Crystal Structure and Conformation of 17α-Ethynyl-17β-hydroxy-6,6-dimethyl-6-sila-5α-estr-1(10)-en-3-one

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The crystal and molecular structure of the title compound (I) has been established by *X*-ray analysis. Crystals are monoclinic, space group $P2_1/c$, with $a = 12.87(2)$, $b = 6.61(1)$, $c = 23.32(3)$ Å, $\beta = 97.87(10)°$, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares calculations to R 0.114 over 1729 reflections from photographic data. Ring A adopts a semiplanar conformation, rings B and C are in chair forms, and ring D has a C(13) envelope conformation. The endocyclic C–Si–C angle is 100.1(3)°. The steroid conformation is significantly modified in the A/B region from that usually found.

THE search for new potential contraceptive agents has led to numerous synthetic modifications of the structures of natural steroid hormones. In the past these have included several examples in which a heteroatom, generally nitrogen, oxygen, or sulphur, has replaced a steroid-ring carbon atom.[1] In order to assess the influence which the introduction of these various heteroatoms has upon the overall steroid conformation a few compounds have been subjected to single-crystal analysis.[2] Recently, Pitt *et al.*[3] synthesized a number of

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[1] H. O. Huisman in ' MTP International Review of Science,' ed. W. F. Johns, Butterworths, London, 1973, vol. 8.

[2] See *e.g.* J. N. Brown and L. M. Trefonas, *J. Amer. Chem. Soc.*, 1972, **94**, 4311; H. Schenk, W. M. B. Könst, W. N. Speckamp, and H. O. Huisman, *Tetrahedron Letters*, 1970, 4937; J. S. McKechnie, L. Kubina, and I. C. Paul, *J. Chem. Soc.* (*B*), 1970, 1476.

[3] C. G. Pitt, A. E. Friedman, D. Rector, and M. C. Wani, *Tetrahedron*, in the press.

6,6-dimethyl-6-silasteroids and established that the estrogenic, anti-estrogenic, and post-coital activity of these compounds was significantly less than that exhibited by the normal series. We here report the *X*-ray analysis of one of these compounds, 17α-ethynyl-17β-hydroxy-6,6-dimethyl-6-sila-5α-estr-1(10)en-3-one (I). The study was undertaken to verify that the synthetic scheme had provided the desired stereochemical products and to establish the detailed molecular conformation, knowledge of which might account, in part at least, for the reduced activity.

EXPERIMENTAL

Crystal Data.—$C_{21}H_{30}O_2Si$, $M = 342.6$. Monoclinic, $a = 12.87(2)$, $b = 6.61(1)$, $c = 23.32(3)$ Å, $\beta = 97.87(10)°$, $U = 1\,965$ Å^3, $D_m = 1.16$, $Z = 4$, $D_c = 1.158$, $F(000) = 752$, Cu-K_α radiation, $\lambda = 1.542$ Å; μ(Cu-K_α) = 11.0 cm^{-1}. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$.

TABLE 1

Fractional atomic co-ordinates (× 10⁴) and anisotropic temperature factor parameters * (× 10⁴) for the natural enantiomer, with estimated standard deviations in parentheses

