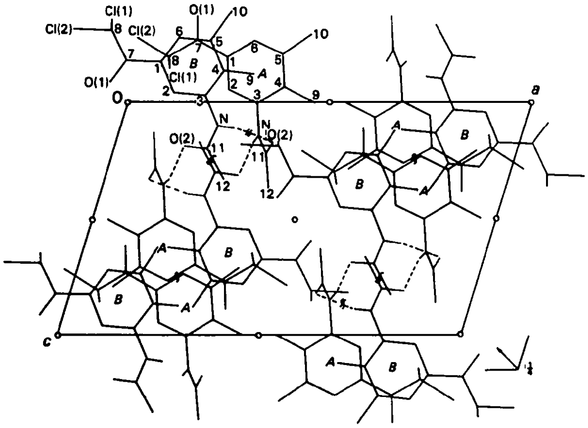

Fig. 2. Perspective view of the molecular packing.

tween the asymmetric units related by the twofold screw axis at $x = \frac{1}{4}$ and $z = \frac{1}{4}$ result in the formation of infinite chains. In the chains the benzene-ring planes of the molecules *A* and *B* lie nearly perpendicular to **b** and parallel with each other, the dihedral angle being 4·8 (1)°. The Cl(2) atoms of molecules *A* and *B* lie in the respective ring planes, and the Cl(1)—C(8) bonds in the molecules *A* and *B* extend nearly parallel to the twofold screw axis, but in opposite directions, resulting in compact packing of the molecules in the chain. The chains are held together by van der Waals interactions to form a sheet in (100). In the sheet the methyl groups at C(4) and C(5) of molecule *B* are sandwiched between the benzene rings of molecules *A* related by the twofold screw axis at $x = \frac{1}{4}$ and $z = \frac{3}{4}$. The sheets are stacked along **a** by weak van der Waals interactions to complete the structure.

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Structure of 14a,17α-Epoxy-3-methoxy-14-methyl-14α-estra-1,3,5(10)-trien-17β-ol

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Abstract. $\mathrm{C_{20}H_{26}O_3}$, $M_r = 314\cdot4$, trigonal, $P3_221$, $a = b = 7\cdot1677\ (5)$, $c = 55\cdot370\ (5)$ Å, $V = 2463\cdot6$ Å^3, $Z = 6$, $D_x = 1\cdot27$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot54184$ Å, $\mu = 5\cdot8$ cm^{-1}, $F(000) = 1020$, $T = 293$ K, $R = 0\cdot0387$ for 2098 unique reflections. The atoms forming ring *A* do not deviate significantly from the least-squares plane. Ring *B* is found to adopt a $^2H_3$ half-chair conformation, whereas ring *C* is in the expected $^4C_1$ chair form. The molecules are linked by O—H···O hydrogen bonds.

Introduction. A novel cycloaddition approach to the synthesis of estrone analogues bearing functionalized 14α-alkyl groups has recently been described (Bull & Thomson, 1986). Selective reduction of 3-methoxy-17-oxo-1,3,5(10)-estratriene-14α-carbaldehyde results in formation of the corresponding 14α-hydroxymethyl compound (I), the spectroscopic properties of which revealed that it exists in solution as an equimolar mixture of (I) and the title hemiacetal (II).

An X-ray crystallographic structure determination

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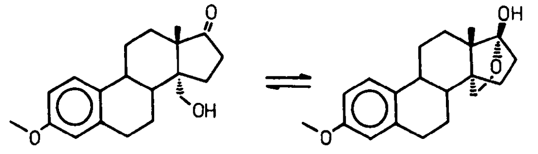
was carried out in order to ascertain the preferred form of the molecule in the solid state.



(I) (II)

Experimental. Colorless, plate-shaped crystals by slow evaporation of a diluted acetone solution. Crystal *ca* 0·2 × 0·2 × 0·4 mm used for data collection.

