

C15—N—C20	126.5 (2)	N—C20—C21	108.5 (3)
O2—C1—C2	109.6 (3)	N—C20—C22	111.9 (2)
C1—C2—C3	118.4 (3)	N—C20—C23	106.9 (3)
C1—C2—C7	123.3 (3)	C21—C20—C22	109.6 (3)
O3—C8—C9	111.9 (3)	C21—C20—C23	108.8 (3)
C8—C9—C10	119.5 (4)	C22—C20—C23	111.0 (3)
C8—C9—C14	121.8 (4)		

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *BEGIN* in *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM* in *SDP-Plus*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

The authors are grateful to Drs M. Pierrot and M. Giorgi (Service Commun Cristallochimie St Jérôme) for the X-ray data collection. The authors also thank ELF ATOCHEM and CNRS for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1002). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). **C54**, 1714–1716

## 13,13-Ethylenedithio-3-mesyloxy-18-nor-13,17-secoestra-1,3,5(10)-triene-17-nitrile

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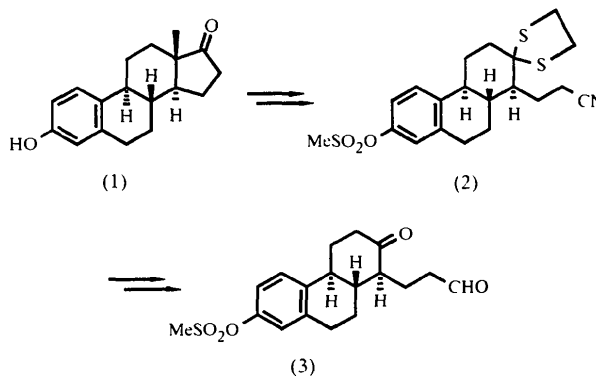
(Received 26 February 1998; accepted 14 April 1998)

## Abstract

In the course of the partial synthesis of 18-norestradiol, an X-ray analysis of an appropriately crystallizing intermediate, C<sub>20</sub>H<sub>25</sub>NO<sub>3</sub>S<sub>3</sub>, was carried out in order to determine its absolute configuration. The unusual D-seco steroid displays configurations at C8, C9 and C14 not altered in comparison with the starting material, estrone.

## Comment

In the context of our investigations directed towards the synthesis of 18-norsteroids, we examined an intramolecular coupling reaction of (3), a D-seco steroid prepared by a seven-step sequence starting from naturally occurring estrone, (1) (Kuhl, 1998). Since our first attempts to determine the configuration of (3) by NMR techniques led to ambiguous results and (3) was obtained as a non-crystallizing oil, we undertook the X-ray analysis of the title compound, (2), as a precursor of (3).



Although (2) displays in its D-seco moiety an unusual feature for steroids, some distortion effects typical of aromatic estrane derivatives are observed concerning rings A and B. Ring A displays typical characteristic aromaticity, with delocalization of  $\pi$  electrons producing an average C—C bond length of 1.381 (3) Å (Duax, 1972), with the exception of the C<sub>2</sub>—C<sub>3</sub> bond, which is significantly shortened [1.325 (6) Å]. Additionally, the C<sub>5</sub>—C<sub>10</sub>—C<sub>1</sub> bond angle is reduced to a value of

117.2(4)°. These facts are due to a strong interaction of the aromatic H1 and equatorial H11 atoms of ring C, indicated by an interatomic distance of 2.112(5) Å. The steric repulsive hindrance is reduced by a twisting about the C9—C10 bond (Cooper *et al.*, 1969), leading to a slightly deformed half-chair conformation for ring B (Cody *et al.*, 1971). In contrast to usual aromatic estranes, ring C is in an ideal chair conformation, with the C9 atom lying 0.672(4) Å below and C13 0.696(4) Å above the plane through atoms C8, C11, C12 and C14. The spiro-fused ring E at C13 displays puckering parameters  $\varphi_m$  and  $\Delta$  (Altona *et al.*, 1968) of 29.6 and  $-1.5^\circ$ , respectively. The conformation, therefore, approximates an ideal half-chair. From a chemical point of view, it is significant that the C14 side chain retains a *trans* configuration with respect to the H9 atom, thus reflecting the original stereochemical relationship of the starting compound, estrone (1). The displacement parameters of atoms C1', O2 and O3 indicate disorder. The crystal structure contains solvent-accessible voids of 29.0 Å<sup>3</sup>, which are too small for the methanol crystallization solvent.

