Distances to the plane from the atoms out of the plane

Cl1	−1.217 (5)	O1	−3.455 (6)
O2	1.122 (7)	O3	0.463 (8)

The high *R* value is due to the small crystal size. Computations were carried out using programs of the *NRCVAX* package (Gabe, Le Page, Charland, Lee & White, 1989).

This work was funded in part by the Ontario Ministry of the Environment.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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17β-Hydroxy-3-methoxyestra-1,3,5(10)-triene-6,7-dione 7-Oxime

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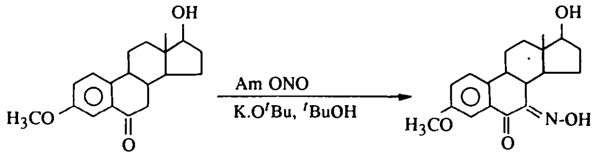
Abstract

X-ray structure analysis of the title compound, $C_{19}H_{23}NO_4$, showed an unexpected *anti* orientation for the 6-oxo-7-oximino function. After molecular-mechanics calculations, the H atom of the 17-hydroxy moiety, which participates in a strong hydrogen bond formed in the crystalline state, changed its orientation substantially. Some change in the conformation of ring *B* was also observed.

Comment

To prepare a suitably functionalized estradiol derivative for further chemical transformations into a 6,7-seco steroid system, synthesis of 17β-hydroxy-3-methoxyestra-1,3,5(10)-triene-6,7-dione 7-oxime was carried out by the base-catalysed action of amyl nitrate on 17β-hydroxy-3-methoxyestra-1,3,5(10)-triene-6-one, (1):



(1) (2)

The chemical structure of (2) was deduced by spectroscopic data (the ^{1}H NMR spectrum showed a signal at 11.65 p.p.m., corresponding to HO—N<; the signal in the ^{13}C NMR spectrum at 153.18 p.p.m. originates from C7=N—OH), but the exact geometry of the oximino function still remained undefined. Therefore, an X-ray structural analysis of the title compound was undertaken.

From the analysis, it was found that compound (2) possesses the *anti* geometry for the 6-oxo-7-oximino function. In addition, molecular-mechanics calculations were performed to establish possible changes in the conformation and distances between the functional groups in the molecule of (2) when released from the interactions with surrounding molecules in the crystalline state.

A perspective view of the molecule, computed from the final atomic coordinates listed in Table 1, is shown in Fig. 1. Unusually high displacement factors for the O4 atom were found. Ring-puckering parameters (Cremer & Pople, 1975) and asymmetry parameters (Duax, Weeks & Rohrer, 1976), listed in Table 3, define the ring conformations (Fig. 2).

Ring *B* exhibits an 8β-envelope (sofa) conformation. The distance of C8 from the best plane of the remaining five atoms is 0.696 (5) Å. Ring *C* has an 8β,12α-chair conformation, while the five-membered ring *D* adopts a 13β,14α-half chair conformation [the distances of C13 and C14 from the best plane of the remaining three atoms are 0.499 (5) and −0.316 (5) Å, respectively], slightly distorted towards a 13β-envelope conformation. After energy minimization, there were no noticeable changes in the conformation of rings *C* and *D*. However, the envelope conformation of ring *B*, the only

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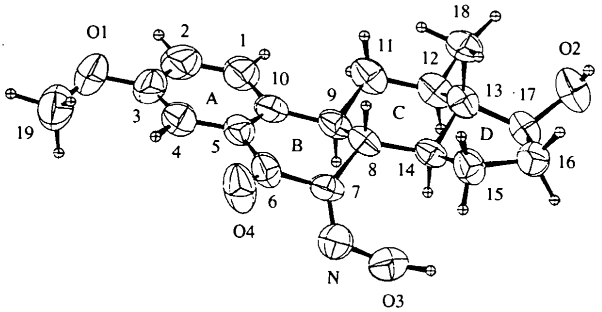

Fig. 1. A perspective view of the molecule with atomic labelling. Displacement ellipsoids are shown at the 30% probability level; H atoms (not labelled) are drawn as spheres of arbitrary radii.