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	4 511(7)	7 448(16)	3 905(4)	75(6)	410(35)	20(2)	−76(27)	15(6)	16(14)
C(2)	4 889(7)	7 618(20)	3 333(4)	81(7)	622(47)	18(2)	−149(31)	17(6)	−30(16)
C(3)	4 233(7)	6 434(17)	2 875(3)	73(6)	433(36)	16(1)	43(27)	20(5)	20(13)
C(4)	3 804(7)	4 477(14)	3 068(3)	70(6)	280(29)	19(2)	36(24)	20(5)	4(13)
C(5)	3 190(6)	4 853(14)	3 581(3)	71(6)	245(25)	14(1)	24(23)	1(5)	0(11)
Si(6)	1 810(2)	5 913(4)	3 402(1)	62(1)	236(6)	16(1)	−8(6)	5(1)	−19(3)
C(7)	1 402(6)	5 958(14)	4 141(3)	65(6)	268(27)	17(1)	−40(22)	−6(5)	−28(12)
C(8)	2 210(6)	7 078(12)	4 586(3)	54(5)	226(24)	14(1)	−10(20)	2(4)	7(10)
C(9)	3 345(6)	6 225(13)	4 624(3)	67(6)	244(25)	12(1)	30(22)	−5(5)	−11(11)
C(10)	3 756(7)	6 233(13)	4 041(3)	76(6)	220(24)	15(1)	57(22)	−1(5)	11(11)
C(11)	4 100(7)	7 250(14)	5 107(3)	76(6)	253(27)	19(2)	−8(23)	19(5)	−27(12)
C(12)	3 703(6)	7 268(13)	5 696(3)	61(5)	221(24)	17(2)	−22(21)	3(5)	−28(11)
C(13)	2 616(6)	8 173(12)	5 654(3)	77(6)	160(21)	13(1)	−7(20)	15(4)	−2(10)
C(14)	1 885(6)	7 032(12)	5 188(3)	60(5)	176(23)	14(1)	−4(19)	10(4)	−20(9)
C(15)	774(6)	7 736(14)	5 265(3)	59(5)	318(29)	19(1)	50(23)	14(5)	−22(12)
C(16)	840(7)	8 395(14)	5 907(3)	71(6)	242(25)	24(2)	45(23)	21(5)	−27(13)
C(17)	1 992(7)	7 966(11)	6 176(3)	84(6)	122(21)	16(1)	66(20)	10(5)	−3(9)
C(18)	2 651(7)	10 505(13)	5 507(3)	101(7)	175(24)	20(2)	−84(23)	17(6)	−11(11)
C(19)	2 033(6)	5 841(13)	6 398(3)	76(6)	210(23)	16(1)	75(22)	13(5)	13(11)
C(20)	2 067(8)	4 129(15)	6 575(4)	120(9)	243(29)	23(2)	89(28)	13(7)	12(14)
O(21)	4 114(5)	7 004(11)	2 369(2)	84(5)	494(26)	18(1)	−94(19)	16(4)	25(10)
C(22)	1 834(8)	8 504(16)	3 107(4)	112(9)	272(29)	24(2)	57(30)	−17(7)	25(15)
C(23)	940(8)	4 321(17)	2 890(4)	78(7)	434(38)	22(2)	−61(30)	2(6)	−42(15)
O(24)	2 306(5)	9 306(8)	6 642(2)	96(5)	194(16)	17(1)	12(15)	16(3)	−35(7)

* In the form: $B\sin^2\theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$.

Crystallographic Measurements.—Unit-cell dimensions were obtained from precession photographs taken with Mo-K_α ($\lambda = 0.7107$ Å) radiation. A crystal of dimensions *ca*. 0.2 × 0.2 × 1.0 mm was oriented to rotate about the crystallographic b axis and three-dimensional intensity data of the $h0$—$6l$ reciprocal lattice nets were recorded photographically by the equi-inclination multiple-film Weissenberg method. Intensities were estimated visually by comparison with a calibrated intensity scale, and corrected for spot-shape, Lorentz, and polarization factors; no allowance was made for absorption. In all, 1 729 non-zero structure amplitudes were derived. Initially the various layers of data were assumed to be on a common scale as each had been given approximately equal exposure times. Absolute layer scales were established at the end of the isotropic refinement stage (*vide infra*) by correlation with the observed structure amplitudes.

Structure Analysis.—The structure was solved by direct phase-determining methods by use of MULTAN [4] with 277 $|E|$ values > 1.34. Reflections in the starting set were 3,5,$\bar{3}$; 4,5,15; 6,1,2; 0,2,17; 1,1,0; 3,4,15; and 5,0,0. An E map calculated from the values of the phase constants produced by that set having the lowest residual and highest figure of merit clearly revealed the positions of all non-hydrogen atoms. Atomic positional and thermal parameters, at first isotropic and subsequently anisotropic, were refined to R 0.140 by a number of full-matrix least-squares calculations. A difference-Fourier synthesis was evaluated and showed significant positive electron density at positions calculated for hydrogen atoms. Inclusion of the thirty hydrogen atoms, with the isotropic temperature factors of their bonded carbon or oxygen atoms, reduced R to 0.122. Following several further least-squares iterations during which the non-hydrogen parameters were varied, the refinement converged at R 0.114. Final atomic positional and thermal parameters are listed in Tables 1 and 2. A Table of observed and calculated structure factors has been deposited in Supplementary Publication No. SUP 21336 (10 pp., 1 microfiche).*

For the structure-factor calculations, scattering factors for carbon, oxygen, and silicon were taken from ref. 5, and for hydrogen from ref. 6. In the least-squares calculations $\Sigma w\Delta^2$ was minimized, with weights w given by

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[4] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] R. F. Stewart, E. R. Davidson, and W.T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

$\sqrt{w} = 1$ for $|F_o| \leqslant 13.0$ and $\sqrt{w} = 13.0/|F_o|$ for $|F_o| > 13.0$.

