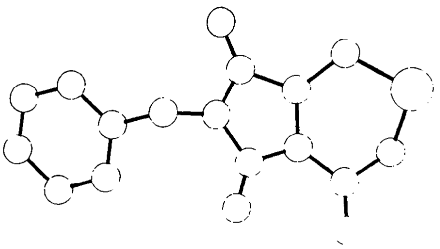

Fig. 2. Perspective view of the molecule.

The bond lengths and angles in the hydantoin ring are comparable with those in DL-allantoin (Mootz, 1965) and 3-benzyl-5-(methoxycarbonylmethylthiomethyl)hydantoin (hereafter 5CM3BH) (Dhaneshwar, Tavale & Guru Row, 1985). The C(5)—N(1) bond involving the tetrahedral C atom has a length of 1·459 (4) Å, close to the corresponding values of 1·461 Å in DL-allantoin and 1·46 (1) Å in 5CM3BH. The C(4)—C(5) bond distance of 1·509 (7) Å is close to the sp^2—sp^3 C—C single-bond value of 1·501 (4) Å (Lide, 1962). The three carbonyl bonds are shorter than the mean value of 1·216 Å quoted for 12 barbiturates (Craven, Cusatis, Gartland & Vizzini, 1973) due to the absence of any hydrogen bonding, as in the case of phenobarbitone (Williams, 1974). The hydantoin ring is planar in the present case as in DL-allantoin and 5CM3BH. Atoms O(1), O(2) and C(10) lie within 0·01 Å of the ring plane, while O(3), C(8) and C(9) deviate from the ring plane by 0·1 Å.

The thiazine ring has a boat form (Hendrickson, 1964). Angles C(6)—S—C(8) and C(5)—N(1)—C(9) are 100·6 (2) and 122·1 (3)°, comparable with the corresponding angles 100·2 (1) and 122·1 (2)° in 10-(2-nitrophenyl)phenothiazine (Jovanovic, Biehl, de Meester & Chu, 1984). The two C—S bonds, C(6)—S and C(8)—S are 1·806 (5) and 1·817 (4) Å, very close to the C—S single-bond value of 1·82 Å (Sutton, 1965).

The aromatic ring is planar and makes a dihedral angle of 113·9 (4)° with the hydantoin ring.

We thank Drs T. Ravindranathan and V. S. Hiremath and Mr D. R. Reddy for supplying the compound, and Drs A. P. B. Sinha, L. M. Pant and Mrs V. G. Puranik for their keen interest and useful discussions.

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Acta Cryst. (1985). C**41**, 1530–1532

10β-Hydroxy-1,4-estradiene-3,17-dione

By J. H. Bieri* and R. Prewo

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, *CH*-8057 *Zürich, Switzerland*

and J. L. Briansó and J. F. Piniella

Departamento de Cristalografía, Universidad Autónoma de Barcelona, Cerdanyola (*Barcelona*), *Spain*

(*Received* 15 *March* 1985; *accepted* 1 *July* 1985)

Abstract. $C_{18}H_{22}O_3$, $M_r = 286{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}014\,(2)$, $b = 12{\cdot}176\,(4)$, $c = 17{\cdot}648\,(4)$ Å, $V = 1507{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}079$ mm^{-1}, $F(000) = 616$, T *ca* 130 K, $R = 0{\cdot}109$ for all 2506 unique reflections within $\lambda^{-1}\sin\theta = 0{\cdot}70$ Å^{-1}; the absolute configuration was not determined. The relative stereochemistry at C(10) is established. The

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* To whom correspondence should be addressed.

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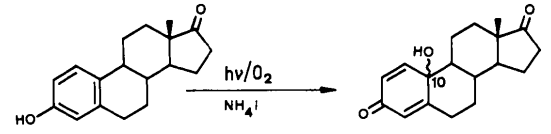
unsaturated ring is essentially planar; the two central rings are in the chair conformation and the five-membered ring adopts the envelope conformation.

Introduction. The photooxygenation of estrone (1) followed by iodide reduction preferentially led to (2*b*) with a small amount of (2*a*) (Lupón, Gómez & Bonet, 1983). The configurations of C(10) were determined by the different ^{1}H NMR chemical shifts of the methyl groups at C(13). In order to confirm this assignment and to know the geometry of these molecules better an X-ray diffraction study of (2*b*) has been carried out. The crystallization of (2*a*) was not possible due to decomposition of the molecule.



