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D-Secoestrone Derivatives. IV. 3-Hydroxy-18-methyl-17-oxaestra-1,3,5(10)-trien-16-one

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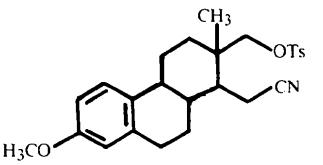
Abstract

X-ray structure analysis of the title compound, $C_{18}H_{22}O_3$, obtained under demethylation reaction conditions from 3-methoxy-17-*p*-toluenesulfonyloxy-16,17-secoestra-1,3,5(10)-triene-16-carbonitrile, revealed an unusual *C/D* ring junction. The molecules are connected in a head-to-tail manner by bifurcated hydrogen bonds, forming twisted chains along the *a* axis.

Comment

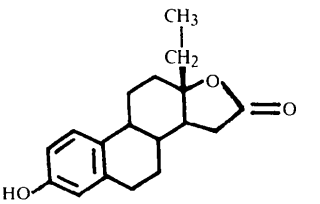
It has been shown that some estrone derivatives with an O atom in ring *D* show significant effects on blood lipids and low estrogenic activity at screening levels (Baran, 1967). These compounds have been prepared either by Baeyer–Villiger oxidation of estrone (Bollinger & Courtney, 1964), or by chemical transformations of some D-seco estrone derivatives (Baran, 1967; Miljković *et al.*, 1978).

In our recent work concerning structure–activity relationships in 16- and 17-substituted estrane derivatives, a D-oxa derivative, (2), was obtained unexpectedly (Petrović *et al.*, 1992) under demethylation reaction conditions from 3-methoxy-17-*p*-toluenesulfonyloxy-16,17-secoestra-1,3,5(10)-triene-16-carbonitrile, (1) (Stanković *et al.*, 1992). The formation of (2) could be explained by a two-step mechanism: demethylation of the 3-methoxy function and hydrolysis of the CN group, followed by a neopentyl rearrangement and a five-membered lactone ring formation. However, the structure of lactone (2) could not be determined unambiguously on the basis of spectroscopic data. Therefore, an X-ray structural analysis has been undertaken.



(1)

38% HBr
CH_3COOH



(2)

The title molecule is shown in Fig. 1. The bond lengths and valence angles are within the range of mean values for steroid structures (Duax *et al.*, 1976).

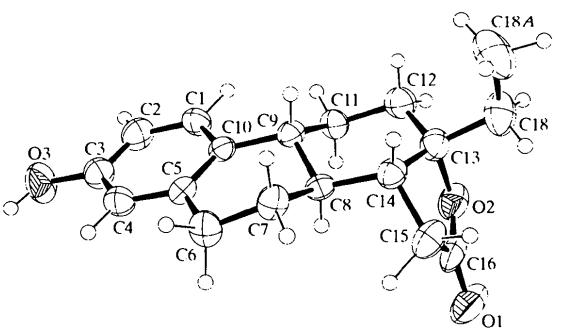


Fig. 1. A perspective view of the title molecule with the atomic labelling. Displacement ellipsoids are shown at the 30% probability level; H atoms (not labelled) are drawn as spheres of arbitrary radii.

Ring-puckering parameters (Cremer & Pople, 1975) and asymmetry parameters (Duax *et al.*, 1976) define the usual ring conformations in the 1,3,5(10)-estratriene steroid system, which are 7α,8β-half-chair for ring *B* and 8β,12α-chair for ring *C*. However, the *C/D cis* ring junction has significantly altered the conformation of ring *C* towards the 9α,11β-half-chair conformation. The five-membered lactone ring is intermediate between a 14β-envelope and a 13α,14β-half chair. As expected, the lactone moiety is planar (within the standard deviations) and α-oriented. The ethyl moiety is β-oriented [C12—C13—C18—C18*A* 72.8 (5)°]. The twist along the length of the steroid molecule is negligible [C1—C10···C13—C18 88.0 (7)°].

Screw-axis-related molecules are connected in a head-to-tail manner by bifurcated O···O hydrogen bonds, forming twisted chains (Fig. 2). The O3—H hydroxy group participates simultaneously in both strong (O3—H···O1) and weak (O3—H···O2) hydrogen bonds. The chains, connected to each other by van der Waals contacts, lie parallel to the *a* axis.

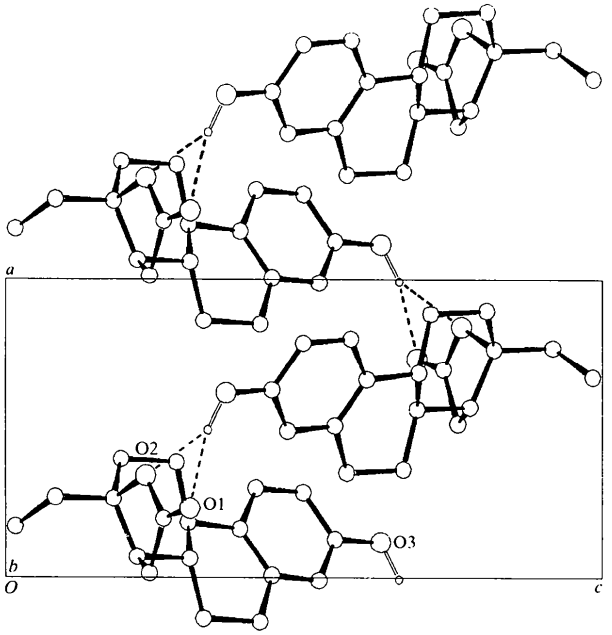


Fig. 2. The packing arrangement of the molecules that form the single chain, viewed down the *b* axis. Hydrogen bonds are indicated by dotted lines.