TABLE 2

Calculated fractional co-ordinates ($\times 10^3$) and isotropic temperature factors for the hydrogen atoms labelled according to the carbon or oxygen atom to which they are bonded

Atom	x	y	z	B/Å^2
H(1)	489	841	422	4.3
H(2α)	487	914	320	5.1
H(2β)	566	707	333	5.1
H(4α)	334	381	274	3.6
H(4β)	445	349	318	3.6
H(5)	308	343	377	3.4
H(7α)	67	671	414	3.6
H(7β)	129	445	427	3.6
H(8)	224	858	444	3.2
H(9)	329	474	475	3.1
H(11α)	482	646	511	4.3
H(11β)	423	875	498	4.3
H(12α)	368	578	586	3.9
H(12β)	420	815	598	3.9
H(14)	191	551	531	2.6
H(15α)	55	893	498	3.9
H(15β)	22	653	520	3.9
H(16α)	69	998	593	3.9
H(16β)	29	763	615	3.9
H(18α)	308	1 067	514	3.9
H(18β)	185	1 097	545	3.9
H(18γ)	297	1 123	588	3.9
H(20)	213	268	674	3.5
H(22α)	108	913	301	5.3
H(22β)	224	935	344	5.3
H(22γ)	230	841	275	5.3
H(23α)	18	495	279	5.1
H(23β)	139	424	253	5.1
H(23γ)	91	297	310	5.1
H(24)	292	886	689	3.5

RESULTS AND DISCUSSION

The results of the X-ray analysis verify that the synthetic route employed by Pitt *et al.*[3] produces the desired *trans-anti-trans* BCD ring fusions and establish that the proton on C(5) is α-oriented.[*] Figure 1 shows the molecular conformation and the atom numbering scheme. Interatomic distances, valency angles, and torsion angles[7] for the natural enantiomer are reported in Table 3.

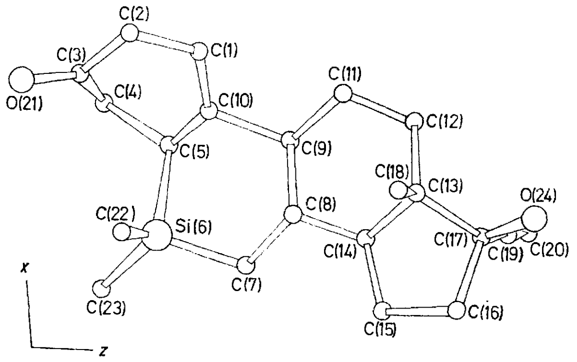

FIGURE 1 Atom numbering scheme and molecular conformation in the enantiomer corresponding to the natural chirality

TABLE 3

Interatomic distances (Å) and angles (deg.), with estimated standard deviations in parentheses

(*a*) Bond lengths

C(1)–C(2)	1.486(12)	C(9)–C(10)	1.527(10)
C(1)–C(10)	1.331(13)	C(9)–C(11)	1.540(11)
C(2)–C(3)	1.489(14)	C(11)–C(12)	1.529(11)
C(3)–C(4)	1.500(14)	C(12)–C(13)	1.512(11)
C(3)–O(21)	1.227(10)	C(13)–C(14)	1.534(10)
C(4)–C(5)	1.540(11)	C(13)–C(17)	1.554(10)
C(5)–Si(6)	1.901(9)	C(13)–C(18)	1.581(11)
C(5)–C(10)	1.515(11)	C(14)–C(15)	1.536(11)
Si(6)–C(7)	1.870(8)	C(15)–C(16)	1.550(11)
Si(6)–C(22)	1.848(11)	C(16)–C(17)	1.555(12)
Si(6)–C(23)	1.850(10)	C(17)–C(19)	1.495(11)
C(7)–C(8)	1.552(11)	C(17)–O(24)	1.417(9)
C(8)–C(9)	1.556(11)	C(19)–C(20)	1.203(13)
C(8)–C(14)	1.518(10)		