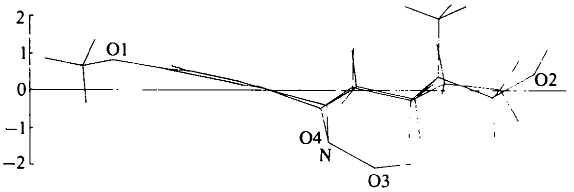

Fig. 2. The conformation of the molecule viewed perpendicular to the C8—C14 bond with the scale in Å.

flexible ring in the 1,3,5(10)-estratriene steroid system, became significantly altered towards a 7α,8β-half chair. The non-bonded torsion angle C1—C10···C13—C18 of 78.1 (6)° (after energy minimization 77.0°) indicates a certain twist along the principal axis of the molecule, caused by bulky substituents at C6 and C7. The non-bonded O1···O2 distance is 10.936 (7) Å in the crystalline state and 10.880 Å after energy minimization.

During energy minimization the H atom at 17β-OH, whose position was very well defined in the Δ*F* map and satisfactorily refined, changes its orientation from +synclinal to −antiperiplanar (C13—C17—O2—HO2 is 79.3 and −173.1°, respectively) taking C13 as the reference atom. The energetically unfavourable orientation of the aforementioned H atom in the crystalline state is probably a result of its participation in the strong intermolecular hydrogen bond [O2···O3(*y*, *x*−1, −*z*) = 2.62 (1) Å, O2—HO2···O3 = 165 (1)°].

Experimental

Crystal data

$C_{19}H_{23}NO_4$
$M_r = 329.40$
Tetragonal
$P4_12_12$
$a = 9.441\ (1)$ Å
$c = 39.253\ (5)$ Å
$V = 3498\ (1)$ Å^3
$Z = 8$
$D_x = 1.25$ Mg m^{-3}

Cu *Kα* radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 14.7 - 27.5°$
$\mu = 0.675$ mm^{-1}
$T = 295$ K
Prism
0.275 × 0.100 × 0.050 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: refined from Δ*F* (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.9510$, $T_{\max} = 0.9995$
2526 measured reflections

2195 independent reflections
1448 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 50°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 39$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on *F*
$R = 0.060$
$wR = 0.063$
$S = 1.9$
1442 reflections
229 parameters
$w = 0.7017/[\sigma^2(F) + 0.00265F^2]$

$(\Delta/\sigma)_{\max} = 0.676$
$\Delta\rho_{\max} = 0.123$ e Å^{-3}
$\Delta\rho_{\min} = -0.155$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for H atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	*y*	*z*	$U_{\rm iso}/U_{\rm eq}$
C1	0.4685 (8)	0.5063 (8)	0.1506 (2)	0.070 (2)
C2	0.3889 (9)	0.6016 (10)	0.1697 (2)	0.087 (3)
C3	0.3724 (8)	0.7404 (10)	0.1586 (2)	0.080 (2)
C4	0.4295 (7)	0.7814 (8)	0.1280 (2)	0.068 (2)
C5	0.5093 (7)	0.6850 (7)	0.1091 (1)	0.056 (2)
C6	0.5788 (8)	0.7391 (8)	0.0783 (2)	0.063 (2)
C7	0.6796 (7)	0.6420 (7)	0.0614 (2)	0.055 (2)
C8	0.6361 (7)	0.4879 (5)	0.0625 (1)	0.050 (2)
C9	0.6280 (7)	0.4455 (6)	0.1006 (1)	0.053 (2)
C10	0.5337 (6)	0.5459 (7)	0.1203 (1)	0.055 (2)
C11	0.5842 (7)	0.2887 (6)	0.1057 (2)	0.064 (2)
C12	0.6751 (7)	0.1882 (6)	0.0835 (2)	0.061 (2)
C13	0.6684 (6)	0.2283 (6)	0.0462 (1)	0.054 (2)
C14	0.7244 (6)	0.3811 (6)	0.0420 (1)	0.048 (2)
C15	0.7381 (8)	0.3971 (7)	0.0035 (2)	0.067 (2)
C16	0.7966 (8)	0.2497 (7)	−0.0073 (2)	0.073 (2)
C17	0.7796 (7)	0.1557 (7)	0.0238 (2)	0.061 (2)
C18	0.5200 (7)	0.2026 (7)	0.0317 (2)	0.065 (2)
C19	0.3029 (9)	0.9742 (11)	0.1735 (2)	0.107 (3)
N	0.7911 (7)	0.7071 (6)	0.0508 (1)	0.072 (2)
O1	0.2962 (6)	0.8273 (7)	0.1794 (1)	0.107 (2)
O2	0.7472 (6)	0.0137 (5)	0.0134 (1)	0.085 (2)
O3	0.8996 (6)	0.6233 (6)	0.0397 (2)	0.085 (2)
O4	0.5571 (7)	0.8591 (6)	0.0676 (2)	0.097 (2)
HO2	0.700 (14)	−0.011 (14)	−0.001 (3)	0.016 (6)
HO3	0.934 (14)	0.579 (16)	0.017 (3)	0.030 (7)

