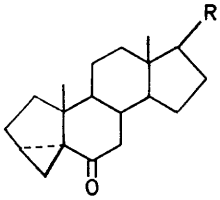
An *X*-Ray Examination of Geometrical Factors affecting Conjugative Overlap between a Cyclopropane Ring and an Adjacent Chromophore in Two 3,5-Cyclosteroid Derivatives

By **Roger C. Pettersen,***† and **Olga Kennard,**‡ University Chemical Laboratory, Lensfield Road, Cambridge
William G. Dauben, Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.

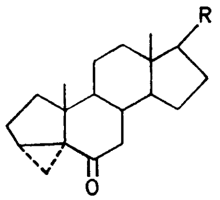
The structure of 6-oxo-3α,5-cycloandrostan-17-yl *p*-bromobenzoate, $C_{26}H_{31}O_3Br$ (3), was solved by the heavy-atom method from Weissenberg film data and refined to *R* 0·17 (1643 observed reflections). The structure of 6-oxo-3β,5-cycloandrostan-17-yl acetate, $C_{21}H_{30}O_3$ (4), was solved by direct-phasing methods from diffractometer data and refined to *R* 0·10 (1888 observed reflections). Crystal data: (3), monoclinic, space group $P2_1$, $a = 6{\cdot}45(1)$, $b = 28{\cdot}69(2)$, $c = 6{\cdot}690(4)$ Å, $\beta = 109{\cdot}97(10)°$, $Z = 2$; (4), orthorhombic, space group $P2_12_12_1$, $a = 7{\cdot}423(1)$, $b = 11{\cdot}184(1)$, $c = 22{\cdot}110(1)$ Å. Both compounds possess the normal steroidal nucleus for rings B, C, and D. The introduction of the C(3)–C(5) bond into the steroidal nucleus changes greatly the general shape of ring A and the two different orientations of the hydrogen at C(3) considerably affect the geometry of the two molecules in the region of the A and B rings. The valency angles at C(5) are distorted in both molecules to accommodate the strain of the 3,5-cyclization. The u.v. spectra of the two parent compounds [(1) and (2)] indicate a greater amount of conjugative overlap between the cyclopropane ring and the carbonyl group for (1) than for (2). The spectral differences could not be attributed to a difference in the torsion angle O(1)–C(6)–C(5)–C(3) since these were found to be the same in (3) and (4). They may, however, be due to decreased *p* character for the C(3)–C(5) bond in compound (4) as the valency angle, C(3)–C(5)–C(6) increases from 114 in (3) to 130° in (4).

Cyclopropane has chemical properties somewhere between those of normal saturated hydrocarbons and those of olefins. Such a ring system has been shown to exhibit conjugative effects when adjacent to carbonyl, methylene, or other unsaturated groups.[1] For maximum interaction between a cyclopropane ring and a carbonyl group, the plane containing the carbonyl group and the adjacent carbon of the ring should bisect the three-membered ring, but can be in either the *cis*- or *trans*-conformation.[2,3] This geometrical effect has been evaluated by solvolysis studies employing 2-substituted derivatives of 1-adamantyl tosylate.[3] The substituents were 2-spirocyclopropene and 2-methylene respectively, and the solvolysis rates of these compounds were compared with the solvolysis rates for 1-adamantyl tosylate and 2,2-dimethyl-1-adamantyl tosylate. The rigidity of the adamantyl ring system permits the evaluation of the geometrical requirements in a qualitative way, although the exact structures had not been determined. A recent and very similar solvolysis study also using the adamantane skeleton as a substrate, stresses the importance of the geometry of the system and discusses in some detail how all the conjugation is lost when the conformation is 'perpendicular.'[4] The latter conformation is in contrast to the 'bisected' mentioned previously.

The present work was undertaken to investigate precisely the geometry of the cyclopropane–carbonyl system as found in the steroid isomers, (1) 3α,5-cyclocholestan-6-one, and (2) 3β,5-cyclocholestan-6-one. The u.v. spectra indicate good conjugative overlap for (1) [$\lambda_{max.}$ (EtOH) 207 nm], but show no maximum for (2) above 194 nm, the latter being the lowest wavelength which is physically possible to measure with present equipment. The geometry of these molecules is expected to be unusual because of the strain introduced into the steroid skeleton by the three-membered ring. A suitable crystalline derivative of each compound was prepared (3) and (4) and *X*-ray structure analyses were undertaken to look for unusual features in each and differences between the two.



R
(1) C_8H_{17}
(3) $O{\cdot}CO{\cdot}C_6H_4{\cdot}Br$



R
(2) C_8H_{17}
(4) OCOMe

EXPERIMENTAL

(a) *6-Oxo-3α,5-cycloandrostan-17-yl* p-*Bromobenzoate* (3).—*Crystal data.* $C_{26}H_{31}O_3Br$, $M = 440{\cdot}2$. Monoclinic, $a = 6{\cdot}45(1)$, $b = 28{\cdot}69(2)$, $c = 6{\cdot}690(4)$ Å, $\beta = 109{\cdot}97(10)°$, $U = 1163{\cdot}6$ Å^3, $D_m = 1{\cdot}28$, $Z = 2$, $D_{calc} = 1{\cdot}29$, $F(000) = 592$. Space group $P2_1$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$. Crystal dimensions for data collection: $0{\cdot}25 \times 0{\cdot}25 \times 0{\cdot}35$ mm, μ(Cu-K_α) = 22·6 cm^{-1}, $\mu l = 0{\cdot}75$ for longest dimension.