Intensities measured at 293 K; Enraf–Nonius CAD-4F diffractometer; graphite-monochromated Cu $K\alpha$ radiation; ω–2θ scan; variable scan speed with a maximum of 8·24° min^{-1}, and a minimum corresponding to a measuring time of 50 s per reflection; ω-scan angle changed as $(0{\cdot}60 + 0{\cdot}14\tan\theta)°$, horizontal aperture as $(1{\cdot}37 + 0{\cdot}1\tan\theta)°$, limited to 1·3–5·0 mm; vertical slit fixed to 4 mm.

Unit-cell parameters determined with 25 reflections in the θ range 11–38°; intensity control every hour using 3 standard reflections (loss 0·7%); orientation control every 200 reflections.

Monoclinic data set collected up to $\sin\theta/\lambda = 0{\cdot}609$ Å^{-1} (h = 0–9, k = 0–9, l = −70–70) resulting in 3897 reflections of which 234 were unobserved $[I < \sigma(I)]$.

Data were corrected for Lorentz and polarization effects only. The structure was solved with *MULTAN*80 (Main *et al.*, 1980); all H atoms were located from subsequent Fourier maps. Non-H atoms were refined anisotropically, H atoms with a common isotropic temperature factor $U = 0{\cdot}059\,(2)$ Å^2; *SHELX*76 (Sheldrick, 1976); full-matrix method with $1/\sigma^2(F)$ weights; 2098 unique reflections and 287 refined variables; $R_{\rm int} = 0{\cdot}0165$; $(\Delta/\sigma)_{\rm max} = 0{\cdot}15$; $(\Delta\rho)_{\rm max} = 0{\cdot}20$ e Å^{-3}, $(\Delta\rho)_{\rm min} = -0{\cdot}16$ e Å^{-3}; final $R = 0{\cdot}0387$, $wR = 0{\cdot}0335$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates and equivalent isotropic parameters are given in Table 1.* The numbering of atoms and a perspective view of the molecule is shown in Fig. 1.

The cell dimensions are very unusual – the ratio of the axis is 7·72 – but more extreme values have been

Table 1. *Fractional coordinates* (×10^4) *and equivalent isotropic thermal parameters* (×10^3 Å^2)

