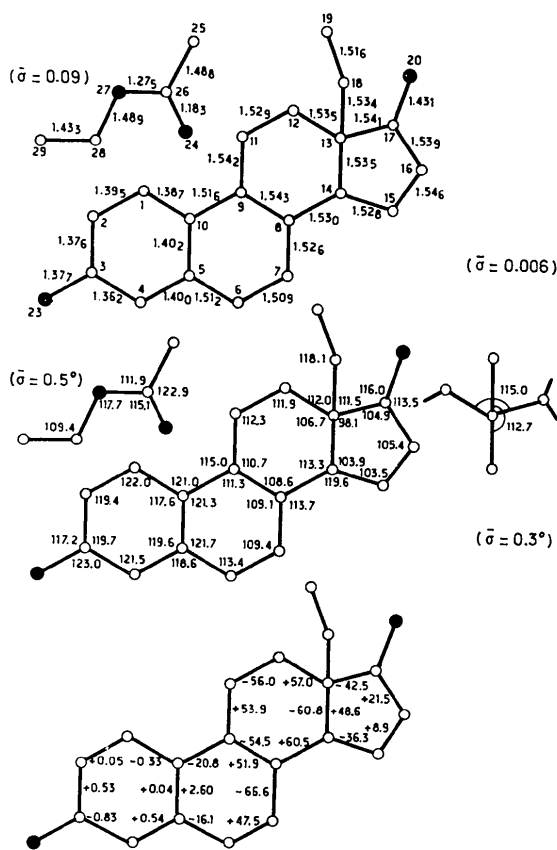


Fig. 1. Conformation of the molecule.

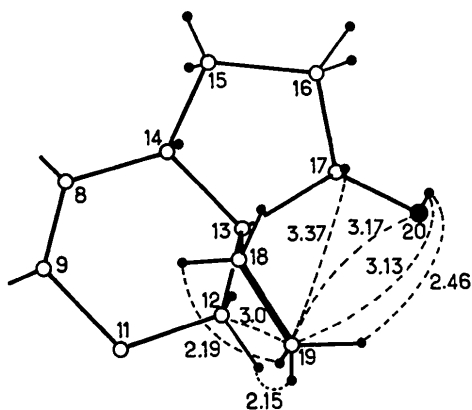


Fig. 2. Environment of the ethyl group.

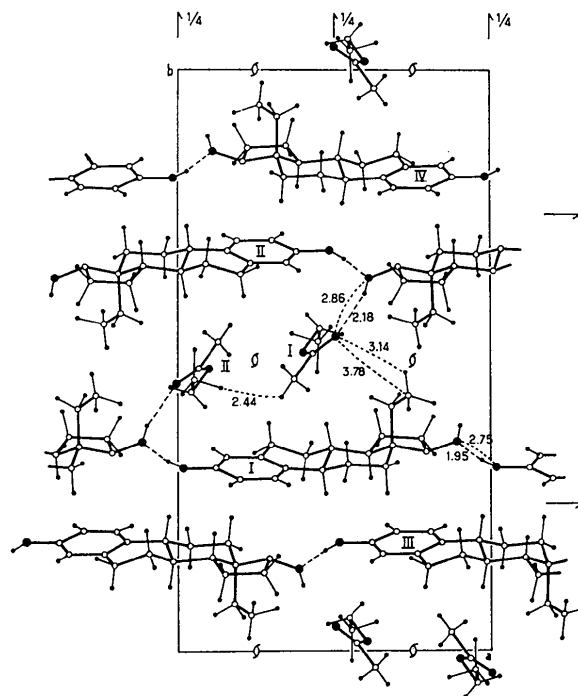


Fig. 3. Projection of the structure along  $c$ .