The *a* cell dimension was determined from a rotation photograph, and the *b* and *c* dimensions from an aluminium-calibrated 0*kl* Weissenberg photograph. The angle β was measured from an *h*0*l* precession photograph taken with Cr radiation. Layers 0—5*kl* were recorded by the equi-inclination Weissenberg method using multiple film packs. Intensities were measured visually and no corrections for absorption or spot shape were applied. 1887 Independent reflections were measured of which 244 were considered unobserved [$(\sin\theta/\lambda)_{max.}$ 0·646]. Intensities were corrected

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† *Present address:* Department of Chemistry, Northeast Louisiana University, Monroe, Louisiana 71201, U.S.A.

‡ External Staff, Medical Research Council.

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for Lorentz and polarization factors. No attempt was made to scale reflections between layers.

The x and z co-ordinates for the Br atom were located from a Harker section at $V = 0{\cdot}50$. A Fourier map phased on the Br atom alone (R 54%) gave the position of the benzoate group and its mirror image. One group was chosen which was confirmed at a later stage to be the correct enantiomorph. A new Fourier map was computed (R 47%) from which the remainder of the structure was evident. Eight cycles of block-diagonal least-squares calculations reduced R to 18·2%, and no further work was done for about 4 years.

After the solution of (4), (3) was refined further with a full-matrix least-squares program. A weighting scheme of the form, $w = 1/\sigma^2$, where $\sigma = A + B|F_o| + C|F_o|^2 + D|F_o|^3$ and $A = 2{\cdot}0$, $B = 1{\cdot}0$, $C = 0{\cdot}02$, $D = 0{\cdot}005$ was applied. The quantity minimized in the least-squares refinement was $\Sigma w(F_o - F_c)^2$. An analysis of the data divided into twelve equal groups of reflections over the range of F_o indicated a relatively constant $\Sigma w(F_o - F_o)^2$. The atomic scattering factors were taken from ref. 5 and the Br was corrected for anomalous dispersion according to ref. 6. After four cycles of refinement, R factor was 17·0%: A difference-Fourier map did not indicate the positions for any of the hydrogen atoms. Structural parameters are listed in Table 1.*

TABLE 1

Fractional co-ordinates ($\times 10^4$) and thermal parameters for (3)

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Br	13186(6)	0000	12375(5)	8·3(1)
C(1)	2858(55)	4052(11)	5397(50)	7·2(6)
C(2)	2353(58)	4240(12)	3107(55)	7·5(7)
C(3)	−103(46)	4147(9)	1987(42)	6·4(5)
C(4)	−1542(44)	4242(9)	3300(42)	6·3(5)
C(5)	−611(37)	3756(8)	3275(33)	5·0(4)
C(6)	−2082(35)	3403(7)	2031(31)	4·6(4)
C(7)	−1103(34)	2940(7)	1568(30)	4·5(3)
C(8)	780(34)	2774(7)	3517(30)	4·7(3)
C(9)	2521(34)	3173(7)	4426(29)	4·4(3)
C(10)	1448(36)	3599(7)	5119(32)	4·6(4)
C(11)	4528(42)	2976(9)	6254(38)	5·5(4)
C(12)	5570(41)	2537(9)	5680(36)	5·9(4)
C(13)	3813(38)	2173(7)	4851(32)	5·0(4)
C(14)	2004(31)	2367(6)	2941(26)	4·1(3)
C(15)	641(43)	1946(9)	1870(39)	6·0(5)
C(16)	2418(49)	1542(10)	2298(41)	6·0(5)
C(17)	4622(39)	1766(8)	3788(35)	5·4(4)
C(18)	3037(37)	1986(8)	6632(35)	5·1(4)
C(19)	808(45)	3520(9)	7173(41)	6·3(5)
C(20)	7178(38)	1134(8)	4836(33)	5·0(4)
C(21)	8599(45)	851(9)	6563(40)	6·0(5)
C(22)	8020(37)	782(7)	8498(31)	4·7(3)
C(23)	9406(41)	520(8)	10116(37)	5·6(4)
C(24)	11129(41)	325(8)	10060(35)	5·4(4)
C(25)	11892(53)	404(11)	8230(48)	6·9(6)
C(26)	10459(45)	648(9)	6464(39)	6·0(5)
O(1)	−4142(30)	3445(6)	1313(28)	6·4(4)
O(2)	5881(25)	1431(6)	5370(23)	5·6(3)
O(3)	7311(37)	1112(8)	3001(35)	7·5(5)

(b) 6-*Oxo*-3β,5-*cycloandrostan*-17-*yl Acetate* (4).—*Crystal data*. $C_{21}H_{30}O_3$, $M = 330{\cdot}23$. Orthorhombic, $a = 7{\cdot}423(1)$, $b = 11{\cdot}184(1)$, $c = 22{\cdot}110(1)$ Å, $U = 1835{\cdot}5$ Å^3, $D_m = 1{\cdot}18$, $Z = 4$, $D_c = 1{\cdot}20$, $F(000) = 720$. Space group, $P2_12_12_1$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å. Crystal dimensions for data collection, 0·20 × 0·20 × 0·40 mm, μ(Cu-K_α) = 5·21 cm^{-1}, $\mu l = 0{\cdot}21$ for longest crystal dimension.

Unit-cell dimensions were determined from a least-squares refinement of accurately measured values of 2θ for 27 high-angle reflections. Intensity measurements were made on an automated General Electric XRD 5 spectrogoniometer equipped with a NaI scintillation counter and pulse-height discriminator. The θ—2θ scan technique [7] was used with a scan rate of 2·0° min^{-1}. A total of 2237 reflections was measured to $\sin\theta/\lambda = 0{\cdot}6332$ ($2\theta = 150°$). Relative structure factors (F_o) and their statistical variances (σF_o) were computed according to the scheme of ref. 8. 349 Reflections having $I_0 \leqslant 2\sigma(I_0)$ were considered unobserved.

