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The Crystal and Molecular Structure of (±)-14-β-Androsta-4,8-diene-3,17-dione

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The crystal and molecular structure of (±)-14-β-androsta-4,8-diene-3,17-dione ($C_{19}H_{24}O_2$) has been determined from three-dimensional diffractometer data (2θ scan) in order to establish the geometrical isomerism of the molecule. The compound crystallizes in the monoclinic space group, $P2_1/c$, with four molecules in a unit cell of dimensions $a=7{\cdot}338$ (3), $b=18{\cdot}641$ (5), $c=12{\cdot}432$ (4) Å, $\beta=114{\cdot}89$ (4)°. The structure was refined by the full-matrix least-squares method to a final R value of 0·045 for 2151 reflections $>3\sigma(I)$. The molecule has a *cis* junction between rings *C* and *D*, and the two methyl groups are in the *cis* configuration.

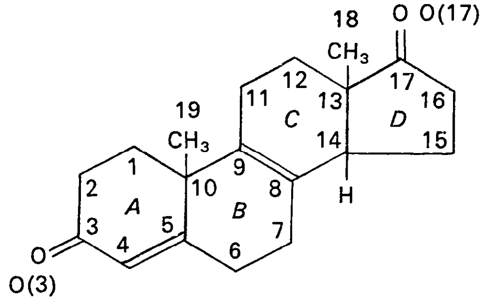
Introduction

The crystal structure determination of (±)-14-β-androsta-4,8-diene-3,17-dione was undertaken to determine the positions of the double bonds, the steric relationship of the methyl groups, and the configuration at the junction of the *C*, *D* rings. The results were crucial for unequivocally establishing a new total synthesis of androstadienediones (Danishefsky, Solomon, Crawley, Sax, Yoo, Abola & Pletcher, 1972).

Experimental

The crystals of the androstadienedione were provided for this analysis by Professor S. Danishefsky of the University of Pittsburgh Chemistry Department. They are colorless, and their habit is tabular with **a** parallel to the long axis. The space group was obtained from oscillation and Weissenberg photographs. The unit-cell dimensions were deduced from manual 2θ scans of the observable axial reflections using a Picker FACS I diffractometer equipped with a scintillation detector. The crystal was mounted so that its *a* axis coincided with the φ axis of the full-circle orienter. Ni-filtered Cu $K\alpha$ radiation was used throughout the analysis. Table 1 contains the crystal data.

Table 1. *Crystal data for* (±)-14-β-*androsta-*4,8-*diene*-3,17-*dione*



$C_{19}H_{24}O_2$, M.W. 284·42, m.p. 143 ~ 144 °C

Monoclinic, space group $P2_1/c$ from systematic absences: $h0l$ absent for l odd; $0k0$ absent for k odd.

$a=7{\cdot}338$ (3) Å	measured at 24 °C	λ(Cu $K\alpha$) = 1·5418 Å
$b=18{\cdot}641$ (5)		λ(Cu $K\alpha_1$) = 1·54051
$c=12{\cdot}432$ (4)		λ(Cu $K\alpha_2$) = 1·5443
$\beta=114{\cdot}89$ (4)°		μ(Cu $K\alpha$) = 6·1 cm^{-1}
$V=1542{\cdot}5$ Å^3		$F(000)=616$
$Z=4$		

$d_x=1{\cdot}225$ g cm^{-3}
$d_m=1{\cdot}221$ g cm^{-3} measured by flotation method in aqueous potassium iodide solution at 20 °C.
Crystal dimensions: 0·8 × 0·4 × 0·2 mm.

The integrated intensity measurements were made by scanning reflections in the θ–2θ mode at a rate of 2° min^{-1} over a 2θ range of 2°. The background was counted for 10 sec at each of the scan limits. Eight reflections were chosen as standards, and two of these were monitored at intervals of approximately 2 hr. Examination of the standards during the data collection showed an 8 % decrease in intensity after a total exposure of ~80 hr. Accordingly, scale factors based on the standard reflections were applied to the intensity data to correct for the time-dependent decrease.