(*b*) Valency angles

C(2)–C(1)–C(10)	126.6(9)	C(1)–C(10)–C(9)	124.5(7)
C(1)–C(2)–C(3)	112.5(8)	C(5)–C(10)–C(9)	115.9(7)
C(2)–C(3)–C(4)	115.6(7)	C(9)–C(11)–C(12)	113.9(7)
C(2)–C(3)–O(21)	120.8(9)	C(11)–C(12)–C(13)	111.3(6)
C(4)–C(3)–O(21)	123.5(8)	C(12)–C(13)–C(14)	108.9(6)
C(3)–C(4)–C(5)	110.1(7)	C(12)–C(13)–C(17)	119.1(6)
C(4)–C(5)–Si(6)	116.9(5)	C(12)–C(13)–C(18)	110.2(7)
C(4)–C(5)–C(10)	113.5(7)	C(14)–C(13)–C(17)	110.4(6)
Si(6)–C(5)–C(10)	106.1(6)	C(14)–C(13)–C(18)	111.1(6)
C(5)–Si(6)–C(7)	100.1(3)	C(17)–C(13)–C(18)	106.8(6)
C(5)–Si(6)–C(22)	111.1(4)	C(8)–C(14)–C(13)	115.1(6)
C(5)–Si(6)–C(23)	113.3(4)	C(8)–C(14)–C(15)	118.7(6)
C(7)–Si(6)–C(22)	110.4(4)	C(13)–C(14)–C(15)	105.0(6)
C(7)–Si(6)–C(23)	112.5(4)	C(14)–C(15)–C(16)	105.6(6)
C(22)–Si(6)–C(23)	109.0(5)	C(15)–C(16)–C(17)	105.2(6)
Si(6)–C(7)–C(8)	112.1(5)	C(13)–C(17)–C(16)	103.4(6)
C(7)–C(8)–C(9)	113.7(6)	C(13)–C(17)–C(19)	110.8(6)
C(7)–C(8)–C(14)	111.3(6)	C(13)–C(17)–O(24)	115.0(6)
C(9)–C(8)–C(14)	108.4(6)	C(16)–C(17)–C(19)	107.3(7)
C(8)–C(9)–C(10)	112.7(6)	C(16)–C(17)–O(24)	110.6(6)
C(8)–C(9)–C(11)	112.0(6)	C(19)–C(17)–O(24)	109.3(6)
C(10)–C(9)–C(11)	112.9(7)	C(17)–C(19)–C(20)	180.0(6)
C(1)–C(10)–C(5)	119.4(7)		

(*c*) Intermolecular distances $\leqslant$3.7 Å

O(24) · · · O(21$^{\mathrm{I}}$)	2.82	C(20) · · · C(18$^{\mathrm{II}}$)	3.61
C(20) · · · O(24$^{\mathrm{II}}$)	3.20	C(17) · · · O(21$^{\mathrm{I}}$)	3.62
O(21) · · · C(4$^{\mathrm{III}}$)	3.41	C(2) · · · O(21$^{\mathrm{III}}$)	3.65
C(19) · · · O(21$^{\mathrm{I}}$)	3.56	O(24) · · · C(4$^{\mathrm{I}}$)	3.70
O(24) · · · C(3$^{\mathrm{I}}$)	3.56		