Solution of (4). Normalized structure factors were computed from the observed structure factors in the usual way.[9] This and the phasing calculations at Mellon Institute were carried out using S. R. Hall's series of programs.[10] The following statistics were observed:

	Obs.	Calc. for centrosymmetric [11]	Calc. for non-centrosymmetric
$\langle E\rangle$	0·901	0·798	0·886
$\langle E^2\rangle$	1·020	1·0	1·0
$\langle E^2 - 1\rangle$	0·722	0·968	0·736

A complete list of the Σ_2 relationships was generated by computer for all E values $\gtrsim 1{\cdot}60$ (151 reflections). From this list a set of four reflections was chosen to define the origin (3) and enantiomorph (1) by use of criteria suggested by Karle and Hauptman for space group $P2_12_12_1$.[12] The following reflections were chosen:

	h	k	l	E	No. of Σ_2	Phase assigned
Origin	0	5	2	4·41	32	$\pi/2$
	5	0	12	3·13	31	0
	0	1	7	2·60	29	$\pi/2$
Enantiomorph	6	0	5	2·33	20	$\pi/2$

These four phases were used to initiate the tangent refinement in a manner similar to that described by Oh and Maslen.[10] After several attempts to solve the structure (11 E-maps), the problem was set aside for a time when a fresh approach might give better results.

A successful starting set was eventually obtained using a program [13] which is particularly useful in conjunction with direct methods employing a multiple-solution approach. A total of 150 reflections with $E \gtrsim 1{\cdot}60$ were used as input with the origin and enantiomorph defining reflections listed above coded with known phases. Of the remaining reflections, the 50 highest $|E|$ values were tested as potential symbols to generate additional phases. Three symbols were chosen from the list; 5 1 1 ($|E| = 2{\cdot}16$), 4 7 2 ($|E| = 2{\cdot}71$), and 5 6 18 ($|E| = 2{\cdot}62$). The technique of the multiple-solution approach has been described elsewhere.[14] Although a successful starting set was found by this

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* Tables of observed and calculated structure factors are listed in Supplementary Publication No. SUP 20455 (20 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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method, the first E-map did not indicate the structure unambiguously. However, except for three atoms of the acetate group, the entire structure was determined from a subsequent E-map based on the phases of 199 reflections with $|E| < 1{\cdot}52$ obtained from a tangent refinement calculation. The 21 atomic positions, deduced from this map, were refined two cycles by full-matrix least-squares calculations and a Fourier map gave the position of the remaining atoms.

Refinement was continued with full-matrix least-squares calculations with atomic scattering factors of ref. 5 for non-hydrogen atoms, and of ref. 15 for hydrogen. The carbon and oxygen atoms were refined for two cycles with anisotropic temperature factors. Positions for hydrogen atoms except one were determined from a subsequent difference-Fourier map. Each hydrogen atom was assigned an isotropic temperature factor equivalent to the temperature factor of the bonded carbon atom and their scattering contribution was then included with a further refinement of the carbon and oxygen atoms.

TABLE 2

Fractional co-ordinates ($\times 10^4$) and thermal parameters * for (4)

Atom	x/a	y/b	z/c	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
C(1)	3465(10)	−548(5)	2001(3)	272(17)	67(5)	22(1)	−6(8)	−20(4)	8(2)
C(2)	2287(12)	−1692(6)	2093(3)	351(21)	77(6)	23(2)	2(10)	−16(5)	7(3)
C(3)	367(11)	−1260(6)	2019(3)	274(17)	74(5)	26(2)	−38(9)	−2(5)	10(3)
C(4)	−105(12)	−122(7)	2349(3)	313(19)	109(7)	20(1)	−38(11)	22(5)	7(3)
C(5)	427(9)	−95(5)	1686(2)	220(13)	58(5)	15(1)	−26(7)	−1(3)	0(2)
C(6)	−923(8)	457(6)	1282(3)	130(11)	81(5)	23(1)	−1(7)	27(3)	−7(2)
C(7)	−636(8)	1799(5)	1214(3)	174(11)	60(4)	16(1)	−6(6)	−9(3)	−4(2)
C(8)	1332(7)	2172(5)	1106(2)	110(9)	53(4)	12(9)	−5(5)	13(3)	−3(2)
C(9)	2638(8)	1550(5)	1557(2)	167(11)	60(4)	11(9)	12(6)	−13(3)	−1(2)
C(10)	2384(9)	188(5)	1525(3)	194(13)	45(4)	18(1)	−3(7)	−2(4)	2(2)
C(11)	4563(9)	1979(5)	1482(3)	202(13)	57(5)	22(1)	5(7)	−6(4)	6(2)
C(12)	4754(8)	3341(5)	1506(3)	114(10)	47(4)	33(2)	−7(6)	−8(4)	−5(2)
C(13)	3504(8)	3940(5)	1047(3)	182(11)	56(4)	16(1)	−11(6)	2(3)	1(2)
C(14)	1584(8)	3533(5)	1176(2)	167(11)	49(4)	15(1)	24(6)	−4(3)	−2(2)
C(15)	398(10)	4358(5)	805(3)	229(15)	53(5)	33(2)	1(8)	−21(5)	8(2)
C(16)	1385(11)	5584(7)	867(4)	239(17)	81(6)	42(3)	7(9)	−15(6)	12(3)
C(17)	3239(9)	5317(5)	1132(3)	213(14)	52(4)	23(1)	−2(7)	−9(4)	13(2)
C(18)	4151(9)	3685(6)	412(3)	218(14)	95(6)	20(1)	−18(8)	10(4)	−1(3)
C(19)	2784(9)	−321(5)	889(3)	223(14)	53(4)	20(1)	5(7)	6(4)	−7(2)
C(20)	5980(10)	6437(6)	1064(3)	228(16)	64(5)	29(2)	8(8)	−22(5)	−3(3)
C(21)	7073(10)	7164(6)	630(4)	248(16)	61(5)	47(2)	−60(9)	4(6)	12(3)
O(1)	−2202(6)	−40(4)	1066(2)	176(9)	84(4)	42(1)	−21(5)	−11(3)	−2(2)
O(2)	4513(7)	6030(4)	802(2)	288(11)	68(4)	24(1)	−46(6)	−13(3)	6(2)
O(3)	6385(8)	6191(6)	1573(3)	356(15)	178(7)	36(2)	−79(9)	−41(5)	20(3)
				$B/\text{Å}^2$					
H(1,1)	4888	−703	1816	4·74					
H(1,2)	3475	−203	2500	4·74					
H(2,1)	2813	−2255	1709	5·23					
H(2,2)	2395	−1982	2500	5·23					
H(3)	−707	−1721	2000	5·22					
H(4,1)	796	216	2667	5·50					
H(4,2)	−1547	0000	2415	5·50					
H(7,1)	−1302	2050	860	3·18					
H(7,2)	−1035	2049	1614	3·18					
H(8)	1656	1933	692	2·60					
H(9)	2207	1798	2000	2·94					
H(11,1)	5090	1801	1051	3·88					
H(11,2)	5155	1630	1843	3·88					
H(12,1)	5841	3671	1546	3·79					
H(12,2)	4201	3954	1667	3·79					
H(14)	1304	3707	1667	3·10					
H(15,1)	297	4058	351	4·86					
H(15,2)	−700	4613	1015	4·86					
H(16,1)	1389	5783	375	6·09					
H(16,2)	661	5980	1330	6·09					
H(17)	3100	5340	1670	4·15					
H(18,1)	3903	2890	167	4·46					
H(18,2)	3401	4027	167	4·46					
H(18,3)	5471	3705	369	4·46					
H(19,1)	2036	0000	524	3·90					
H(19,2)	2476	−1154	917	3·90					
H(19,3)	4066	0000	833	3·90					
H(21,1)	6474	6959	167	5·58					
H(21,2)	6759	8033	667	5·58					