(1) (2a) (10α) (2b) (10β)

Experimental. (2*b*) crystallized from acetone/petroleum ether, platelet of *ca* 0·65 × 0·35 × 0·05 mm selected, Nicolet *R*3 diffractometer with cooling device LT-1 and standard control software. Lattice parameters from restricted least-squares refinement (*XRAY*72, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) of 72 2θ values of 36 automatically centered reflections within $35 < |2\theta| < 48°$. Intensities measured for $0 \le h \le 9$, $0 \le k \le 17$, $0 \le l \le 24$, Wyckoff ω-scan, scan range 1·7° and background offset 1·6° due to peak splitting for reflections with $h > 0$; 2531 intensities measured of which reflection 341 rejected due to uneven backgrounds and 24 reflections systematically extinct; 001 and 010 not measured; 352 reflections with $h = 0$ repeated with scan range 0·9° and background offset 1° of which reflection 008 rejected due to uneven backgrounds and 19 reflections systematically extinct; three standard reflections remeasured periodically after 100 reflections showed no systematic deviation and a maximum random deviation of 3·1% from their initial intensities; usual corrections except for absorption (*SHELXTL*, Sheldrick, 1981); intensities below $0{\cdot}5\sigma_I$ set to $0{\cdot}25\sigma_I$; 2506 unique reflections, *SHELXTL* merging $R_{\rm int} = 0{\cdot}012$; solution by direct methods; blocked-cascade least-squares refinement based on *F*, *ca* 100 variables per block; H atoms except those at C(16) located by difference Fourier synthesis and refined with individual isotropic temperature factors, the latter two calculated and kept riding on C(16) with free isotropic temperature factors, other atoms anisotropically refined; $w = (\sigma_F^2 + 0{\cdot}0004F^2)^{-1}$, all 2506 reflections used, 272 variables, final $R = 0{\cdot}109$, $wR = 0{\cdot}061$, maximum shift to e.s.d. ratio 0·037; maximum height in final difference Fourier synthesis 0·47, minimum $-0{\cdot}44$ e Å^{-3}; scattering factors from

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalized **U** tensor.

	x	*y*	*z*	U_{eq}
C(1)	156 (5)	964 (3)	4072 (2)	25 (1)
C(2)	330 (5)	925 (3)	4824 (2)	26 (1)
C(3)	677 (4)	1937 (3)	5260 (2)	25 (1)
O(3)	961 (3)	1886 (2)	5953 (1)	30 (1)
C(4)	678 (4)	2974 (3)	4848 (2)	22 (1)
C(5)	428 (4)	3023 (3)	4094 (2)	21 (1)
C(6)	429 (5)	4080 (2)	3665 (2)	25 (1)
C(7)	2034 (5)	4084 (2)	3079 (2)	22 (1)
C(8)	2006 (4)	3063 (2)	2578 (1)	19 (1)
C(9)	2000 (4)	2000 (3)	3062 (1)	20 (1)
C(10)	245 (4)	1994 (3)	3610 (1)	21 (1)
C(11)	2104 (4)	949 (2)	2577 (2)	23 (1)
C(12)	3811 (5)	959 (2)	2028 (2)	26 (1)
C(13)	3750 (5)	1991 (3)	1537 (2)	26 (1)
C(14)	3707 (5)	3015 (3)	2051 (2)	23 (1)
C(15)	4144 (7)	3961 (3)	1498 (2)	40 (1)
C(16)	5730 (8)	3466 (3)	1001 (2)	63 (2)
C(17)	5469 (6)	2213 (3)	1049 (2)	41 (1)
C(18)	2047 (6)	1945 (3)	978 (2)	44 (1)
O(19)	−1428 (3)	2043 (2)	3139 (1)	28 (1)
O(20)	6498 (4)	1542 (2)	748 (1)	51 (1)

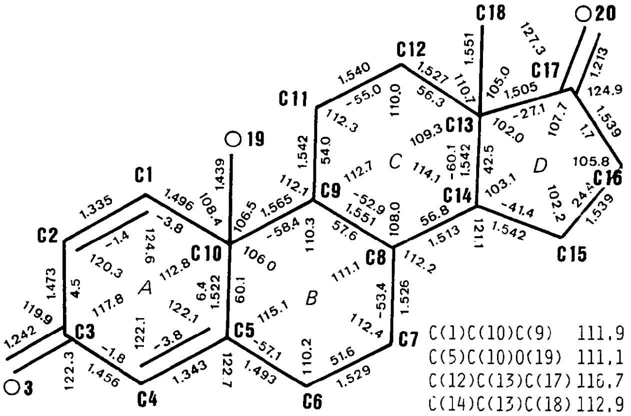


Fig. 1. Schematic structure of (2*b*) with atom numbering, bond lengths (in Å, e.s.d.'s 0·003–0·006 Å), bond angles (in degrees, e.s.d.'s 0·2–0·4°) and intra-annular torsion angles (in degrees, e.s.d.'s 0·3–0·5°).