(*d*) Torsion angles for the natural enantiomer

C(10)–C(1)–C(2)–C(3)	7	C(9)–C(8)–C(14)–C(15)	−178
C(2)–C(1)–C(10)–C(5)	0	C(8)–C(9)–C(10)–C(1)	110
C(2)–C(1)–C(10)–C(9)	−175	C(11)–C(9)–C(10)–C(1)	−18
C(1)–C(2)–C(3)–C(4)	−35	C(8)–C(9)–C(10)–C(5)	−65
C(1)–C(2)–C(3)–O(21)	149	C(11)–C(9)–C(10)–C(5)	167
C(2)–C(3)–C(4)–C(5)	55	C(8)–C(9)–C(11)–C(12)	51
O(21)–C(3)–C(4)–C(5)	−129	C(10)–C(9)–C(11)–C(12)	180
C(3)–C(4)–C(5)–Si(6)	78	C(9)–C(11)–C(12)–C(13)	−53
C(3)–C(4)–C(5)–C(10)	−46	C(11)–C(12)–C(13)–C(14)	55
C(4)–C(5)–Si(6)–C(7)	177	C(11)–C(12)–C(13)–C(17)	169
C(4)–C(5)–Si(6)–C(22)	−66	C(11)–C(12)–C(13)–C(18)	−67
C(4)–C(5)–Si(6)–C(23)	57	C(12)–C(13)–C(14)–C(8)	−59
C(10)–C(5)–Si(6)–C(7)	−55	C(12)–C(13)–C(14)–C(15)	168
C(10)–C(5)–Si(6)–C(22)	62	C(17)–C(13)–C(14)–C(8)	175
C(10)–C(5)–Si(6)–C(23)	−175	C(17)–C(13)–C(14)–C(15)	43
C(4)–C(5)–C(10)–C(1)	20	C(18)–C(13)–C(14)–C(8)	62
C(4)–C(5)–C(10)–C(9)	−164	C(18)–C(13)–C(14)–C(15)	−70
Si(6)–C(5)–C(10)–C(1)	−110	C(12)–C(13)–C(17)–C(16)	−162
Si(6)–C(5)–C(10)–C(9)	66	C(12)–C(13)–C(17)–C(19)	−47

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[*] The synthetic route produces a racemic mixture, and both enantiomers are present in the crystal. All the ensuing discussion and Figure 1 refer to the enantiomer having the natural chirality, and the use of α,β relates to this enantiomer only.

[7] W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

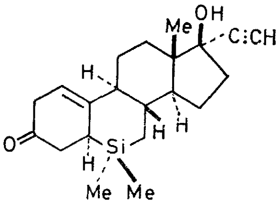
Table 3 (*Continued*)

C(5)–Si(6)–C(7)–C(8)	52	C(12)–C(13)–C(17)–O(24)	77
C(22)–Si(6)–C(7)–C(8)	−65	C(14)–C(13)–C(17)–C(16)	−43
C(23)–Si(6)–C(7)–C(8)	173	C(14)–C(13)–C(17)–C(19)	71
Si(6)–C(7)–C(8)–C(9)	−55	C(14)–C(13)–C(17)–O(24)	−164
Si(6)–C(7)–C(8)–C(14)	−178	C(18)–C(13)–C(17)–C(16)	73
C(7)–C(8)–C(9)–C(10)	56	C(18)–C(13)–C(17)–C(19)	−173
C(7)–C(8)–C(9)–C(11)	−175	C(18)–C(13)–C(17)–O(24)	−48
C(14)–C(8)–C(9)–C(10)	−179	C(8)–C(14)–C(15)–C(16)	−156
C(14)–C(8)–C(9)–C(11)	−51	C(13)–C(14)–C(15)–C(16)	−26
C(7)–C(8)–C(14)–C(13)	−178	C(14)–C(15)–C(16)–C(17)	−2
C(7)–C(8)–C(14)–C(15)	−52	C(15)–C(16)–C(17)–C(13)	28
C(9)–C(8)–C(14)–C(13)	56	C(15)–C(16)–C(17)–C(19)	−89
		C(15)–C(16)–C(17)–O(24)	152

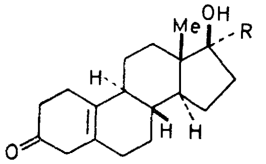
Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1:

I $x, \frac{3}{2} - y, \frac{1}{2} + z$ III $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
II $x, -1 + y, z$

The torsion angles of the β,γ-cyclohexenone ring A indicate that C(1), C(2), C(3), C(5), and C(10) are close to being coplanar, with C(4) displaced to the α-side of the steroid molecule. This approximately semiplanar conformation is similar to the preferred ring A forms found in the 3-keto-$\Delta^{5,10}$-steroids, 17β-hydroxyestr-5(10)-en-3-one (II) [8] and its iodoacetate derivative,[9] and in 17α-ethynyl-17β-hydroxyestr-5(10)-en-3-one (III).[10] Table 4 lists torsion angles for the A rings in (II) and (III), together with those of the appropriate enantiomer of (I) for comparison. The common occurrence of the semiplanar form in these different molecules implies that for β,γ-cyclohexenones this probably represents the most stable conformation and consequently contrasts with the preference of cyclohexenes for the half-chair form.[11] In this respect it should be noted that a half-chair β,γ-cyclohexenone form has a greater number of unfavourable eclipsing C=O/C–H interactions than occur in the semiplanar form. The alternative C(4) β-side displacement is less favoured than the α-side displacement since the former would have more severe non-bonded interactions between the C(4) hydrogen atoms and the silicon methyl groups.