* In the form $T = \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

After an analysis of the data, a weighting scheme was introduced to force $\Sigma w(F_o - F_c)^2$ to be nearly constant for reflections sorted into equal groups of similar intensities with $w = 1/\sigma^2$ and $\sigma^2 = A + B|F_o| + C|F_o|^2 + D|F_o|^3$.[16] The constants were: $A = 4{\cdot}129$, $B = -0{\cdot}307$, $C = 0{\cdot}011$,

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and *D* = 0·000. The carbon and oxygen atom parameters were refined two more cycles with this weighting scheme and fixed hydrogen atom parameters. A second difference-Fourier map was computed with the phase contribution of the hydrogen atoms omitted to obtain an improved set of hydrogen co-ordinates. The carbon and oxygen atoms were then refined for two more cycles with the hydrogen atoms held fixed. The final *R* was 10·0% and the weighted factor, *R′*, 9·8%. The average shift per error in the last cycle was 0·31. A list of the structural parameters is given in Table 2.

RESULTS AND DISCUSSION

The bond lengths for each compound are listed in Table 3; the atom labels are shown in Figure 1[(a) and (b)]. The mean C–H bond length for (4) is 1·04 Å with a range of 0·87—1·24 Å. The torsion or dihedral angles are listed in Table 5 and the bond angles in Table 4. The results indicate that the three-membered ring, C(3)–C(4)–C(5), has markedly changed the geometry of the steroid molecules in the region of the A and B rings as compared to a steroid molecule such as androsterone where the C(3)–C(5) bond is not present.[17]

TABLE 3

Bond distances (Å)

	(3)	(4)		(3)	(4)
C(1)–C(2)	1·56(5)	1·56(1)	C(13)–C(14)	1·52(3)	1·52(1)
C(1)–C(10)	1·56(4)	1·56(1)	C(13)–C(17)	1·55(4)	1·56(1)
C(2)–C(3)	1·54(4)	1·51(1)	C(13)–C(18)	1·53(4)	1·51(1)
C(3)–C(4)	1·50(5)	1·51(1)	C(14)–C(15)	1·53(3)	1·52(1)
C(3)–C(5)	1·51(4)	1·50(1)	C(15)–C(16)	1·59(4)	1·56(1)
C(4)–C(5)	1·52(3)	1·52(1)	C(16)–C(17)	1·58(3)	1·53(1)
C(5)–C(6)	1·45(3)	1·48(1)	C(17)–O(2)	1·46(3)	1·44(1)
C(5)–C(10)	1·55(3)	1·53(1)	C(20)–C(21)	1·46(3)	1·50(1)
C(6)–C(7)	1·54(3)	1·52(1)	C(20)–O(2)	1·32(3)	1·32(1)
C(6)–O(1)	1·26(3)	1·20(1)	C(20)–O(3)	1·26(4)	1·20(1)
C(7)–C(8)	1·54(2)	1·54(1)	C(21)–C(22)	1·47(4)	
C(8)–C(9)	1·58(3)	1·56(1)	C(21)–C(26)	1·35(4)	
C(8)–C(14)	1·53(3)	1·54(1)	C(22)–C(23)	1·38(3)	
C(9)–C(10)	1·55(3)	1·54(1)	C(23)–C(24)	1·26(4)	
C(9)–C(11)	1·57(3)	1·52(1)	C(24)–C(25)	1·48(5)	
C(10)–C(19)	1·58(4)	1·54(1)	C(24)–Br	1·92(2)	
C(11)–C(12)	1·53(4)	1·53(1)	C(25)–C(26)	1·42(4)	
C(12)–C(13)	1·51(3)	1·53(1)			