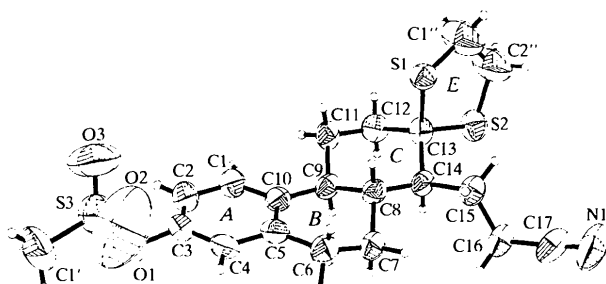


Fig. 1. View (*SHELXTL-Plus*; Sheldrick, 1991) of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of arbitrary radii.

## Experimental

Thioacetal (2) was prepared by treatment of the corresponding ketone with 1.2 equivalents of ethanedithiol and 2.5 equivalents of BF<sub>3</sub>·Et<sub>2</sub>O in a solution of dichloromethane (Jones *et al.*, 1990). Usual work-up led to a 97% yield of thioacetal (2), which was crystallized from methanol (m.p. 435 K).

### Crystal data

C<sub>20</sub>H<sub>25</sub>NO<sub>3</sub>S<sub>3</sub>  
*M<sub>r</sub>* = 423.59  
 Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 7.055(2) Å  
*b* = 12.531(2) Å  
*c* = 24.464(2) Å  
*V* = 2162.8(4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.301 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71069 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 9.66–10.31°  
 $\mu$  = 0.362 mm<sup>-1</sup>  
*T* = 291(1) K  
 Plate  
 0.30 × 0.15 × 0.08 mm  
 Colourless

### Data collection

Nonius MACH3 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 $\psi$  scan (*CORINC*; Dräger & Gattow, 1971)  
 $T_{\min}$  = 0.938,  $T_{\max}$  = 0.971  
 3689 measured reflections  
 3465 independent reflections

1727 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.016  
 $\theta_{\text{max}}$  = 27.47°  
 $h$  =  $-1 \rightarrow 9$   
 $k$  =  $-1 \rightarrow 16$   
 $l$  =  $-1 \rightarrow 31$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 1.3%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)]$  = 0.058  
 $wR(F^2)$  = 0.109  
 $S$  = 1.148  
 3465 reflections  
 244 parameters  
 H atoms constrained, only  
 U's refined

$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}}$  = 0.001  
 $\Delta\rho_{\text{max}}$  = 0.233 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  =  $-0.185$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

C2—C3	1.325(6)		
C5—C10—C1	117.2(4)		
C10—C5—C6—C7	-19.0(6)	S2—C13—S1—C1''	20.7(3)
C5—C6—C7—C8	48.7(5)	C13—S1—C1''—C2''	-27.6(7)
C6—C7—C8—C9	-64.9(5)	S1—C1''—C2''—S2	23.6(9)
C7—C8—C9—C10	50.3(5)	C1''—C2''—S2—C13	-7.0(7)
C6—C5—C10—C9	5.7(6)	S1—C13—S2—C2''	-11.0(4)
C8—C9—C10—C5	-22.0(5)		

The title structure was solved by direct methods (*SHELXS97*; Sheldrick, 1990) and successive difference Fourier syntheses and refined by full-matrix least-squares methods (*SHELXL97*; Sheldrick, 1997). H atoms were placed in calculated positions using a riding model with atomic displacement parameters fixed at 1.2 times those of the C atoms. Refinement of the Flack (1983) parameter resulted in a value of  $x = -0.20(12)$ , which gives only a slight indication that the given configuration is the absolute configuration, but chemical considerations undoubtedly confirm the selected configuration.