(I)

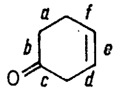


R
(II) H
(III) C:CH

Substitution of the dimethylsilyl group for the methylene at position 6 in the normal steroid nucleus and the presence of the C(1)–C(10) double bond have a profound effect upon the ring B geometry and the overall steroid conformation. In particular, the endocyclic valency angle at silicon, C(5)–Si(6)–C(7) 100.1(3)°, is significantly smaller than tetrahedral. The reasons for this are not immediately apparent and further studies on 6-silasteroids may provide clarification of this point. The torsion angles indicate that the A/B junction is *quasi cis* [11] and that ring B adopts a distorted-chair conformation more puckered around C(10) than usual. The resulting steroid conformation makes the β-face of the C(1)–C(10) double bond relatively inaccessible to heterogeneous catalytic hydrogenation which consequently yields the A/B *cis*-isomer.[12] It is also apparent that any hormonal activity which is heavily dependent upon close approach of the steroid β-face will be significantly diminished from that of the normal steroid series where there is generally only a slight bowing of the steroid skeleton and to the α-side.

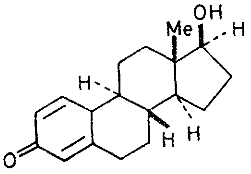
Table 4

Endocyclic torsion angles in β,γ-cyclohexenone steroid A rings

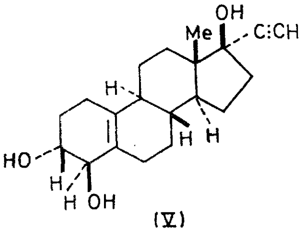


	(II) *	(III) †		(I) ‡
a	48	−44	44	−46
b	−48	45	−51	55
c	21	−23	29	−35
d	7	−2	0	7
e	−6	2	−4	0
f	−22	21	−19	20

* Calculated from the co-ordinates provided in ref. 8 which lists those for the mirror image of the natural series. † Ref. 10; there are two crystallographically independent molecules of the natural enantiomer in the asymmetric crystal unit. ‡ Present work (for the natural enantiomer).



(IV)



(V)

There being no previous structural study of a steroid

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[8] R. R. Sobti, S. G. Levine, and J. Bordner, *Acta Cryst.*, 1972, **B28**, 2292.

[9] J. Bordner, R. R. Sobti, and S. G. Levine. *J. Amer. Chem. Soc.*, 1971, **93**, 5588.

[10] A. T. McPhail, P. A. Luhan, and P. S. W. Tschang, unpublished data.

[11] For a recent review see, R. Bucourt, *Topics Stereochem.*, 1974, **8**, 159.

[12] A. T. McPhail and R. W. Miller, unpublished data.

having a C(1)–C(10) double bond with which to compare the results of the present study, endocyclic torsion angles for the C and D rings of a selection of related steroids [(II)—(V)] possessing a variety of ring A unsaturation patterns are compared in Table 5 with those of (I).

TABLE 5

Endocyclic torsion angles in the C and D rings of several related steroids

	(I)[a]	(II)[b]	(III)[c]	(IV)[d]	(V)[e]
(*a*) Ring C					
C(14)–C(8)–C(9)–C(11)	−51	−57	−59	−60	−54
C(8)–C(9)–C(11)–C(12)	51	55	58	59	53
C(9)–C(11)–C(12)–C(13)	−53	−52	−57	−58	−52
C(11)–C(12)–C(13)–C(14)	55	51	56	57	54
C(12)–C(13)–C(14)–C(8)	−59	−56	−60	−61	−59
C(13)–C(14)–C(8)–C(9)	56	59	61	62	58
(*b*) Ring D					
C(17)–C(13)–C(14)–C(15)	43	46	47	47	47
C(13)–C(14)–C(15)–C(16)	−26	−32	−34	−34	−33
C(14)–C(15)–C(16)–C(17)	2	6	6	8	5
C(15)–C(16)–C(17)–C(13)	28	23	23	22	23
C(16)–C(17)–C(13)–C(14)	−43	−42	−42	−42	−42

