

Table 2. Selected torsion angles ( $^{\circ}$ ) for the  $\alpha$ -silylvinylsulfoximines in series (2)

Compound	R	C=C—S=O	C=C—S=N
(2a)†	<sup>t</sup> Pr	109.98 (15)	-123.66 (15)
(2a)†	<sup>t</sup> Pr	-115.94 (15)	117.76 (15)
(2b)	Ph	108.9 (5)	-125.1 (5)
(2d)	Me	-0.8 (5)	-134.7 (4)

† Two crystallographically independent molecules.

For compounds (1f) and (2d), data collection was restricted to a  $\theta_{\max}$  of  $22.5^{\circ}$ , because higher-angle intensities were very weak. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with  $U_{\text{iso}}$  constrained to be 1.2 (1.5 for methyl groups) times  $U_{\text{eq}}$  of the carrier atom. For compound (1e), twofold disorder of the cyclohexyl group was resolved and refined with essentially equal occupancies [50.6(6):49.4(6)%], without the need for any constraints or restraints.

For compounds (1c), (1d), (1e) and (2a); data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSCIAFC Diffractometer Control Software*; data reduction: *MSCIAFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs. For compounds (1f), (2b), (2d) and (3); data collection: *DIF4* (Stoe & Cie, 1988); cell refinement: *DIF4*; data reduction: local programs; program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1428). Services for accessing these data are described at the back of the journal.

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## A Hexacyclic Estrone Derivative

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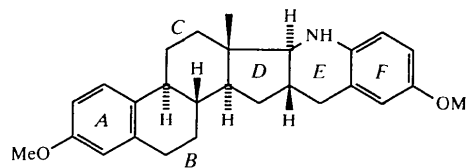
(Received 29 August 1997; accepted 16 February 1998)

### Abstract

The structure of 3,6'-dimethoxy-1',2' $\alpha$ ,3' $\beta$ ,4'-tetrahydroquinolino[3',2':16,17]estra-1,3,5(10)-triene, C<sub>27</sub>H<sub>33</sub>NO<sub>2</sub>, is reported.

### Comment

The synthesis of the title compound, (I), via a boron trifluoride ethyl etherate-initiated cyclization reaction of the corresponding D-secoestrone imine derivative, will



(I)

be published elsewhere (Frank *et al.*, 1998). The structure was investigated to determine the relative configuration of the newly formed stereogenic centres (C16 and C17), which could not be established unambiguously by NMR spectroscopy. The B/C, C/D and D/E ring fusions are all *trans*. Rings A and F are both planar, rings B and E adopt distorted half-chair conformations, ring C a chair conformation and ring D an envelope

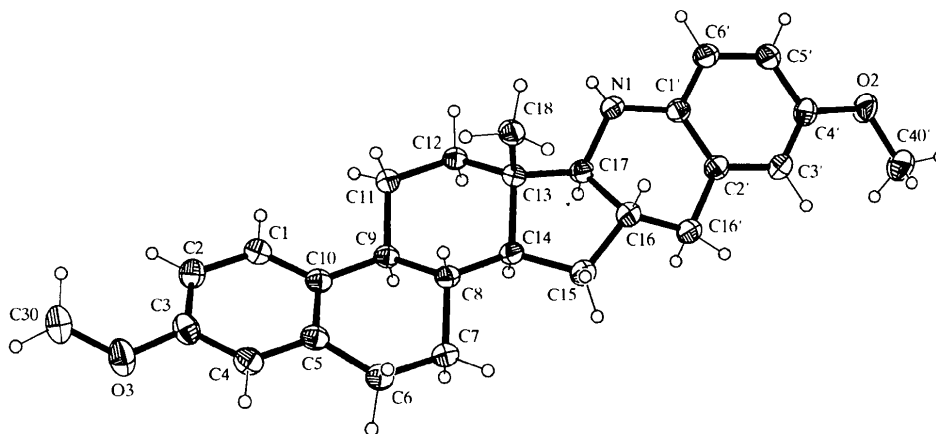


Fig. 1. Molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

conformation. For the crystal structures of some other estrone derivatives see Bes *et al.* (1997), Bolanos-García *et al.* (1996) and Hooft & Kroon (1995); for those of some quinoline derivatives see Ng (1997), Othman *et al.* (1996) and Kelderman *et al.* (1996).

## Experimental

For the synthesis of the title compound, (I), 13 $\alpha$ -formyl-3-methoxy-16,17-secoestra-1,3,5(10),16-tetraene and *p*-anisidine were reacted in dichloromethane in the presence of molecular sieves. The resultant imine derivative (not isolated) was transformed into (I) by treatment with equivalent amounts of boron trifluoride ethyl etherate. After column chromatography on silica gel, the product was crystallized from a 1:1 mixture of acetone/*tert*-butyl methyl ether at 298 K.