Data collection: Nonius MACH3 Argus software. Cell refinement: Nonius MACH3 Argus software. Data reduction: *CORINC* (Dräger & Gattow, 1971). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL97* and *PARST95* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1360). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). C54, 1716–1718

## 1-(2-Mercaptoethyl)-2-methyl-1,2-dicarbaborane(12)

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(Received 22 January 1998; accepted 20 May 1998)

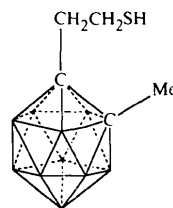
### Abstract

In the title compound, C<sub>5</sub>H<sub>18</sub>B<sub>10</sub>S, the mercaptoethyl and methyl groups are connected to the C atoms of the 1,2-dicarbaborane cage. The C<sub>cage</sub>—C<sub>cage</sub> distance is 1.670 (3) Å and the C—C<sub>cage</sub>—C<sub>cage</sub>—C torsion angle –1.2 (3)°.

### Comment

In earlier papers, we have studied the elongation of the C1—C2 distance in 1,2-dicarbaboranes and suggested an empirically derived equation to calculate this distance (Kivekäs *et al.*, 1994; Kivekäs, Sillanpää *et al.*, 1995). The C1—C2 bond length varies considerably, depending on the number of substituents and the atomic species connected to the cluster C atoms. Thus, values of 1.634 (3) and 1.57 (1)–1.61 (1) Å are reported for the 1,2-dihydrogen compounds 9,12- $\mu$ -[(CH<sub>3</sub>)<sub>2</sub>CS<sub>2</sub>]-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> and CH<sub>2</sub>(9-S-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)<sub>2</sub>, respectively (Šubrtová *et al.*, 1980; Novák *et al.*, 1983). Much larger values of 1.816 (7), 1.826 (5) and 1.858 (5) Å are observed for compounds in which S atoms are connected to both the cluster C atoms (Teixidor, Romerosa *et al.*, 1990; Teixidor, Viñas *et al.*, 1990). Generally, the contribution of C, Si and P to this lengthening is less than that of S and, moreover, it seems that

aryl substituents have a greater tendency to elongate the bond than non-aryl substituents (Lewis & Welch, 1993). In order to study further the contribution of different types of C substituents on the lengthening of the C1—C2 bond, we have synthesized the title compound, (I), and determined its crystal structure.



(I)

In (I), the C14 atom is oriented away from C15, the S atom is *anti* in relation to the cluster C1 atom and, omitting H atoms, the molecule has a pseudo-mirror plane through atoms S, C1, C2, C13–C15, B9 and B12. The intramolecular C13...C15 distance of 3.106 (4) Å is only 0.2–0.3 Å shorter than the sum of the corresponding van der Waals radii (Allinger *et al.*, 1968; Bondi, 1964), indicating the absence of any noteworthy repulsion between C13 and C15. The C13—C1—C2—C15 torsion angle of –1.2 (3)° agrees well with the value of 0.5 (8)° in 1-P<sup>i</sup>Pr<sub>2</sub>-2-Me-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, but significantly higher values have been reported for compounds with bulky substituents connected to both cluster C atoms: for instance, in 1,2-(P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, the value is 12.1 (2)° (Kivekäs, Sillanpää *et al.*, 1995).

The C13—C1—X (X = B or C) angles vary from 116.7 (2) to 123.1 (2)°, and the C15—C2—X angles from 117.6 (2) to 120.8 (2)°. For compounds in which one or two bulky substituents such as P<sup>i</sup>Pr<sub>2</sub> or PPh<sub>2</sub> are connected to cluster C atoms, variations of up to ca 21° on the corresponding angle values have been observed (Kivekäs, Sillanpää *et al.*, 1995; Kivekäs, Teixidor *et al.*, 1995; Sillanpää *et al.*, 1996; Teixidor *et al.*, 1997). This significant variation probably originates from the

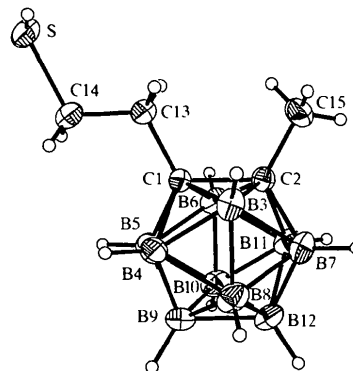


Fig. 1. View of the structure of (I), with displacement ellipsoids at the 30% probability level and H atoms shown as spheres of arbitrary radii.