In all, 2631 reflections were collected; of these, 480 had net intensities, (I), less than $3\sigma(I)$ where $\sigma(I)$ is given by

$$A\{(10S+5)+[(10B_1+5)+(10B_2+5)]\}^{1/2}.$$

S is the total number of decacounts accumulated during the scan, B_1 and B_2 are the background, also in decacounts, while A is the attenuator factor. The intensities were corrected for Lorentz and polarization factors, but not for absorption. The scaling, data processing and reduction were performed using the IBM 1130 programs of Shiono (1971*a*).

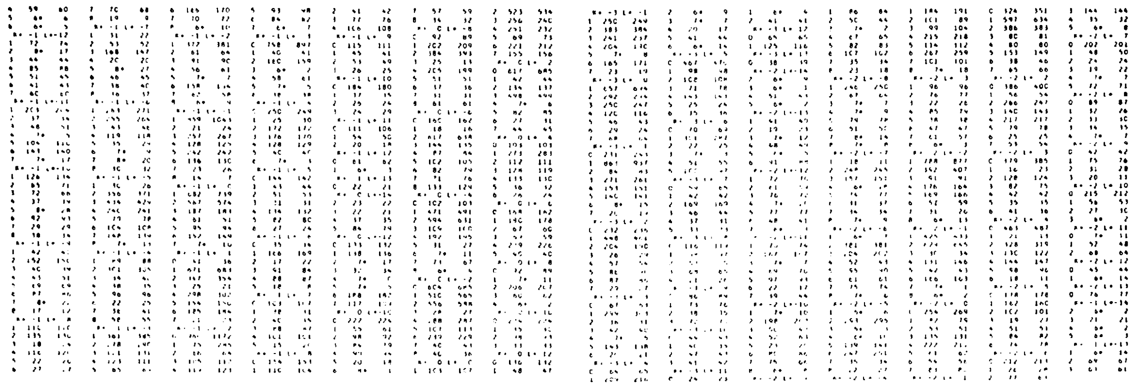
Structure determination and refinement

The X-RAY 70 system of computer programs (Stewart, Kundell & Baldwin, 1970) was used to place the structure factors on an approximately absolute scale by means of a Wilson (1942) plot, to normalize the structure factors to E values, to determine the signs of 296 of the reflections with $E\geq 1{\cdot}50$, and to produce an E map (Karle, Hauptman, Karle & Wing, 1958) which revealed the 21 non-hydrogen atoms in the molecule. The structural parameters were refined by the full-matrix least-squares method, using the program *ORFLS* of Busing, Martin & Levy (1962) as modified by Shiono (1971*b*). The Hughes (1941) weighting scheme was employed with $\sigma(F)=F/11{\cdot}2$ for $|F|>11{\cdot}2$ and with $\sigma(F)=1$ for $|F|\le 11{\cdot}2$. The function mini-

Table 2. *Observed and calculated structure factors*

The columns within each group in order from left to right are: the running index h, $10|F_o|$ and $10|F_c|$. Asterisks indicate unobserved reflections.

Table 2 (*cont.*)



mized was $\sum w(|F_o|-k|F_c|)^2$ where k is a single scale factor and w is the weight. The hydrogen atoms were located in a difference Fourier synthesis computed when the conventional R was 0·11. The positional and isotropic thermal parameters of the hydrogen atoms were varied in additional cycles of the refinement. The

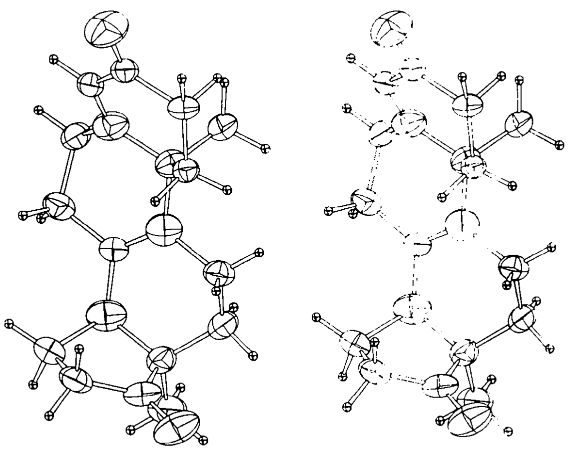


Fig. 1. Stereoscopic view of the molecule.