[a] Present work (for the natural enantiomer). [b] Calculated from the co-ordinates provided in ref. 8 revised to conform to the natural series. [c] Ref. 10; mean values of two crystallographically independent molecules of the natural enantiomer in the asymmetric crystal unit. [d] W. L. Duax, D. A. Norton, S. Pokrywiecki, and C. Eger, *Steroids*, 1971, 526. [e] P. A. Luhan, Ph.D. Dissertation, Duke University, 1973.

In all these compounds ring C is in a chair conformation, that of (I) being slightly more flattened than usual around C(9) due to the ring B conformation already described. The D rings consistently adopt a C(13) envelope (C_s) form for which the maximum torsion angle, ϕ_m 46°, and phase angle of pseudorotation, Δ 39°, of (I) lie close to the standard values, 46.7 and 36°, computed by Altona *et al.*[13]

The mean values of chemically equivalent bonds agree well with accepted values[14] and none of the individual bond lengths departs significantly from the corresponding mean: $C(sp^3)$–Si 1.867, $C(sp^3)$–$C(sp^3)$ 1.543, $C(sp^3)$–$C(sp^2)$ 1.503, $C(sp^3)$–$C(sp)$ 1.495, $C(sp^2)$=$C(sp^2)$ 1.331, $C(sp)$≡$C(sp)$ 1.203, $C(sp^3)$–O 1.417, and $C(sp^2)$=O 1.227 Å.

The arrangement of molecules in the crystal is shown in Figure 2. Intermolecular separations <3.7 Å are listed in Table 3. The shortest of these O(24) · · · O(21) 2.82 Å is indicative of a hydrogen bond between molecules related by the *c* glide plane; other distances correspond to normal van der Waals interactions.

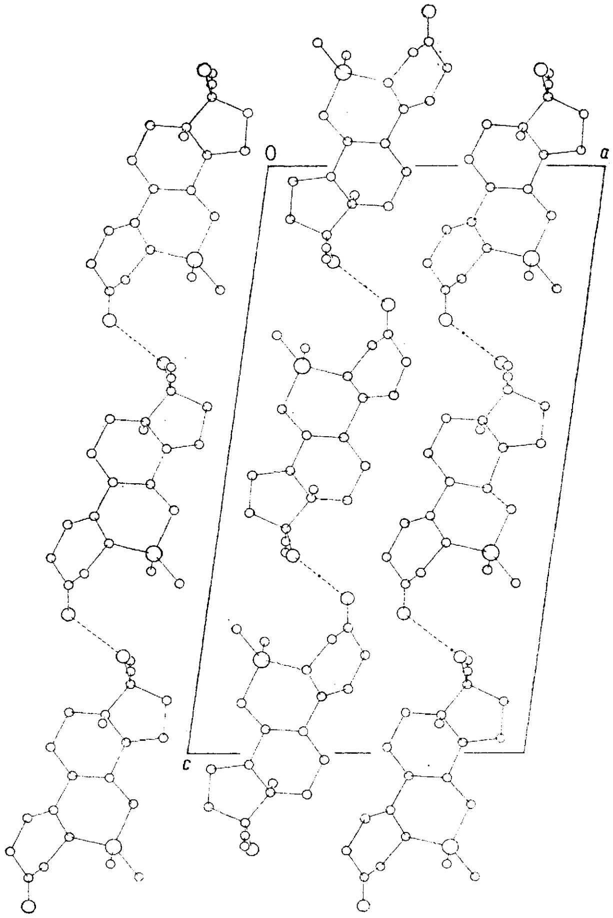

FIGURE 2 Packing of molecules in the crystal, viewed in projection along the *b* axis. Hydrogen bonds are denoted by broken lines

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[4/2606 *Received*, 16*th December*, 1974]

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[14] *Chem. Soc. Special Publ.*, No. 11, 1958; No. 18, 1965.