

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

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(Received 6 April 1973; accepted 18 May 1973)

The crystal and molecular structure of (\pm)-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 $a = 7.338$ (3), $b = 18.641$ (5), $c = 12.432$ (4) Å, $\beta = 114.89$ (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 (\pm)-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

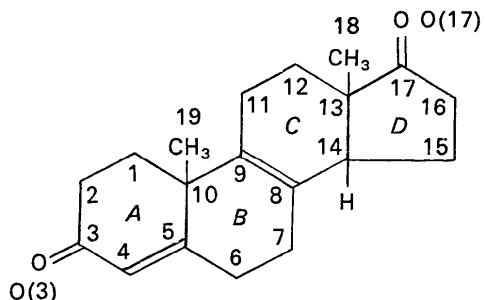
The crystals of the androstadienedione were provided for this analysis by Professor S. Danishefsky of the University of Pittsburgh Chemistry Department. They are colorless, and their habit is tabular with *a* parallel to the long axis. The space group was obtained from oscillation and Weissenberg photographs. 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.

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

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

Table 1. Crystal data for (\pm)-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.

$a = 7.338$ (3) Å	}	measured at 24 °C	$\lambda(Cu K\alpha) = 1.5418$ Å
$b = 18.641$ (5)			$\lambda(Cu K\alpha_1) = 1.54051$
$c = 12.432$ (4)			$\lambda(Cu K\alpha_2) = 1.5443$
$\beta = 114.89$ (4)°			$\mu(Cu K\alpha) = 6.1$ cm $^{-1}$

$V = 1542.5$ Å 3

$Z = 4$

$d_x = 1.225$ g cm $^{-3}$

$d_m = 1.221$ g cm $^{-3}$ measured by flotation method in aqueous potassium iodide solution at 20 °C.

Crystal dimensions: 0.8 × 0.4 × 0.2 mm.

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 (1971a).

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 $E \geq 1.50$, 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 (1971b). The Hughes (1941) weighting scheme was employed with $\sigma(F)=F/11.2$ for $|F|>11.2$ and with $\sigma(F)=1$ for $|F|\leq 11.2$. 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.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	8010	8011	8012	8013	8014	8015	8016	8017	8018	8019	8020	8021	8022	8023	8024	8025	8026	8027	8028	8029	8030	8031	8032	8033	8034	8035	8036	8037	8038	8039	8040	8041	8042	8043	8044	8045	8046	8047	8048	8049	8050	8051	8052	8053	8054	8055	8056	8057	8058	8059	8060	8061	8062	8063	8064	8065	8066	8067	8068	8069	8070	8071	8072	8073	8074	8075	8076	8077	8078	8079	8080	8081	8082	8083	8084	8085	8086	8087	8088	8089	8090	8091	8092	8093	8094	8095	8096	8097	8098	8099	80100	80101	80102	80103	80104	80105	80106	80107	80108	80109	80110	80111	80112	80113	80114	80115	80116	80117	80118	80119	80120	80121	80122	80123	80124	80125	80126	80127	80128	80129	80130	80131	80132	80133	80134	80135	80136	80137	80138	80139	80140	80141	80142	80143	80144	80145	80146	80147	80148	80149	80150	80151	80152	80153	80154	80155	80156	80157	80158	80159	80160	80161	80162	80163	80164	80165	80166	80167	80168	80169	80170	80171	80172	80173	80174	80175	80176	80177	80178	80179	80180	80181	80182	80183	80184	80185	80186	80187	80188	80189	80190	80191	80192	80193	80194	80195	80196	80197	80198	80199	80200	80201	80202	80203	80204	80205	80206	80207	80208	80209	80210	80211	80212	80213	80214	80215	80216	80217	80218	80219	80220	80221	80222	80223	80224	80225	80226	80227	80228	80229	80230	80231	80232	80233	80234	80235	80236	80237	80238	80239	80240	80241	80242	80243	80244	80245	80246	80247	80248	80249	80250	80251	80252	80253	80254	80255	80256	80257	80258	80259	80260	80261	80262	80263	80264	80265	80266	80267	80268	80269	80270	80271	80272	80273	80274	80275	80276	80277	80278	80279	80280	80281	80282	80283	80284	80285	80286	80287	80288	80289	80290	80291	80292	80293	80294	80295	80296	80297	80298	80299	80300	80301	80302	80303	80304	80305	80306	80307	80308	80309	80310	80311	80312	80313	80314	80315	80316	80317	80318	80319	80320	80321	80322	80323	80324	80325	80326	80327	80328	80329	80330	80331	80332	80333	80334	80335	80336	80337	80338	80339	80340	80341	80342	80343	80344	80345	80346	80347	80348	80349	80350	80351	80352	80353	80354	80355	80356	80357	80358	80359	80360	80361	80362	80363	80364	80365	80366	80367	80368	80369	80370	80371	80372	80373	80374	80375	80376	80377	80378	80379	80380	80381	80382	80383	80384	80385	80386	80387	80388	80389	80390	80391	80392	80393	80394	80395	80396	80397	80398	80399	80400	80401	80402	80403	80404	80405	80406	80407	80408	80409	80410	80411	80412	80413	80414	80415	80416	80417	80418	80419	80420	80421	80422	80423	80424	80425	80426	80427	80428	80429	80430	80431	80432	80433	80434	80435	80436	80437	80438	80439	80440	80441	80442	80443	80444	80445	80446	80447	80448	80449	80450	80451	80452	80453	80454	80455	80456	80457	80458	80459	80460	80461	80462	80463	80464	80465	80466	80467	80468	80469	80470	80471	80472	80473	80474	80475	80476	80477	80478	80479	80480	80481	80482	80483	80484	80485	80486	80487	80488	80489	80490	80491	80492	80493	80494	80495	80496	80497	80498	80499	80500	80501	80502	80503	80504	80505	80506	80507	80508	80509	80510	80511	80512	80513</td