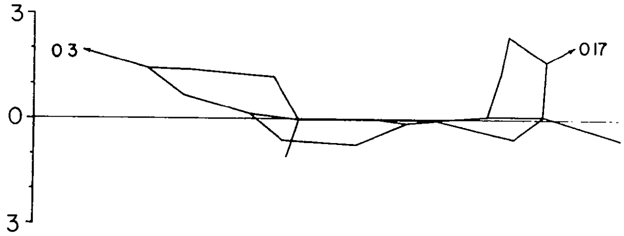


Fig. 2. Side view of the molecule. Ordinate refers to deviation (Å) of atoms from the plane defined by abscissa.

Table 3. *Atomic parameters, their estimated standard deviations and root-mean-square deviations about principal axes of vibration*

Thermal parameters are in the form exp $[-(h^2\beta_{11}+\ldots 2kl\beta_{23})]$.

(*a*) Fractional coordinates ($\times 10^4$), thermal parameters ($\times 10^4$) and root-mean-square deviations $\times 10^4$ (Å) for the non-hydrogen atoms.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$D1$	$D2$	$D3$
O(3)	9035 (4)	−1280 (1)	5269 (2)	407 (7)	39 (1)	99 (2)	30 (2)	66 (3)	33 (1)	1751	3131	3200
C(1)	6284 (3)	262 (1)	3547 (2)	216 (5)	22 (1)	61 (2)	6 (1)	56 (2)	3 (1)	1893	1950	2239
C(2)	6497 (4)	−414 (1)	4281 (2)	218 (6)	27 (1)	67 (2)	−1 (2)	66 (3)	8 (1)	1831	2312	2515
C(3)	8315 (4)	−851 (1)	4452 (2)	263 (6)	22 (1)	68 (2)	−2 (2)	34 (3)	8 (1)	1311	2163	2666
C(4)	9152 (3)	−756 (1)	3586 (2)	219 (5)	20 (1)	82 (2)	12 (1)	43 (3)	5 (1)	1743	2256	2446
C(5)	8331 (3)	−333 (1)	2634 (2)	190 (5)	15 (1)	72 (2)	1 (1)	47 (2)	0 (1)	1636	2063	2166
C(6)	9171 (4)	−281 (1)	1730 (2)	244 (6)	19 (1)	100 (2)	17 (2)	88(3)	3 (1)	1677	2191	2602
C(7)	9705 (3)	496 (1)	1620 (2)	200 (5)	21 (1)	101 (2)	10 (1)	83 (3)	5 (1)	1799	1977	2589
C(8)	8034 (3)	1009 (1)	1483 (2)	171 (5)	16 (1)	61 (2)	0 (1)	48 (2)	−1 (1)	1669	1892	2006
C(9)	6565 (3)	830 (1)	1800 (2)	157 (4)	15 (1)	54 (2)	1 (1)	33 (2)	−1 (1)	1633	1836	1976
C(10)	6461 (2)	112 (1)	2374 (1)	158 (5)	16 (1)	55 (2)	−3 (1)	37 (3)	1 (1)	1663	1866	1940
C(11)	4876 (3)	1349 (1)	1619 (2)	192 (5)	20 (1)	85 (2)	11 (1)	71 (3)	8 (1)	1758	1913	2431
C(12)	4546 (3)	1891 (1)	636 (2)	201 (5)	21 (1)	78 (2)	14 (1)	48 (2)	7 (1)	1645	2227	2311
C(13)	6494 (3)	2262 (1)	700 (2)	227 (5)	16 (1)	61 (2)	4 (1)	52 (2)	5 (1)	1616	2014	2264
C(14)	8186 (3)	1728 (1)	952 (2)	230 (6)	18 (1)	80 (2)	−4 (1)	79 (3)	1 (1)	1735	1962	2393
C(15)	2139 (4)	1748 (1)	223 (3)	223 (6)	21 (1)	149 (3)	−13 (2)	80 (4)	4 (1)	1770	2310	3152
C(16)	9554 (4)	2531 (1)	2626 (2)	288 (6)	22 (1)	99 (2)	−9 (2)	26 (3)	3 (1)	1932	2226	3000
C(17)	7373 (4)	2702 (1)	1943 (2)	315 (7)	16 (1)	71 (2)	7 (2)	65 (3)	5 (1)	1645	2130	2698
C(18)	6100 (4)	2779 (1)	−239 (2)	350 (8)	25 (1)	72 (2)	7 (2)	65 (3)	13 (1)	1755	2409	2850
C(19)	4639 (3)	−330 (1)	1527 (2)	200 (5)	21 (1)	72 (2)	−12 (1)	38 (3)	1 (1)	1700	2095	2385
O(17)	461 (4)	30 (1)	110 (2)	461 (8)	29 (1)	110 (2)	35 (2)	100 (3)	−9 (1)	1872	2725	3399