Table 2. Hydrogen atom coordinates ( $\times 10^4$ ) and thermal parameters

	$x$	$y$	$z$	$B_i$
H(101)	3523 (33)	2773 (17)	-636 (59)	5.2
H(102)	1676 (34)	2865 (18)	97 (61)	5.5
H(104)	1146 (30)	3472 (16)	-4528 (53)	4.7
H(106)	2918 (30)	3920 (15)	-6227 (49)	4.0
H(206)	2444 (33)	3402 (17)	-6859 (54)	5.0
H(107)	4250 (31)	3575 (18)	-7761 (56)	5.0
H(207)	3969 (34)	2936 (18)	-7008 (59)	5.6
H(108)	4744 (29)	3894 (15)	-4875 (51)	3.4
H(109)	4706 (30)	2685 (15)	-4020 (50)	3.6
H(111)	5313 (33)	2927 (18)	-1220 (55)	5.0
H(211)	5379 (31)	3589 (17)	-1614 (54)	4.9
H(112)	6686 (32)	2708 (17)	-3077 (57)	4.5
H(212)	6990 (32)	3237 (17)	-1672 (55)	4.8
H(114)	6168 (30)	2964 (15)	-5846 (53)	3.8
H(115)	6322 (35)	4147 (18)	-7308 (58)	5.5
H(215)	6321 (31)	3555 (17)	-8235 (55)	4.8
H(116)	8182 (32)	4021 (18)	-7285 (58)	5.3
H(216)	8179 (33)	3377 (19)	-7981 (59)	5.9
H(117)	8026 (30)	2973 (16)	-5245 (54)	4.3
H(118)	6157 (34)	4377 (18)	-3646 (57)	5.7
H(218)	7079 (32)	4405 (17)	-4650 (57)	5.2
H(119)	8181 (35)	4263 (19)	-2083 (62)	6.7
H(123)	-303 (36)	3260 (19)	-2404 (62)	6.0
H(120)	9020 (34)	3879 (18)	-4807 (62)	5.8
H(125)	3335 (36)	4374 (19)	-1004 (64)	7.0
H(219)	7255 (34)	4787 (17)	-1725 (59)	6.1
H(319)	7372 (37)	4159 (18)	-1415 (59)	6.6
H(228)	4137 (33)	5852 (18)	-3936 (57)	5.9
H(128)	5215 (38)	5425 (19)	-4105 (64)	7.5
H(225)	4126 (36)	4499 (20)	2 (65)	7.2
H(325)	3356 (36)	4889 (19)	524 (62)	6.6
H(129)	4441 (39)	4796 (21)	-6237 (69)	8.8
H(229)	3615 (41)	5469 (21)	-6329 (69)	8.2
H(329)	4843 (40)	5572 (21)	-7093 (66)	8.0

plane; in the **b** direction, we meet in succession two sheets of steroid molecules and one sheet made up of the included solvent. The steroid molecules in the same sheet are linked in the **a** direction by a hydrogen bond ( $O \cdots O = 2.75 \text{ \AA}$ ,  $O-H \cdots O = 166^\circ$ ). Each inclusion molecule is linked to a steroid molecule by a hydrogen bond involving the  $17\beta$ -ol function ( $O \cdots O = 2.86 \text{ \AA}$ ,  $O-H \cdots O = 158^\circ$ ).

In the **b** and **c** directions, crystal cohesion is ensured by attractive van der Waals forces. No repulsive contacts are observed.

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**Reply to Comment on 'Struktur des tetragonalen  $(B_{12})_4B_2Ti_{1.3-2.0}$ ' by E. Amberger and K. Polborn.** By E. AMBERGER and K. POLBORN, *Institut für Anorganische Chemie der Universität, D-8000 München 2, Meiserstrasse 1, Deutschland (BRD)*

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Reduction of  $BCl_3$  and  $TiCl_4$  with  $H_2$  on boron nitride substrate produces the analytically controlled carbon-free  $(B_{12})_4B_2Ti_{1.3-2.0}$ . Therefore the tetragonal unit cell contains boron on special equivalent point  $2(b)$  and titanium on  $2(a)$ .

In the paper *Struktur des tetragonalen  $(B_{12})_4B_2Ti_{1.3-2.0}$*  (Amberger & Polborn, 1975) the synthesis and structure of the berthollide titanium boride were described. The unit cell was found to contain four  $B_{12}$  icosahedra, two single boron atoms on special equivalent point  $2(b)$ , and a maximum of two titanium atoms on  $2(a)$ . Now Ploog (1976) in a comment on this paper argues that carbon is more likely to occupy the  $2(b)$  position than boron.

But there are convincing arguments against this: (i) The crystal used for X-ray investigation was taken from a certain crystalline region of the boride deposit. The chemical analysis showed that this region was free from carbon. (ii) Furthermore each synthesis (reduction of gaseous  $BCl_3$  and  $TiCl_4$  with  $H_2$ ) yielded the carbon-free titanium boride. An *I*-tetragonal titanium boride carbide  $(B_{12})_4C_{\sim 2}Ti_{1.5-2.0}$  (Amberger, Polborn & Gerster, in preparation) was pro-

duced – and in fact is reproducible – under these conditions but only with an additional amount of  $CCl_4$ . In the latter cell, carbon occupies the  $2(b)$  position and titanium the  $2(a)$ . (iii) The structure of the titanium boride was derived from photometrically measured X-ray patterns. The figures resulting from this procedure are not precise enough to signify a formula of the investigated compound other than the formula  $(B_{12})_4B_2Ti_{1.3-2.0}$ , derived from chemical and analytical findings.

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