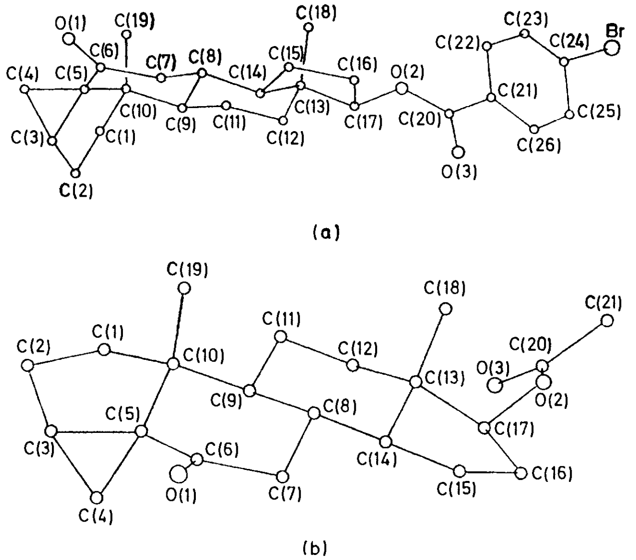

FIGURE 1 (a) Compound (3), 6-oxo-3α,5-cycloandrostan-17-yl *p*-bromobenzoate; note that the 'new' ring A is bent away from the general plane of the steroid nucleus; and (*b*) compound (4), 6-oxo-3β,5-cycloandrostan-17-yl acetate

TABLE 4

Bond angles (deg.)

	(3)	(4)
C(2)–C(1)–C(10)	104(2)	103·4(6)
C(1)–C(2)–C(3)	106(3)	104·6(5)
C(2)–C(3)–C(4)	115(3)	115·9(6)
C(2)–C(3)–C(5)	103(2)	107·6(6)
C(4)–C(3)–C(5)	61(2)	60·8(4)
C(3)–C(4)–C(5)	60(2)	59·3(4)
C(3)–C(5)–C(4)	59(2)	60·0(4)
C(3)–C(5)–C(6)	114(2)	129·9(6)
C(3)–C(5)–C(10)	112(2)	108·8(5)
C(4)–C(5)–C(6)	117(2)	114·6(6)
C(4)–C(5)–C(10)	120(2)	118·4(5)
C(6)–C(5)–C(10)	119(2)	114·7(5)
C(5)–C(6)–C(7)	119(2)	112·1(5)
C(5)–C(6)–O(1)	124(2)	125·7(6)
C(7)–C(6)–O(1)	117(2)	121·9(6)
C(6)–C(7)–C(8)	111(2)	114·6(5)
C(7)–C(8)–C(9)	112(2)	111·8(4)
C(7)–C(8)–C(14)	111(2)	111·6(4)
C(9)–C(8)–C(14)	107(2)	107·6(4)
C(8)–C(9)–C(10)	111(2)	109·7(4)
C(8)–C(9)–C(11)	110(2)	112·0(4)
C(10)–C(9)–C(11)	113(2)	115·1(5)
C(1)–C(10)–C(5)	100(2)	102·9(5)
C(1)–C(10)–C(9)	113(2)	115·4(5)
C(1)–C(10)–C(19)	109(2)	108·7(5)
C(5)–C(10)–C(9)	110(2)	108·1(5)
C(5)–C(10)–C(19)	110(2)	108·5(5)
C(9)–C(10)–C(19)	115(2)	112·6(4)
C(9)–C(11)–C(12)	115(2)	113·5(5)
C(11)–C(12)–C(13)	109(2)	110·9(5)
C(12)–C(13)–C(14)	109(2)	108·2(5)
C(12)–C(13)–C(17)	112(2)	115·3(5)
C(12)–C(13)–C(18)	111(2)	109·9(5)
C(14)–C(13)–C(17)	100(2)	98·9(5)
C(14)–C(13)–C(18)	115(2)	114·6(5)
C(17)–C(13)–C(18)	110(2)	109·7(5)
C(8)–C(14)–C(13)	113(2)	112·9(4)
C(8)–C(14)–C(15)	117(2)	118·5(5)
C(13)–C(14)–C(15)	106(2)	105·1(5)
C(14)–C(15)–C(16)	103(2)	102·4(6)
C(15)–C(16)–C(17)	105(2)	106·6(6)
C(13)–C(17)–C(16)	103(2)	105·1(5)
C(13)–C(17)–O(2)	111(2)	113·8(5)
C(16)–C(17)–O(2)	111(2)	106·8(5)
C(21)–C(20)–O(2)	116(2)	110·8(6)
C(21)–C(20)–O(3)	121(2)	126·3(7)
O(2)–C(20)–O(3)	123(2)	122·8(7)
C(17)–O(2)–C(20)	119(2)	120·9(5)
C(20)–C(21)–C(22)	120(2)	
C(20)–C(21)–C(26)	122(3)	
C(22)–C(21)–C(26)	118(2)	
C(21)–C(22)–C(23)	118(2)	
C(22)–C(23)–C(24)	125(3)	
C(23)–C(24)–C(25)	120(2)	
C(23)–C(24)–Br	124(2)	
C(25)–C(24)–Br	114(2)	
C(24)–C(25)–C(26)	117(3)	
C(21)–C(26)–C(25)	121(3)	

Except for the hydrogen atom at position 3, the configuration of both molecules is 8β,9α,10β,13β,14α,17β. A ball and stick model of one compound can be converted into a model of the other by disconnecting the C(2)–C(3) bond and re-connecting C(2) to C(4). The atom labels for C(3) and C(4) are interchanged and the acetate group at position 17 is replaced with a *p*-bromo-

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[17] D. F. High and J. Kraut, *Acta Cryst.*, 1966, **21**, 88.

benzoate group or *vice versa*. Atoms C(3) and C(4) remain in approximately the same relative position in both structures, but the labels are reversed. This is made clearer by inspection of the Newman projections in Figures 2 and 3.