Table 3 (*cont.*)

(*b*) Fractional coordinates ($\times 10^3$) and isotropic temperature factors for the hydrogen atoms.

	x	*y*	*z*	*B*
H(C1)	738 (2)	61 (1)	404 (1)	2·9 (3)
H'(C1)	495 (2)	49 (1)	336 (2)	3·9 (4)
H(C2)	539 (4)	−76 (1)	389 (2)	5·8 (6)
H'(C2)	660 (3)	−29 (1)	529 (2)	4·9 (4)
H(C4)	1038 (3)	−105 (1)	376 (2)	5·1 (4)
H(C6)	1033 (3)	−60 (1)	194 (2)	4·3 (4)
H'(C6)	808 (3)	−46 (1)	92 (2)	4·3 (4)
H(C7)	1010 (4)	57 (1)	96 (2)	5·6 (5)
H'(C7)	1096 (3)	62 (1)	235 (2)	4·4 (4)
H(C11)	518 (3)	160 (1)	239 (2)	4·2 (4)
H'(C11)	361 (3)	109 (1)	144 (2)	4·5 (4)
H(C12)	362 (3)	226 (1)	61 (2)	3·6 (4)
H'(C12)	369 (3)	164 (1)	−19 (2)	4·8 (5)
H(C14)	817 (3)	168 (1)	61 (2)	4·0 (4)
H(C15)	1043 (3)	250 (1)	126 (2)	5·2 (5)
H'(C15)	1143 (4)	184 (1)	217 (2)	6·0 (6)
H(C16)	955 (3)	221 (1)	325 (2)	5·5 (5)
H'(C16)	1050 (4)	293 (2)	302 (2)	7·2 (6)
H(C18)	550 (3)	250 (1)	−101 (2)	5·0 (5)
H'(C18)	507 (4)	315 (1)	−26 (2)	6·6 (6)
H''(C18)	743 (4)	302 (2)	−13 (3)	7·3 (7)
H(C19)	466 (3)	−82 (1)	190 (2)	5·9 (5)
H'(C19)	476 (3)	−41 (1)	75 (2)	5·4 (5)
H''(C19)	335 (3)	−8 (1)	136 (2)	5·5 (5)

final *R* index is 0·053 for all 2631 independent reflections and 0·045 for the 2151 reflections $> 3\sigma(I)$. The structure amplitudes are listed in Table 2. The atomic coordinates and thermal parameters with their e.s.d.'s are given in Table 3. The atomic scattering factors used for carbon and oxygen atoms were taken from *International Tables for X-ray Crystallography* (1962), while those of Stewart, Davidson & Simpson (1965) were used for the hydrogen atoms.