Table 2 (cont.)

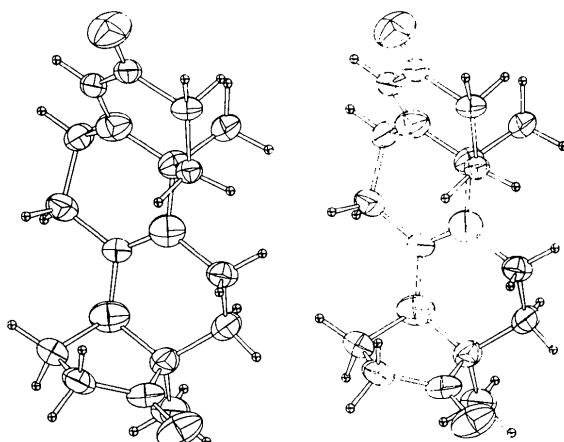


Fig. 1. Stereoscopic view of the molecule.

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

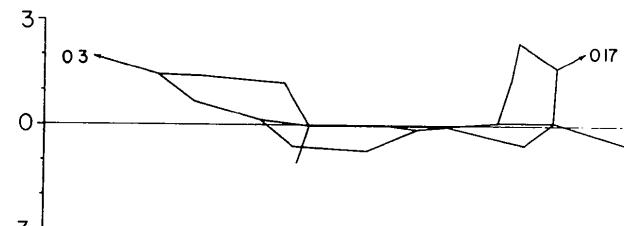


Fig. 2. Side view of the molecule. Ordinate refers to deviation (\AA) of atoms from the plane defined by abscissa.

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

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

(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.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	<i>D1</i>	<i>D2</i>	<i>D3</i>
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.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
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'(C18)	1.02 (3)
C(18)—H''(C18)	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

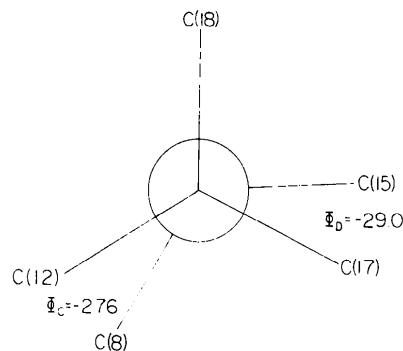


Fig. 3. Newman projection along C(13)-C(14)

Table 5. Valency angles ($^{\circ}$)

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 ($\text{Å} \times 10^3$)