Experimental

The title compound, (2), was obtained under demethylation reaction conditions from (1) (see *Comment*).

Crystal data

$C_{18}H_{22}O_3$
M_r = 286.36
Orthorhombic
$P2_12_12_1$
a = 7.178 (2) Å
b = 14.268 (3) Å
c = 14.795 (3) Å
V = 1515.2 (6) Å^3
Z = 4
D_x = 1.255 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 11.3–30.1°
μ = 0.672 mm^{-1}
T = 293 K
Prism
0.46 × 0.36 × 0.22 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: none
1287 measured reflections
1287 independent reflections
937 reflections with $I > 2\sigma(I)$
θ_{max} = 59.92°
h = 0 → 7
k = 0 → 16
l = 0 → 16
3 standard reflections every 120 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0428
$wR(F^2)$ = 0.1855
S = 1.133
1234 reflections
202 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.2327P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.054
$\Delta\rho_{max}$ = 0.138 e Å^{-3}
$\Delta\rho_{min}$ = −0.125 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C13—O2	1.493 (5)	C15—C16	1.487 (6)
C13—C14	1.528 (6)	C16—O1	1.224 (5)
C14—C15	1.539 (5)	C16—O2	1.342 (5)
O2—C13—C14	102.2 (3)	O1—C16—C15	129.7 (5)
C13—C14—C15	101.6 (3)	O2—C16—C15	111.5 (4)
C16—C15—C14	101.6 (4)	C18*A*—C18—C13	116.0 (4)
O1—C16—O2	118.7 (5)	C16—O2—C13	109.0 (3)

H atoms were generated and refined as riding groups (overall isotropic displacement parameters were refined for different CH types, except those attached to the O atoms, whose positions were found in the ΔF map and refined isotropically). Refinement of the Flack (1983) parameter was not successful. The data were collected to a θ_{max} value of 60°, which was the criterium at the time of submission. As the measurements were carried out elsewhere, for practical reasons, the data cannot be recollected.

Structure solution used *SHELX*76 (Sheldrick, 1976) and structure refinement used *SHELXL*93 (Sheldrick, 1993). Other programs used include *CSU* (Vicković, 1988).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1029). Services for accessing these data are described at the back of the journal.

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1*H*-Tetrazol-5(4*H*)-one

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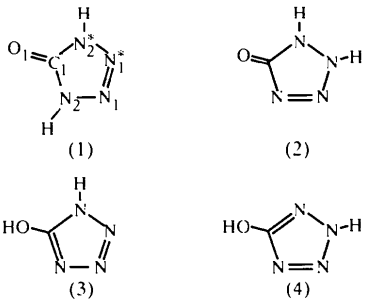
Abstract

The molecular structure determination of the title compound, CH_2N_4O, determined by X-ray crystallography reveals it to be 1*H*-tetrazol-5(4*H*)-one, not 5-hydroxytetrazole which had been generally accepted; 1*H*-tetrazol-5(4*H*)-one is the keto form with C_{2v} symmetry. *Ab initio* calculations at the MP2/6–31G* level also indicate that 1*H*-tetrazol-5(4*H*)-one is the most stable tautomer.

Comment

Four structural isomers, (1)–(4), can be written for the title compound. Hattori *et al.* (1953) reported that 5-hydroxytetrazole, (3), was the generally accepted form and that the crystal system was tetragonal. Furthermore, they studied another unstable form, the crystal system of which was probably triclinic (Hattori *et al.*, 1953). However, recent studies suggested that isomer (1) is acceptable because this compound has a keto group. We have identified the molecular structure of this compound by X-ray crystallography.



The most stable isomer obtained in the solid state is the keto form with C_{2v} symmetry. The ring is essentially planar, the largest deviation from the least-squares plane being 0.005 Å (N1). The bond lengths are quite different from normal ones. The N1—N2 length of 1.351 (2) Å is clearly shorter than other N—N single-bond lengths. The N—N bond lengths in hydrazine (H_2N—NH_2) and *N,N,N′,N′*-tetramethylhydrazine [$(CH_3)_2N$—$N(CH_3)_2$] are 1.449 and 1.42 Å, respectively (Sasada, 1984). Similarly, the C1—N2 bond length of 1.348 (2) Å is shorter than that of 1.47 Å in ethylenediamine ($NH_2C_2H_4NH_2$) and that of 1.46 Å in *N,N,N′,N′*-tetramethylhydrazine. Also, the N1=N1* double-bond length of 1.275 (3) Å is longer than the normal ones; for example, the N=N bond length in azomethane (CH_3N=NCH_3) is 1.247 Å (Sasada, 1984). Such intermediate lengths between single- and double-bond lengths should arise because the electrons in the π orbitals are delocalized over the ring. The C1=O1 bond length of 1.241 (3) Å is longer than expected; for example, that in acetone is 1.213 Å. However, this is not due to the delocalization of the electrons, but to intermolecular electrostatic interactions. The shortest intermolecular distance between the O atom and an H atom is 1.93 Å.

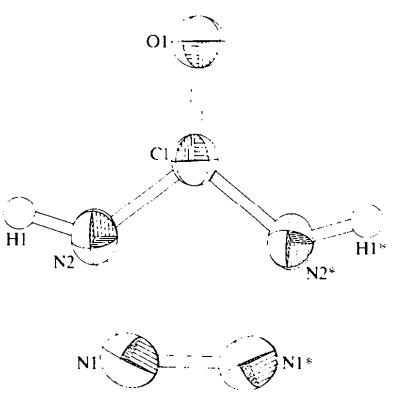


Fig. 1. View of the title molecule with the atomic numbering scheme and with non-H atoms represented by 50% probability ellipsoids. Superscript * denotes the symmetry transformation *y, x, −z, i.e.* code (i) in Table 2.