Discussion of the structure

A stereogram (Johnson, 1965) of the molecule is shown in Fig. 1. The interatomic distances, valency angles, and their e.s.d.'s are presented in Tables 4 and 5. The interatomic distances appear normal except for a significant shortening of the bond between C(15) and C(16). This may be a consequence of the molecular thermal motions, although strain introduced by the *cis* fusion of the *C* and *D* rings may have an effect also.

Table 6 lists torsion angles, and Table 7 gives the best least-squares planes through selected atoms in the molecule. An analysis of these data shows that rings *A*, *B* and *C* are in half-chair conformations but that rings *B* and *C* taken together are in the form of an extended boat. The five-membered ring is in the half-chair form also. Rings *D* and *C* are α-*cis* fused with C(15), C(16) and C(17) lying 1·292, 2·328 and 1·541 Å, respectively, below the planar region of rings *B* and *C*. The methyl carbon atoms, C(18) and C(19), are *cis*-related and project 0·623 and 1·340 Å, respectively, above the planar region of the *B* and *C* rings. Fig. 2 shows the extent of flattening of the *B* and *C* rings caused by the trigonal centers at C(8) and C(9).

Table 4. *Interatomic distances* (Å)

C(1)—C(2)	1·524 (3)
C(1)—C(10)	1·543 (3)
C(2)—C(3)	1·500 (3)
C(3)—C(4)	1·457 (3)
C(4)—C(5)	1·336 (3)
C(5)—C(6)	1·495 (3)
C(5)—C(10)	1·517 (3)
C(6)—C(7)	1·522 (3)
C(7)—C(8)	1·506 (3)
C(8)—C(9)	1·334 (3)
C(8)—C(14)	1·519 (3)
C(9)—C(10)	1·535 (3)
C(9)—C(11)	1·512 (3)
C(10)-C(19)	1·545 (3)
C(11)-C(12)	1·524 (3)
C(12)-C(13)	1·522 (3)
C(13)-C(14)	1·539 (3)
C(13)-C(17)	1·529 (3)
C(13)-C(18)	1·538 (3)
C(14)-C(15)	1·549 (4)
C(15)-C(16)	1·510 (4)
C(16)-C(17)	1·496 (3)
O(3)—C(3)	1·223 (3)
O(17)-C(17)	1·209 (3)
C(1)—H(C1)	1·01 (2)
C(1)—H'(C1)	1·00 (2)
C(2)—H(C2)	1·00 (3)
C(2)—H'(C2)	1·00 (2)
C(4)—H(C4)	1·00 (2)
C(6)—H(C6)	0·97 (2)
C(6)—H'(C6)	1·05 (2)
C(7)—H(C7)	1·00 (3)
C(7)—H'(C7)	1·00 (3)
C(11)-H(C11)	1·01 (2)
C(11)-H'(C11)	0·98 (2)
C(12)-H(C12)	0·96 (2)
C(12)-H'(C12)	1·04 (2)
C(14)-H(C14)	0·99 (2)
C(15)-H(C15)	0·99 (2)
C(15)-H'(C15)	1·04 (3)
C(16)-H(C16)	0·98 (3)
C(16)-H'(C16)	1·00 (3)
C(18)-H(C18)	1·02 (3)
C(18)-H'C(18)	1·02 (3)
C(18)-H''C(18)	1·03 (3)
C(19)-H(C19)	1·02 (2)
C(19)-H'(C19)	1·02 (2)
C(19)-H''(C19)	1·00 (2)

The conformation of ring *D* may be characterized by the parameters φ_m, the measure of puckering, and Δ, the phase (Altona, Geise & Romers, 1968). The