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 3β -*p*-bromo-benzoyloxy-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

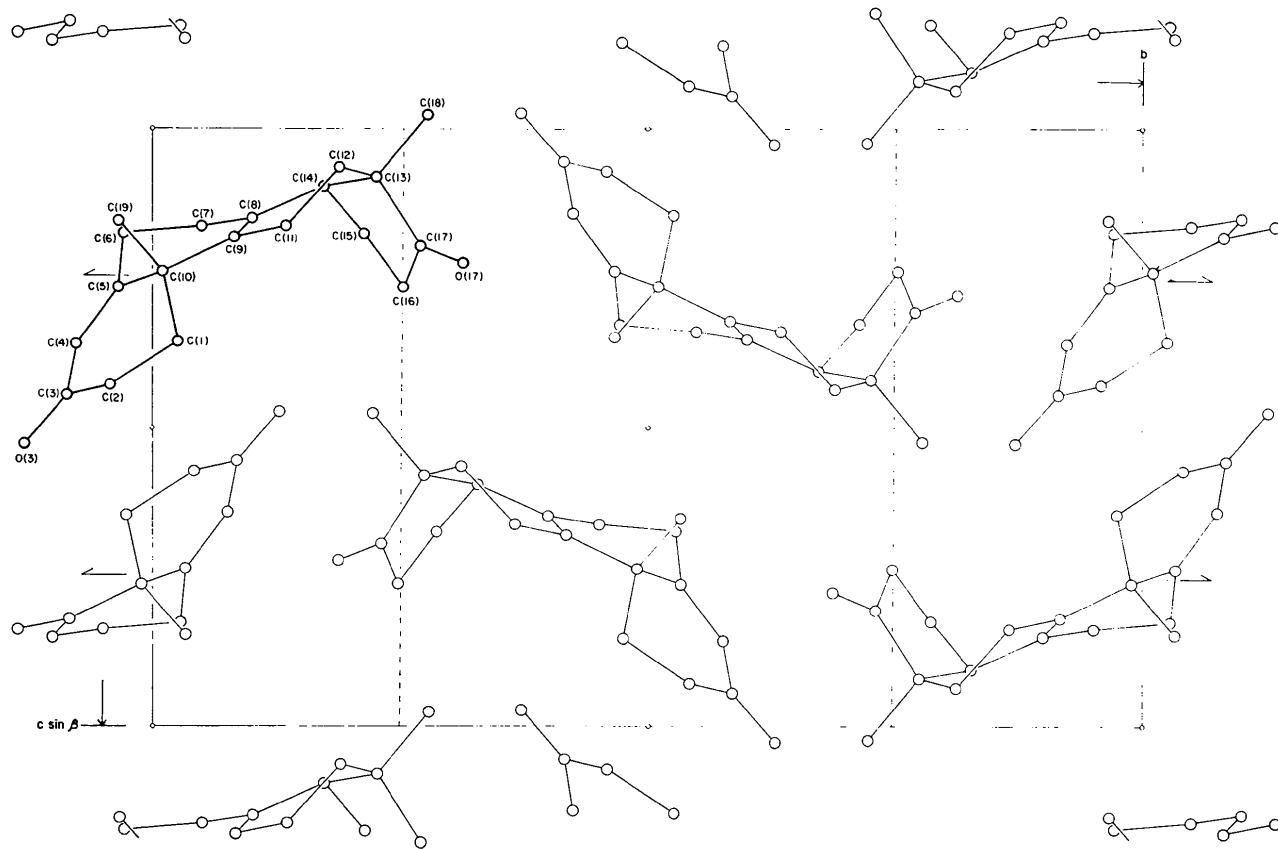


Fig. 4. Projection of one unit cell along the α axis. Hydrogen atoms are omitted.

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 α axis, illustrating the packing of the molecules, is shown in Fig. 4. The distances between neighboring molecules correspond to normal van der Waals contacts.

This research was supported by the U. S. Public Health Service, National Institutes of Health, under Grant No. NS-09178. The computing facilities of the Department of Crystallography and the Computing Center of the University of Pittsburgh were used throughout this research. We gratefully acknowledge the assistance of Professor S. Danishefsky with this research.

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