TABLE 5

Torsional angles (deg.) *

	(3)	(4)
C(10)–C(1)–C(2)–C(3)	38	−34
C(2)–C(1)–C(10)–C(5)	−36	34
C(2)–C(1)–C(10)–C(9)	80	152
C(1)–C(2)–C(3)–C(4)	41	−46
C(1)–C(2)–C(3)–C(5)	−22	20
C(2)–C(3)–C(4)–C(5)	−92	97
C(2)–C(3)–C(5)–C(4)	111	−110
C(2)–C(3)–C(5)–C(6)	−140	152
C(2)–C(3)–C(5)–C(10)	−1	2
C(4)–C(3)–C(5)–C(6)	109	−98
C(4)–C(3)–C(5)–C(10)	−112	113
C(3)–C(4)–C(5)–C(6)	−104	123
C(3)–C(4)–C(5)–C(10)	100	−96
C(3)–C(5)–C(6)–C(7)	100	160
C(3)–C(5)–C(6)–O(1)	−81	−14
C(4)–C(5)–C(6)–C(7)	167	90
C(4)–C(5)–C(6)–O(1)	−14	−84
C(10)–C(5)–C(6)–C(7)	−36	−52
C(10)–C(5)–C(6)–O(1)	143	134
C(3)–C(5)–C(10)–C(1)	23	−23
C(4)–C(5)–C(10)–C(1)	−43	42
C(6)–C(5)–C(10)–C(9)	42	60
C(5)–C(6)–C(7)–C(8)	40	45
C(6)–C(7)–C(8)–C(9)	−51	−47
C(7)–C(8)–C(9)–C(10)	61	55
C(14)–C(8)–C(9)–C(11)	−53	−53
C(8)–C(9)–C(10)–C(5)	−53	−59
C(11)–C(9)–C(10)–C(1)	74	59
C(8)–C(9)–C(11)–C(12)	53	53
C(9)–C(11)–C(12)–C(13)	−55	−54
C(11)–C(12)–C(13)–C(14)	58	57
C(12)–C(13)–C(14)–C(8)	−66	−62
C(17)–C(13)–C(14)–C(15)	49	47
C(12)–C(13)–C(17)–O(2)	83	91
C(14)–C(13)–C(17)–C(16)	−43	−38
C(13)–C(14)–C(15)–C(16)	−34	−38
C(14)–C(15)–C(16)–C(17)	5	13
C(15)–C(16)–C(17)–C(13)	23	16
C(13)–C(17)–O(2)–C(20)	−162	−96
C(16)–C(17)–O(2)–C(20)	84	148
C(21)–C(20)–O(2)–C(17)	172	−179

* The torsional angle ϕ(1–2–3–4) is the dihedral angle between the plane of atoms (1), (2), and (3) and the plane of atoms (2), (3), and (4). It is positive if the bond in front has to be rotated clockwise to eclipse the rear bond.

The ' new ' A ring of (3) is found to be bent away from the general plane of the steroid nucleus [Figure 1(a)]. The dihedral angle between the best least-squares planes of C(2), C(3), C(5), C(10) (ring A), and C(5), C(7), C(8),-C(10) (ring B), is 37·6°, whereas it is 23·7° for (4). The corresponding angle is 33° for i-cholesteryl chloroacetate,[18] a steroid also containing a 3α,5-bond, but the substituents attached to C(6) and C(17) are a β-chloroacetyl group and a β-C_8 hydrocarbon chain respectively. For comparison Figure 1(b) is a stereographic diagram of (4).

The C(5)–C(6) bond is 1·45(3) in (3) and 1·48(1) Å in (4). The difference from the usual value of 1·54 Å for an sp^3–sp^3 bond is only just significant for (3) and probably

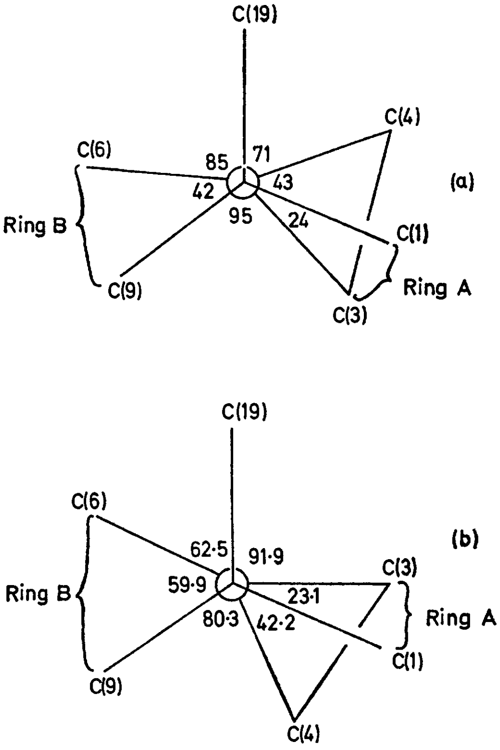

FIGURE 2 Newman projections along the C(5)–C(6) bond for (a) (3) and (b) (4)

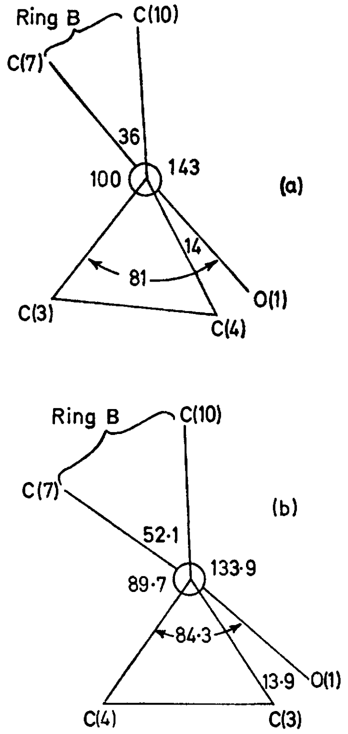

FIGURE 3 Newman projections along the C(5)–C(6) bond for (a) (3) and (b) (4)