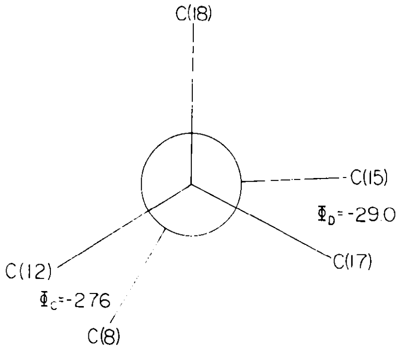


Fig. 3. Newman projection along C(13)–C(14)

Table 5. *Valency angles* (°)

C(1)—C(2)—C(3)	113·2 (2)
C(1)—C(10)–C(5)	109·0 (2)
C(1)—C(10)–C(9)	108·9 (2)
C(1)—C(10)–C(19)	110·3 (2)
C(2)—C(1)—C(10)	112·9 (2)
C(2)—C(3)—C(4)	117·1 (2)
C(3)—C(4)—C(5)	123·6 (2)
C(4)—C(5)—C(6)	122·0 (2)
C(4)—C(5)—C(10)	122·8 (2)
C(5)—C(6)—C(7)	109·4 (2)
C(5)—C(10)–C(9)	111·0 (2)
C(5)—C(10)–C(19)	107·4 (2)
C(6)—C(5)—C(10)	115·2 (2)
C(6)—C(7)—C(8)	112·7 (2)
C(7)—C(8)—C(9)	121·9 (2)
C(7)—C(8)—C(14)	113·8 (2)
C(8)—C(9)—C(10)	124·0 (2)
C(8)—C(9)—C(11)	120·7 (2)
C(8)—C(14)–C(13)	114·9 (2)
C(8)—C(14)–C(15)	112·0 (2)
C(9)—C(8)—C(14)	124·3 (2)
C(9)—C(10)–C(19)	110·3 (2)
C(9)—C(11)–C(12)	112·7 (2)
C(10)–C(9)—C(11)	115·3 (2)
C(11)–C(12)–C(13)	111·7 (2)
C(12)–C(13)–C(14)	112·8 (2)
C(12)–C(13)–C(17)	112·0 (2)
C(12)–C(13)–C(18)	109·8 (2)
C(13)–C(14)–C(15)	103·5 (2)
C(13)–C(17)–C(16)	110·2 (2)
C(14)–C(13)–C(17)	103·3 (2)
C(14)–C(13)–C(18)	111·4 (2)
C(14)–C(15)–C(16)	104·1 (2)
C(15)–C(16)–C(17)	104·3 (2)
C(17)–C(13)–C(18)	107·5 (2)
C(2)—C(3)—O(3)	121·3 (2)
O(3)—C(3)—C(4)	121·6 (2)
O(17)–C(17)–C(13)	123·9 (2)
O(17)–C(17)–C(16)	126·0 (2)

Table 7. *Some least-squares planes through groups of atoms*

Coefficients ($\times 10^4$) in $Ax+By+Cz-D=0$ referred to the crystallographic axes (x,y,z in Å).

Plane	No.	*A*	*B*	*C*	*D*
C(2) C(3) C(4) C(5) C(10)	1	3877	7555	3160	29344
C(5) C(7) C(8) C(9) C(10)	2	1627	4310	7367	30880
C(8) C(9) C(11) C(13) C(14)	3	1580	3598	7677	30241
C(13) C(14) C(15) C(16) C(17)	4	4033	7213	−6804	41604
C(5) C(7) C(8) C(9) C(10) C(11) C(13) C(14)	5	1634	3905	7531	31110

