

Acta Cryst. (1998). **C54**, 372–373

A Steroidal Dihydro-1,3-oxazine Derivative

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(Received 9 June 1997; accepted 11 November 1997)

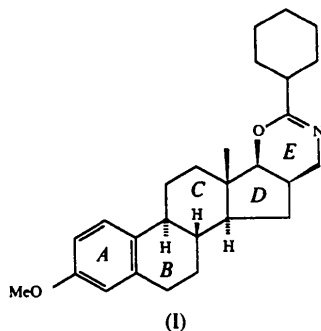
Abstract

The structure of 2'-cyclohexyl-16 α ,17 α -dihydro-3-methoxy-4H-[1,3]oxazino[5',6':16,17]estra-1,3,5(10),16-tetraene, C₂₇H₃₇NO₂, synthesized *via* a Ritter reaction, is reported. A *cis*-fused dihydrooxazine ring, condensed to the known estrane skeleton, was found in the title compound.

Comment

The oxetane ring condensed to the estrane skeleton in the 16 β ,17 β -positions, investigated by us (Hajnal *et al.*, 1997), is transformed into the oxonium ion in acid media. The substitution of a nucleophilic aliphatic or aromatic nitrile can take place at both the C16 methylene and C17 atoms. The 'normal' Ritter reaction product would be the one obtained by the attack at the C atom of higher order, assuming the general observation (Ritter & Minieri, 1948). However, the attack at C17 would involve inversion, and stabilization of the carbocation formed would yield the sterically unfavoured *trans*-annellated dihydrooxazine. The attack at C16 is sterically favoured and the carbocation developed forms a dihydrooxazine ring condensed to the estrane skeleton. The reason for the present study was to prove this 'anomalous' occurrence of the reaction.

The crystal structure of the title compound, (I), reveals that the *B/C* ring fusion is *trans*, whereas the *D/E* fusion is *cis*. Ring *A* is planar (mean deviation



0.0186 Å), ring *B* adopts a distorted half-chair conformation, ring *C* a chair conformation, ring *D* a β -envelope conformation and ring *E* a boat conformation. For structures of some other estrone derivatives, see Burns & Hagaman (1993), Hooft & Kroon (1995) and Bolanos-García *et al.* (1996).

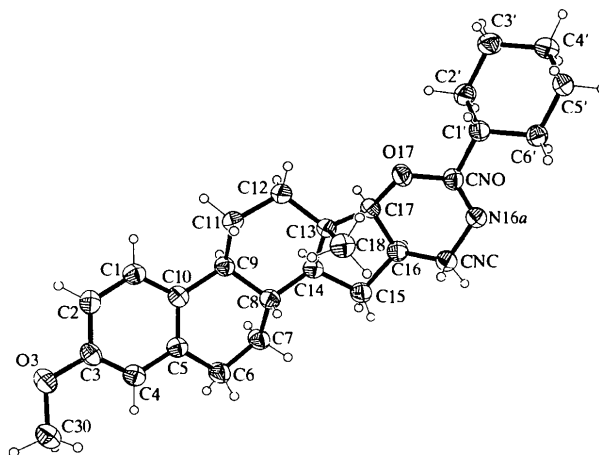


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

The synthesis of the title compound was carried out by reaction of 16 β ,17 β -epoxymethylene-3-methoxyestra-1,3,5(10)-triene and cyclohexanecarbonitrile in the presence of an equivalent amount of HBF₄-diethyl etherate. The dihydrooxazine-HBF₄ salt which formed was dissolved in CH₂Cl₂ and a saturated aqueous solution of NaHCO₃ was layered over it. The organic phase was separated and evaporated to dryness. The residue was crystallized from acetone at room temperature.