Table 2. *Selected geometric parameters* (Å, °)

O1—C3	1.362 (8)	C7—N	1.288 (8)
O1—C19	1.407 (9)	O4—C6	1.225 (8)
O2—C17	1.435 (8)	O2—HO2	0.75 (13)
O3—N	1.365 (8)	O3—HO3	1.04 (12)
C2—C3—O1	116.0 (7)	C8—C7—N	133.7 (6)
C7—C8—C14	118.0 (5)	C7—N—O3	116.1 (6)
C14—C13—C17	97.0 (4)	C17—O2—HO2	129 (9)
C13—C17—O2	115.8 (5)	N—O3—HO3	137 (7)
C2—C3—O1—C19	166.0 (7)	C8—C7—N—O3	−4.5 (11)
C4—C5—C6—O4	−7.1 (11)	C12—C13—C17—O2	80.9 (7)
O4—C6—C7—N	38.9 (10)		

Table 3. *Ring-puckering and asymmetry parameters*

Ring	Q (Å)	φ (°)	θ (°)	C_s (°)	C_2 (°)	
B	0.512 (8)	172 (1)	54.0 (9)	8.6 (C5)	19.4 (C5—C10)	E_4
B*	0.552	166	52.3	14.3 (C5)	13.7 (C5—C10)	$E_4 \leftrightarrow {}^3H_4$
C	0.572 (8)	238 (6)	7.0 (8)	6.9 (C8)	4.7 (C8—C9)	${}^1C_4$
				0.4 (C9)	5.4 (C9—C11)	${}^1C_4$
				7.2 (C11)	10.0 (C11—C12)	${}^1C_4$
C*	0.568	249	10.5	10.6 (C8)	8.8 (C8—C9)	${}^1C_4$
				2.2 (C9)	5.0 (C9—C11)	${}^1C_4$
				8.5 (C11)	13.4 (C11—C12)	${}^1C_4$
D	0.503 (8)	194 (1)		15.2 (C13)	5.8 (C16)	${}^2H_1 \rightarrow E_1$
D*	0.483	193		14.2 (C13)	6.0 (C16)	${}^2H_1 \rightarrow E_1$

* Values resulting from molecular-mechanics calculations.

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.

Program used to solve the structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine the structure: *SHELX*76 (Sheldrick, 1976). Software to prepare material for publication: *CSU* (Vicković, 1988). Software for performing molecular-mechanics calculations: *PCMODEL* (Serena Software, 1989).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KA1093). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Imino-1,4,4-triphenylimidazolidin-2-one: an Imidazolidine with an Exocyclic Imino Group

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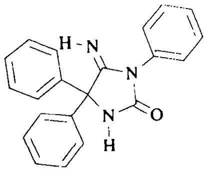
Abstract

The conformation of the imidazolidine ring in the title compound, $C_{21}H_{17}N_3O$, is almost flat with a maximum deviation of ±0.031 (8) Å from the least-squares plane through the ring. The structure is stabilized by an intermolecular hydrogen bond. This type of compound can be used in addition reactions with isocyanates.

Comment

In the past, 5-iminoimidazolidin-2-ones were only reported as intermediates of hydantoins, without further investigation of their structure. In order to characterize one such reaction product unambiguously, an X-ray structure determination of the title compound, (I), has been undertaken.



(I)

Heterocycles with an imino group next to the ring N atom can undergo Dimroth rearrangement (Dimroth, 1909). During this rearrangement the group bound to the ring N atom moves to the exocyclic N atom (Brown & Ienega, 1974). The resulting product no longer has a free imino function. Furthermore, the only published NMR shift for the imino group of a 4,4-disubstituted 5-imidazolidin-2-one differs by about 1.4 p.p.m. from

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