### Crystal data

C<sub>27</sub>H<sub>33</sub>NO<sub>2</sub>  
*M<sub>r</sub>* = 403.54  
 Monoclinic  
*P*2<sub>1</sub>  
*a* = 9.847 (3) Å  
*b* = 10.242 (3) Å  
*c* = 10.866 (3) Å  
 $\beta$  = 101.40 (4)°  
*V* = 1074.2 (5) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.248 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 48 reflections  
 $\theta$  = 10.0–12.5°  
 $\mu$  = 0.077 mm<sup>-1</sup>  
*T* = 153 (2) K  
 Block  
 0.75 × 0.75 × 0.60 mm  
 Colourless

### Data collection

Siemens–Stoe AED four-circle diffractometer  
 2 $\theta$ / $\omega$  scans  
 Absorption correction: none  
 3269 measured reflections  
 2006 independent reflections  
 1953 reflections with *I* > 2 $\sigma$ (*I*)

*R*<sub>int</sub> = 0.036  
 $\theta_{\max}$  = 25°  
*h* = -11 → 11  
*k* = -12 → 12  
*l* = -12 → 12  
 3 standard reflections  
 frequency: 90 min  
 intensity decay: <3%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 0.101  
*S* = 1.015  
 3124 reflections  
 278 parameters  
 H atoms: riding model  
 $w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.1363P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{\max} = 0.207 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.184 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL96*  
 Extinction coefficient: 0.016 (6)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

The structure was solved by direct methods using *SHELXS96* (Sheldrick, 1990). All-non H atoms were refined anisotropically using *SHELXL96* (Sheldrick, 1996). Floating-origin restraints are generated automatically by *SHELXL96*, according to the method of Flack & Schwarzenbach (1988). The H atoms were refined using a riding model and their isotropic displacement parameters were set to 1.2 times (1.5 times for CH<sub>3</sub> groups) the equivalent displacement parameter of their parent atoms.

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL96*.

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Supplementary data for this paper are available from the IUCR electronic archives (Reference: KA1260). Services for accessing these data are described at the back of the journal.

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### Some 1,3-Dipolar Adducts from Benzodiazepine. II.† Condensation of Nitrilimines with [1,4]Benzodiazepine and [1,4]Benzodiazepin-2-one

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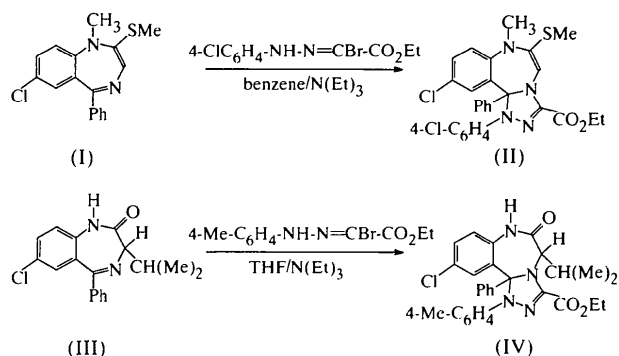
#### Abstract

The structure of the diadduct ethyl 10-chloro-1-(4-chlorophenyl)-7-methyl-6-methylthio-11b-phenyl-7,11b-dihydro-1*H*-[1,2,4]triazolo[4,3-*d*][1,4]benzodiazepine-3-carboxylate, C<sub>27</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>S, has been established by X-ray crystallographic study. The central seven-membered ring is fused with chlorobenzene and triazolo rings to form the core of the molecule.

† Part I: Essaber *et al.* (1998).

#### Comment

Several benzodiazepine derivatives containing an additional ring are of pharmacological interest (Sternbach, 1978). In connection with our investigation on possible approaches to the synthesis of novel benzodiazepine derivatives with an additional fused heterocyclic ring (Capozzi *et al.*, 1985), we have condensed 7-chloro-1-methyl-2-methylthio-5-phenyl-1*H*-[1,4]benzodiazepine, (I) (Early *et al.*, 1974), and 7-chloro-3-isopropyl-5-phenyl[1,4]benzodiazepine-2(3*H*)-one, (III) (Sternbach *et al.*, 1962), with nitrilimines (Huisgen & Koch, 1955) generated *in situ* to give compounds (II) and (IV), respectively (see scheme below). The structures of compounds (II) and (IV) have been determined unambiguously from X-ray diffraction studies. However, the poor quality of the structure determination for compound (IV) does not enable us to give a detailed description of its conformation.



In compound (II) (Fig. 1), the seven-membered ring is composed of two planar fragments: N9–C10a–C10b–N11 (r.m.s. deviation 0.030 Å), which includes

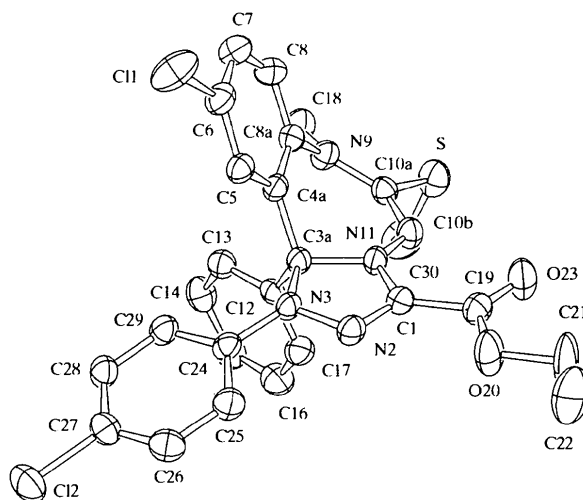


Fig. 1. View of compound (II) with the atom-numbering scheme (C15 partly obscured by C24). Displacement ellipsoids are shown at the 50% probability level.