Crystal data

C₂₇H₃₇NO₂
M_r = 407.58
Orthorhombic
*P*2₁2₁2₁
a = 6.781 (1) Å
b = 15.530 (3) Å
c = 21.179 (4) Å
V = 2230.3 (7) Å³
Z = 4
D_x = 1.214 Mg m⁻³
D_m not measured

Mo *K* α radiation
 λ = 0.71073 Å
Cell parameters from 6579 reflections
 θ = 1.92–25.09°
 μ = 0.075 mm⁻¹
T = 133 (2) K
Block
0.50 × 0.40 × 0.40 mm
Colourless

Data collection

Stoe-Siemens-Huber four-circle diffractometer with CCD detector

2280 independent reflections
2063 reflections with *I* > 2 σ (*I*)

ψ scan $R_{\text{int}} = 0.041$
 Absorption correction: $\theta_{\text{max}} = 25.09^\circ$
 multi-scan (SADABS; $h = 0 \rightarrow 8$
 Sheldrick, 1997a) $k = 0 \rightarrow 18$
 $T_{\text{min}} = 0.964$, $T_{\text{max}} = 0.971$ $l = 0 \rightarrow 25$
 25 360 measured reflections

Refinement

Refinement on F^2 $\Delta\rho_{\text{max}} = 0.148 \text{ e } \text{\AA}^{-3}$
 $R[F^2 > 2\sigma(F^2)] = 0.040$ $\Delta\rho_{\text{min}} = -0.175 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.099$ Extinction correction:
 $S = 1.116$ *SHELXL97*
 2280 reflections Extinction coefficient:
 274 parameters 0.0086 (12)
 H atoms treated by a Scattering factors from
 mixture of independent *International Tables for*
 and constrained refinement *Crystallography* (Vol. C)
 $w = 1/[\sigma^2(F_o^2) + (0.0484P)^2$ Absolute structure: Flack
 $+ 0.6498P]$ (1983)
 where $P = (F_o^2 + 2F_c^2)/3$ Flack parameter = 4 (2)
 $(\Delta/\sigma)_{\text{max}} < 0.001$

The data collection nominally covered over a hemisphere of reciprocal space, by a combination of five sets of exposures; each set had different χ and ω angles, and each exposure covered 0.5° in φ . The crystal-to-detector distance was 5 cm. Coverage of the unique set was over 99% complete to at least 25° in θ . Crystal decay was monitored by repeating the initial frames between runs and analysing the duplicate reflections. The structure was solved by direct methods using *SHELXS97* (Sheldrick, 1990). All non-H atoms were refined anisotropically using *SHELXL97* (Sheldrick, 1997b). The H atoms were refined using a riding model. The isotropic displacement parameters were set to 1.2 (1.5 for CH_3 groups) times the equivalent displacement parameter of the atom to which they are attached.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Molecular graphics: *SHELXTL* (Siemens, 1995). Software used to prepare material for publication: *SHELXL97*.

This research was supported by the National Science Foundation of Hungary (OTKA Grant N. T016122 and F016119). MTB thanks the European Community for a postdoctoral fellowship (N. ERBCHBGCT 940731). JW thanks an Alexander von Humboldt fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1249). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 373–376

2-(Isopropoxy)-4,12-diphenyl-4-(trifluoromethyl)-1,13-dithia-3,11-diazadisp[4.0.4.3]trideca-2,11-diene

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(Received 24 October 1997; accepted 12 November 1997)

Abstract

The title compound, $\text{C}_{25}\text{H}_{25}\text{F}_3\text{N}_2\text{OS}_2$, is one of two isomeric 1:1 cycloadducts of a thermally generated isopropoxy-substituted nitrile ylide and 2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione. The structure shows the regiochemistry of the formation of the major isomer. The cyclopentane ring is disordered and shows both a half-chair and an envelope conformation. The heterocyclic rings have envelope conformations. The C—C bonds involving the heterocyclic spiro C atom are elongated due to electronic effects from the neighbouring S atoms. Delocalization effects result in asymmetric S—C bond lengths.

Comment

The regioselectivity of 1,3-dipolar cycloadditions of nitrile ylides is of theoretical (Houk, 1979) and preparative interest (Hansen & Heimgartner, 1984). It has been shown that substituents at C1 and C3 of the nitrile ylide, (I), have a distinct influence on the geometry of the ylide (propargyl-type A versus allenyl-type B; Caramella *et al.*, 1977).

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