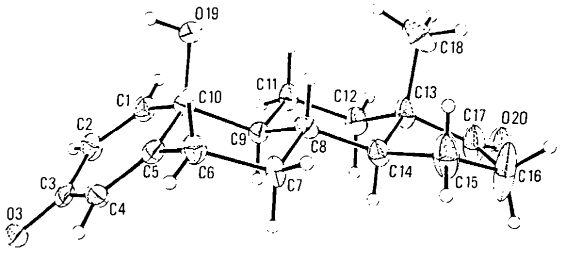


Fig. 2. Perspective view of (2*b*). The H atoms are drawn with arbitrary radius; the other atoms are represented by their 50% probability ellipsoids.

International Tables for X-ray Crystallography (1974). C(18) has been assigned the β-position in accord with Lupón *et al.* (1983).

Discussion. Fractional atomic coordinates are given in Table 1.* The numbering scheme, bond lengths, bond angles and intra-annular torsion angles are given in Fig. 1. As can been seen from the molecular drawing in Fig. 2, O(19) is also in the β-position. This confirms the assignment based on NMR-shift experiments (Lupón *et al.*, 1983).

As in other 1,4-dien-3-one steroids the *A* ring is almost planar. C(10) [0·036 (3) Å] and C(5) [−0·034 (3) Å] have the largest deviations from a mean plane through the C atoms of ring *A*. The *B* and *C* rings have the usual chair conformation. Ring *D* may be described as an envelope with C(14) out of the plane. However, a few thermal parameters, in particular at C(16), indicate some disorder in this ring. There is a hydrogen bond from H(19) to O(3) of a neighboring molecule; O(20) is not involved in hydrogen bonding.

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42315 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1985). C**41**, 1532–1535

Structure Analysis of Minaprine Analogs: 3-Morpholinium Ethylamino-5-methyl-6-phenylpyridazinium Oxalate, Oxalic Acid (1/1)*

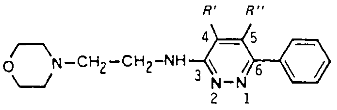
By Christine Van der Brempt, François Durant, Bernadette Norberg and Guy Evrard

Laboratoire de Chimie Moléculaire Structurale, Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles 61, B-5000 Namur, Belgium

(*Received* 25 *January* 1985; *accepted* 9 *July* 1985)

Abstract. $C_{17}H_{24}N_4O^{2+}.C_2O_4^{2-}.C_2H_2O_4$, $M_r = 478{\cdot}5$, triclinic, $P\bar{1}$, $a = 9{\cdot}949\ (1)$, $b = 16{\cdot}477\ (6)$, $c = 8{\cdot}345\ (1)$ Å, $\alpha = 87{\cdot}75\ (2)$, $\beta = 109{\cdot}88\ (1)$, $\gamma = 116{\cdot}59\ (2)$°, $V = 1139{\cdot}9\ (13)$ Å^3, $Z = 2$, $D_x = 1{\cdot}39$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}70$ cm^{-1}, $F(000) = 504$, $T = 293$ K, final $R = 0{\cdot}037$ for 1268 observed reflections. By comparison with the previously studied 4-demethyl and 4-phenyl analogs, the presence of a methyl group on position 5 results in an important torsion of the phenyl ring with regard to the adjacent pyridazine, but has no influence on the bond lengths and angles.

Introduction. This work is part of a general study on structural and molecular properties of a series of analogs of minaprine (commercial name: Cantor–Clin-Midy, France), an antidepressant drug belonging to the aminopyridazine family (Wermuth, 1985). The crystal structure of the title compound, hereafter abbreviated as the '5-methyl' analog, has been studied by X-ray diffraction and compared with those of the 4-demethyl and 4-phenyl analogs (Michel, Gustin, Evrard & Durant, 1982*a,b*). The comparison has been undertaken in order to ascertain the influence of the substituent on the phenyl torsion and the bond length between pyridazine and phenyl rings, in correlation with the activity evolution.



$R' = CH_3$, $R'' = H$: Minaprine

$R' = H$, $R'' = CH_3$: 5-Methyl analog

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* 4-{2-[(4-Methyl-3-phenyl-6-pyridazinio)amino]ethyl}-morpholinium oxalate–oxalic acid (1/1).

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