Plane No.	Displacement from the plane (Å × 10^3)
1	C(1) 615; C(2) 12; C(3) −19; C(4) 13; C(5) 0; C(10) −7
2	C(5) 51; C(6) −635; C(7) −47; C(8) 40; C(9) 9; C(10) −53
3	C(8) 0; C(9) 9; C(11) −9; C(12) −622; C(13) 9; C(14) −8
4	C(13) 126; C(14) −219; C(15) 233; C(16) −151; C(17) 11
5	C(5) 111; C(6) −597; C(7) −69; C(8) −25; C(9) −37; C(10) −33; C(11) −29; C(12) −594; C(13) 63; C(14) 19

values found for the androstadienedione are listed below and are compared to those found for 3*β*-*p*-bromobenzoyloxy-13*α*-androst-5-en-17-one (hereafter APBA) (Portheine & Romers, 1970), which is another steroid with *C*/*D* *cis* fusion.

	Androstadienedione	APBA
φ_m	38·3°	41°
Δ	−81·6	−34

Table 6. *Torsion angles*

The sign convention for the torsion angle is that of Klyne & Prelog (1960). The torsion angles in the other enantiomorph are opposite in sign. φ in (*a*) is the torsion angle about the specified bond. The other two atoms required to define the angle are attached to the ends of the bond and are in the ring in question.

(*a*) Steroid nucleus

Ring *A*		Ring *B*		Ring *C*		Ring *D*	
Bond	φ	Bond	φ	Bond	φ	Bond	φ
C(1)–C(2)	50·3°	C(5)–C(6)	59·1°	C(8)—C(9)	1·0°	C(13)–C(14)	−29·0°
C(1)–C(10)	−49·9	C(5)–C(10)	−36·7	C(8)—C(14)	0·5	C(13)–C(17)	9·3
C(2)–C(3)	−22·9	C(6)–C(7)	−48·6	C(9)—C(11)	24·6	C(14)–C(15)	38·9
C(3)–C(4)	−3·4	C(7)–C(8)	19·7	C(11)–C(12)	−51·2	C(15)–C(16)	−32·7
C(4)–C(5)	1·8	C(8)–C(9)	2·8	C(12)–C(13)	52·8	C(16)–C(17)	14·7
C(5)–C(10)	24·9	C(9)–C(10)	5·1	C(13)–C(14)	−27·6		

(*b*) Ring junctions

A/*B* junction	φ	*B*/*C* junction	φ	*C*/*D* junction	φ
C(1)–C(10)–C(5)—C(6)	−156·6°	C(7)—C(8)–C(9)–C(11)	−178·3°	C(12)–C(13)–C(14)–C(15)	−150·0°
C(4)–C(5)—C(10)–C(9)	144·8	C(10)–C(9)–C(8)–C(14)	−177·9	C(8)—C(14)–C(13)–C(17)	93·4

(*c*) Extra-nuclear

O(3)—C(3)—C(2)—C(1)	158·7°	C(19)–C(10)–C(5)—C(4)	−94·7°
O(3)—C(3)—C(4)—C(5)	175·0	C(19)–C(10)–C(5)—C(6)	83·9
C(18)–C(13)–C(12)–C(11)	177·7	C(19)–C(10)–C(9)—C(8)	−113·8
C(18)–C(13)–C(14)–C(8)	−151·5	C(19)–C(10)–C(9)—C(11)	67·3
C(18)–C(13)–C(14)–C(15)	86·1	O(17)–C(17)–C(13)–C(12)	−49·9
C(18)–C(13)–C(17)–C(16)	−108·5	O(17)–C(17)–C(13)–C(14)	−171·4
C(19)–C(10)–C(1)—C(2)	67·8	O(17)–C(17)–C(13)–C(18)	−70·7
		O(17)–C(17)–C(16)–C(15)	−164·5