	x	y	z	$U_{\rm eq}$
C(1)	7982 (4)	6796 (4)	7167 (1)	35 (1)
C(2)	8431 (4)	7584 (4)	6934 (1)	38 (1)
C(3)	7760 (4)	6144 (4)	6741 (1)	36 (1)
C(4)	6742 (4)	3969 (4)	6786 (1)	36 (1)
C(5)	6316 (4)	3176 (4)	7023 (1)	31 (1)
C(6)	5232 (5)	751 (4)	7056 (1)	37 (1)
C(7)	5250 (5)	91 (4)	7316 (1)	36 (1)
C(8)	4610 (4)	1370 (4)	7484 (1)	27 (1)
C(9)	6383 (4)	3769 (4)	7477 (1)	28 (1)
C(10)	6880 (4)	4583 (4)	7218 (1)	29 (1)
C(11)	5780 (4)	5126 (4)	7640 (1)	32 (1)
C(12)	5252 (4)	4270 (4)	7901 (1)	32 (1)
C(13)	3480 (4)	1904 (4)	7904 (1)	28 (1)
C(14)	4097 (4)	551 (4)	7741 (1)	27 (1)
C(15)	2214 (5)	−1772 (4)	7786 (1)	37 (1)
C(16)	1742 (5)	−1751 (4)	8061 (1)	38 (1)
C(17)	3340 (4)	599 (4)	8130 (1)	31 (1)
C(18)	1317 (5)	1758 (5)	7850 (1)	40 (2)
C(19)	6007 (4)	675 (5)	7887 (1)	34 (1)
O(20)	5478 (3)	787 (3)	8137 (1)	36 (1)
O(21)	2915 (3)	1167 (3)	8352 (1)	38 (1)
O(22)	8209 (3)	7051 (3)	6516 (1)	45 (1)
C(23)	7490 (5)	5647 (5)	6314 (1)	46 (2)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(1)–C(2)	1·379 (3)	C(1)–C(10)	1·402 (3)
C(2)–C(3)	1·395 (3)	C(3)–C(4)	1·373 (3)
C(3)–O(22)	1·369 (2)	C(4)–C(5)	1·402 (3)
C(5)–C(6)	1·519 (3)	C(5)–C(10)	1·393 (3)
C(6)–C(7)	1·519 (3)	C(7)–C(8)	1·528 (3)
C(8)–C(9)	1·546 (3)	C(8)–C(14)	1·516 (3)
C(9)–C(10)	1·521 (3)	C(9)–C(11)	1·540 (3)
C(11)–C(12)	1·540 (3)	C(12)–C(13)	1·528 (3)
C(13)–C(14)	1·543 (3)	C(13)–C(17)	1·534 (3)
C(13)–C(18)	1·530 (3)	C(14)–C(15)	1·552 (3)
C(14)–C(19)	1·551 (3)	C(15)–C(16)	1·564 (3)
C(16)–C(17)	1·538 (3)	C(17)–O(20)	1·470 (3)
C(17)–O(21)	1·378 (2)	C(19)–O(20)	1·449 (3)
O(22)–C(23)	1·420 (3)		
C(2)–C(1)–C(10)	122·4 (2)	C(1)–C(2)–C(3)	119·3 (2)
C(2)–C(3)–C(4)	119·6 (2)	C(2)–C(3)–O(22)	115·8 (2)
C(4)–C(3)–O(22)	124·7 (2)	C(3)–C(4)–C(5)	120·9 (2)
C(4)–C(5)–C(6)	117·4 (2)	C(4)–C(5)–C(10)	120·5 (2)
C(6)–C(5)–C(10)	122·1 (2)	C(5)–C(6)–C(7)	113·1 (2)
C(6)–C(7)–C(8)	109·7 (2)	C(7)–C(8)–C(9)	109·0 (2)
C(7)–C(8)–C(14)	115·2 (2)	C(9)–C(8)–C(14)	111·1 (2)
C(8)–C(9)–C(10)	110·8 (2)	C(8)–C(9)–C(11)	110·7 (2)
C(10)–C(9)–C(11)	113·4 (2)	C(1)–C(10)–C(5)	117·3 (2)
C(1)–C(10)–C(9)	121·0 (2)	C(5)–C(10)–C(9)	121·7 (2)
C(9)–C(11)–C(12)	112·9 (2)	C(11)–C(12)–C(13)	110·8 (2)
C(12)–C(13)–C(14)	110·5 (2)	C(12)–C(13)–C(17)	116·8 (2)
C(14)–C(13)–C(17)	92·6 (2)	C(12)–C(13)–C(18)	109·0 (2)
C(14)–C(13)–C(18)	116·3 (2)	C(17)–C(13)–C(18)	111·2 (2)
C(8)–C(14)–C(13)	113·4 (2)	C(8)–C(14)–C(15)	118·5 (2)
C(13)–C(14)–C(15)	102·3 (2)	C(8)–C(14)–C(19)	115·5 (2)
C(13)–C(14)–C(19)	100·5 (2)	C(15)–C(14)–C(19)	104·4 (2)
C(14)–C(15)–C(16)	102·7 (2)	C(15)–C(16)–C(17)	101·9 (2)
C(13)–C(17)–C(16)	104·6 (2)	C(13)–C(17)–O(20)	102·6 (2)
C(16)–C(17)–O(20)	106·1 (2)	C(13)–C(17)–O(21)	120·3 (2)
C(16)–C(17)–O(21)	113·1 (2)	O(20)–C(17)–O(21)	108·9 (2)
C(14)–C(19)–O(20)	104·6 (2)	C(17)–O(20)–C(19)	105·1 (2)
C(3)–O(22)–C(23)	117·8 (2)		

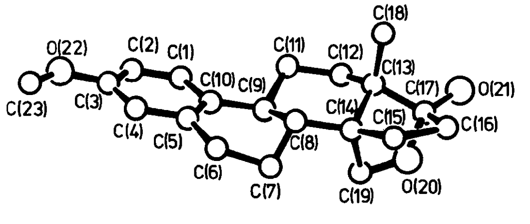


Fig. 1. *ORTEP* (Johnson, 1965) drawing showing atom-numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, least-squares plane data, H-atom coordinates, and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42939 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