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[18] H. R. Harrison, D. C. Hodgkin, E. N. Maslen, and W. D. S. Motherwell, *J. Chem. Soc.* (*C*), 1971, 1275.

significant for the more accurate (4) structure. Bond shortening of this order has been observed in structures containing similar groupings, *e.g.* in cyclopropanecarboxamide[19] and cyclopropanecarbohydrazide[20] where the corresponding bonds are 1·487(7) and 1·48(1) Å. In i-cholesteryl chloroacetate[18] the C(5)–C(6) bond is 1·492(10) Å, although the group adjacent to the cyclopropane ring is an ester.

The bond angles around C(5) are greatly distorted in both compounds (Table 4). For a tetrahedral carbon atom with bond lengths of 1·54 Å and angles of 109·5°, the deviation of C(5) from the plane through C(4), C(6), C(10) is 0·43 Å. In (3), C(5) is displaced by only 0·17 Å from this plane with a consequent enlargement of the C–C–C valency angles to *ca.* 120°. In (4) C(5) is displaced by 0·22 Å from the plane of the corresponding atoms C(3), C(6), C(10). The valency angles around C(5) are again larger than normal except for C(3)–C(5)–C(10) which is constrained by ring A to 109°. As a consequence of this constraint, the angle C(3)–C(5)–C(6) is 130° compared with 117° in (3).

The geometry of ring A is similar in the two structures with the torsion angles approximately equal but opposite in sign (Table 5). The displacement of C(1) from the plane through the remaining atoms of ring A is 0·59 and 0·55 Å in the two molecules, and in both cases ring A is in the envelope conformation. Torsion angles for (3) indicate a slight flattening of ring B in the region of C(10), C(5), C(6), C(7) due possibly to the close approach of the hydrogen atoms attached to C(2) and C(9). The calculated positions for these hydrogen atoms place them only 2·35 Å apart.

TABLE 6

Deviations (Å) of atoms from best least-squares planes

(i) Ring A: C(2), C(3), C(5), C(10)

	(3)	(4)		(3)	(4)
C(1)	0·59	−0·55	C(4)	1·22	−1·22
C(2)	0·00	−0·01	C(5)	0·01	−0·01
C(3)	−0·01	0·01			

(ii) Ring B: C(5), C(7), C(8), C(10)

	(3)	(4)		(3)	(4)
C(5)	0·04	−0·04	C(8)	0·04	−0·04
C(6)	0·43	0·57	C(9)	−0·69	−0·70
C(7)	0·04	0·04	C(10)	0·04	0·04

(iii) Ring C: C(5), C(11), C(13), C(14)

	(3)	(4)		(3)	(4)
C(8)	0·72	0·70	C(12)	−0·68	−0·67
C(9)	0·04	0·03	C(13)	0·04	0·03
C(11)	−0·04	−0·03	C(14)	−0·04	−0·03

(iv) Ring D: C(15)—(17)

	(3)	(4)		(3)	(4)
C(13)	0·60	0·41	C(14)	−0·14	−0·33

The Newman projections along the C(10)–C(5) bond (Figure 2) show a rotation of *ca.* 20° about this bond when (3) is compared with (4). The Newman projections along the C(5)–C(6) bond (Figure 3) indicate that the cyclopropane ring and the carbonyl oxygen maintain the same relative geometry, but the torsion angle C(7)–C(6)–C(5)–C(10) in ring B increases from 36 in (3) to 52° in (4). The smaller torsion angle in (3) is probably the result of the short hydrogen contact (see earlier), the total effect being to flatten one side of the B ring while the other side has larger torsion angles. The flattening is also evident from the least-squares planes calculations (Table 6). The deviations of C(6) and C(9) from the plane through C(5), C(7), C(8), and C(10) are less for (3) than for (4).

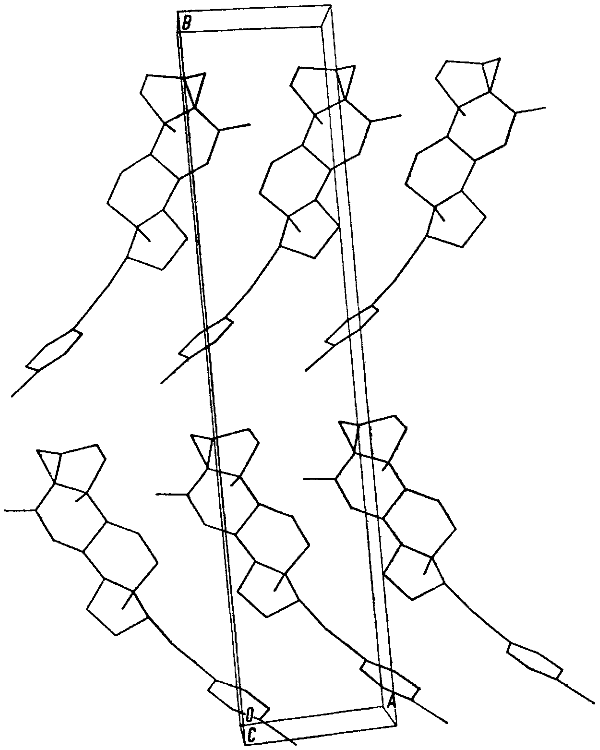

FIGURE 4 A packing diagram of (3) projected on the (001) plane

The geometry of rings C and D of both molecules appears to be normal, most of the strain of the cyclopropane ring having been absorbed in the distortion of rings A and B. The geometry of the *trans* C/D ring junction was discussed by Altona *et al.*,[21] who introduced two parameters to describe the configuration of the D ring: ϕ_m, the maximum torsional angle, and Δ, the angle of pseudorotation. For (3) ϕ_m 50 and Δ 20°, and for (4) ϕ_m 47 and Δ 0·2°. In the latter case, the small value of Δ indicates a nearly symmetrical ring D with a pseudo two-fold axis through atom C(16) and the mid-point of the C(13)–C(14) bond. The out-of-plane distances for C(13) and C(14) from the plane C(15), C(16), C(17) are given in Table 4.