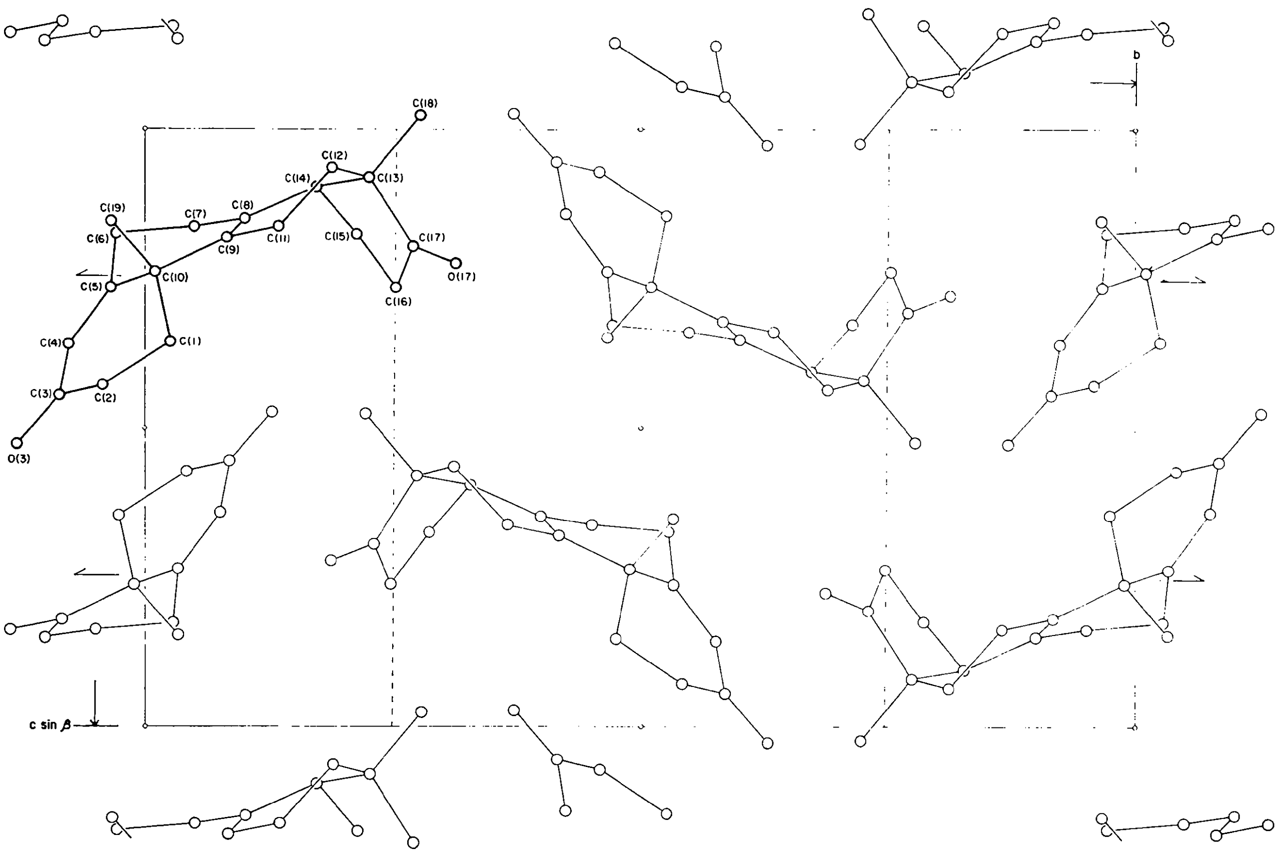


Fig. 4. Projection of one unit cell along the *a* axis. Hydrogen atoms are omitted.

The phase angle for androstadienedione shows that the *D* ring is in the half-chair conformation. The small φ_m found for the androstadienedione as compared with that for ABPA may be due to the ethylenic bond at C(8) and C(9). Fig. 3 shows a Newman projection along C(13)–C(14) for androstadienedione. The corresponding values for φ_C and φ_D in APBA are $-42°$ and $-38°$ respectively (Portheine & Romers, 1970).

A projection of the structure along the *a* axis, illustrating the packing of the molecules, is shown in Fig. 4. The distances between neighboring molecules correspond to normal van der Waals contacts.

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