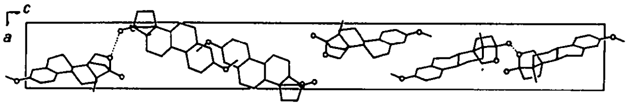

Fig. 2. Packing in the unit cell. Hydrogen bonds are indicated by broken lines.

observed (Alcock & Hough, 1972). The atoms forming ring *A* [C(1), C(2), C(3), C(4), C(5), C(10)] do not deviate significantly from the least-squares plane. Bond lengths and valence angles (Table 2) are comparable with the values found in similar molecules. The C—O bonds involved in the bridged O(20) are slightly elongated because of additional strain.

Puckering parameters (Cremer & Pople, 1975) are $Q = 0{\cdot}538$ Å, $\theta = 128°$ and $\varphi = 262°$ for ring *B* [C(9), C(8), C(7), C(6), C(5), C(10)], and $Q = 0{\cdot}558$ Å and $\theta = 179°$ for ring *C* [C(12), C(13), C(14), C(8), C(9), C(11)]. In the nomenclature of Boeyens (1978), the conformations of rings *B* and *C* are to be described as $^2H_3$ and $^4C_1$, respectively. The molecules are linked by an O—H···O hydrogen bond (Fig. 2), with bond distances O(21)—H(21) = 0·87 (2) Å, O(21)···O(22) $(1-x,\ y-x,\ \frac{5}{3}-z) = 2{\cdot}77$ Å, and H(21)···O(22) = 1·97 Å.

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Structure of an Aminopyridazine Derivative

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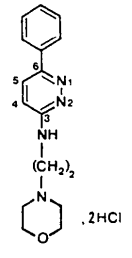
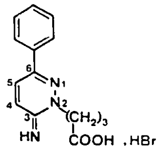
Abstract. 2-(3-Carboxypropyl)-2,3-dihydro-6-phenyl-3-pyridaziniminium bromide, $C_{14}H_{16}N_3O_2^+.Br^-$, $M_r = 338{\cdot}1$, triclinic, $P\bar{1}$, $a = 9{\cdot}711\ (1)$, $b = 14{\cdot}980\ (1)$, $c = 5{\cdot}482\ (1)$ Å, $\alpha = 98{\cdot}12\ (1)$, $\beta = 101{\cdot}42\ (1)$, $\gamma = 98{\cdot}84\ (1)°$, $V = 760{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}48\ \text{g cm}^{-3}$, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 26{\cdot}29\ \text{cm}^{-1}$, $F(000) = 344$, $T = 293$ K, final $wR = 0{\cdot}040$ for 1610 observed reflections. For this molecule, which is a GABA *A* antagonist (GABA is γ-aminobutyric acid), the observed protonation site is the exocyclic N atom, giving rise to electronic delocalization in the aminopyridazine system. Crystal cohesion is assumed by a dense network of intermolecular H bonds involving the Br anion, the carboxylic function and the protonated N atom.

Introduction. The title compound is the demethylated analog of a new selective and competitive antagonist at the GABA *A* receptor site (Chambon, Feltz, Heaulme, Restlé, Schlichter, Bizière & Wermuth, 1985). Its crystal structure analysis has been undertaken in order to account for the structural and electronic features of such 2,6-substituted 3-aminopyridazine derivatives. Our interest was increased by the possibility of comparing these results with those previously observed for several 4,6-substituted 3-aminopyridazines, analogs of minaprine (commercial name: Cantor, Clin-Midy, Montpellier), a potent antidepressant drug (Wermuth, 1985). As the major results reported for this family are similar (Van der Brempt, Evrard & Durant, 1985), these molecules and, for completeness, the dihydrochloride of the demethylated analog of minaprine (Michel, Gustin, Evrard & Durant, 1982), are used for comparative discussion.



Demethylminaprine



Title compound