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[19] R. E. Long, H. Maddox, and K. N. Trueblood, *Acta Cryst.*, 1969, *B*, **25**, 2083.

[20] D. B. Chesnut and R. E. Marsh, *Acta Cryst.*, 1958, **11**, 413.

[21] C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, 1968, **24**, 13.

The overall skeleton of both molecules is slightly convex toward the methyl groups, C(18) and C(19). The vectors C(10) · · · C(19) and C(13) · · · C(18) make an angle of 13° in both compounds. This effect has been observed in several steroid structures.[22]

The results obtained are inconclusive as a method of predicting the amount of conjugative overlap based on the geometry of the cyclopropanecarbonyl system in these two structures. As previously discussed, the cyclopropane ring and the carbonyl oxygen maintain the same relative positions in both structures and thus the torsion angle alone cannot be taken as a measure of the amount of conjugative overlap. The most significant difference between the two structures is the angle C(3)–C(5)–C(6), which is 114 in (3) and 130° in (4). The large increase for (4) indicates that the C(3)–C(5) bond loses more of its *p* character because of the increased valency angle.

TABLE 7

Intermolecular contacts $<3{\cdot}70$ Å excluding hydrogen atoms

	(*a*) Compound (3)		
C(2) · · · O(1^{I})	3·69	C(15) · · · O(3^{I})	3·47
C(9) · · · O(1^{I})	3·56	C(16) · · · O(3^{I})	3·69
C(11) · · · O(1^{II})	3·47	C(16) · · · C(23^{II})	3·54
C(19) · · · O(1^{II})	3·49		
C(22) · · · O(3^{III})	3·33	C(23) · · · O(3^{III})	3·20
C(1) · · · $\mathrm{Br}^{\mathrm{IV}}$	3·68		
C(3) · · · C(24^{V})	3·62	C(4) · · · C(25^{V})	3·47
	(*b*) Compound (4)		
C(7) · · · C(11^{I})	3·62	C(16) · · · C(21^{I})	3·69
C(11) · · · O(1^{I})	3·42		
C(21) · · · O(1^{VI})	3·32		
C(7) · · · C(18^{VII})	3·64		

Roman numerals as superscripts denote the following transformations relative to the reference molecule at x, y, z:

I $1 + x, y, z$
II $1 + x, y, 1 + z$
III $x, y, 1 + z$
IV $2 - x, \frac{1}{2} + y, 2 - z$
V $1 - x, \frac{1}{2} + y, 1 - z$
VI $1 + x, 1 + y, z$
VII $\frac{1}{2} + x, \frac{1}{2} - y, -z$

Crystal Packing.—A packing diagram for (3) projected on the (001) plane is shown in Figure 4. It indicates that the steroid molecules pack in layers approximately parallel to (001). Intermolecular contacts $<3{\cdot}70$ Å (excluding hydrogen atom contacts) are listed in Table 7. None are unusually close. The crystal packing for (4) is unusual in that two-fold screw axes parallel to the *c* axis pass through the A and D rings respectively. This is illustrated in Figure 5, a projection of the cell contents on to the 001 plane. We are unaware of other examples of one or more two-fold screw axes passing through the rings of a steroid molecule.

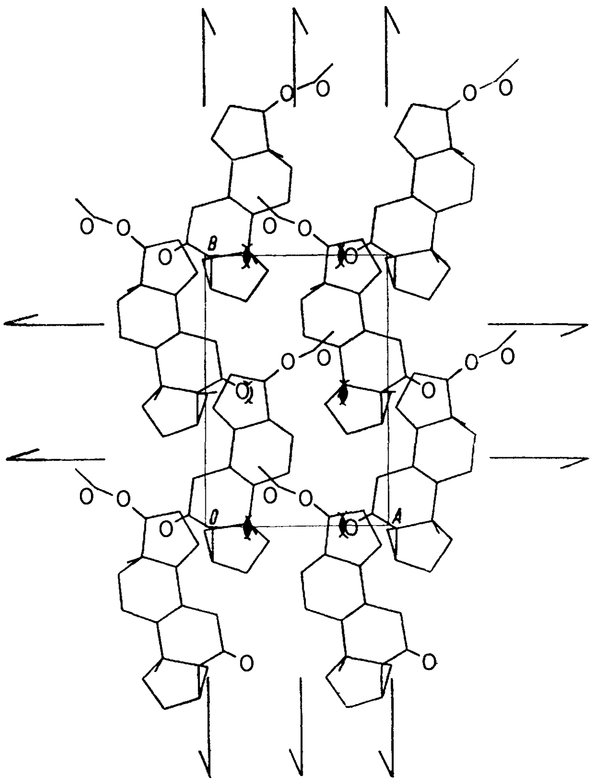

FIGURE 5 A packing diagram of (4) projected on the (001) plane. Note the unusual placement of the molecule with respect to the two-fold screw axes parallel to *c*

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[1/2387 *Received*, 13*th December*, 1971]

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[22] H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, 1963, **23**, 439.