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CONFORMATIONAL ANALYSIS—CXXIV

THE CONFORMATION OF RING A IN THE 4,4-DIMETHYL-3-ANDROSTANONE SYSTEM. THE CRYSTAL STRUCTURE OF 4,4-DIMETHYLANDROSTAN-3-ON-17β-YL BENZOATE[1]

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Abstract—Molecular mechanics calculations indicate that the deformed chair and twisted-boat conformations are similar in energy for a 4,4-dimethyl-3-keto steroid. Earlier dipole moment work on such compounds is discussed. The crystal structure of 4,4-dimethylandrostan-3-on-17β-yl benzoate has been determined. The crystals are orthorhombic, $P2_12_12_1$, $a = 17.096$ (2), $b = 22.136$ (*e*), $c = 6.217$ (1) Å. The structure was solved by direct methods and refined by least squares to $R = 0.039$, $R_w = 0.038$, based on 2168 observed reflections. Ring A is shown to exist in a chair form, deformed as indicated by the calculations.

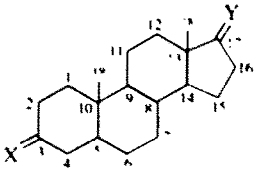
Although the possibility of the existence of a 6-membered ring in a boat or twist form was pointed out as early as 1890 by Sachse,[2] it was not until 1957 that Barton[3] showed that a molecule which was not rigidly constrained to do so, in fact preferentially existed as the boat. The molecule which Barton studied was 2β - bromo-lanost - 8 - en - 3 - one. Subsequently, large numbers of molecules have been shown to have a 6-membered ring preferentially in a conformation other than that of a chair.[4] In all cases except one,[5] however, it has been shown that there are very large steric and/or electrostatic effects which are unfavorable in the chair form, which can be relieved if the molecule adopts a boat or twist conformation.

In the case of Barton's compound, the boat form of ring A here has several factors in its favor. First, serious steric interactions exist between the β substituents at C-2, C-4 and C-10, which are syn-axial on the cyclohexanone ring in the chair form. This repulsion can be largely relieved if the ring goes into the alternative boat-twist conformational continuum. Second, the difference in energy between the chair and boat forms is relatively small for a cyclohexanone ring, compared to a cyclohexane.[6] However, a bromine substituent α to the carbonyl on a cyclohexanone is more stable in the axial than in the equatorial position for electrostatic reasons, which tend in this case to work against the steric effects. Barton clearly showed that the combination of these forces is sufficient in that particular case to give the boat form a greater stability than that of the chair. One might immediately ask which of these interactions are in fact necessary to stabilize the boat form of ring A? 2β - Bromo - 2α - methyl-androstan - 3 - one has ring A in the chair form,[7] so the interaction of the bromine with the 19-methyl alone is insufficient to hold the ring in the boat form, even though it is a cyclohexanone ring. It is noted, however, that an axial bromine would go equatorial as the chair went to a boat. The other compound of interest, 4,4-dimethylandrostan-3-one **2**, which now lacks the bromine, was studied many years ago.[8] It was concluded that the ring was in a flattened chair conformation, on the basis of dipole moment measurements. These dipole moment measurements were interpreted on the basis of the mechanical behavior of Dreiding models, which was the best that could be done at the time. We now know that, although qualitatively very useful, some of the shortcomings of Dreiding models are sufficiently serious that such interpretations are open to considerable question.[9]

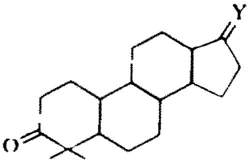
To better determine the structure of a 4,4 - dimethylandrostan - 3 - one system, several alternative procedures are now available. Molecular mechanics calculations, which have been developed to a high degree of reliability, should yield dependable conclusions about such systems.[10] An X-ray crystal structure determination of a suitable compound would yield similar information. The crystal structure of 4,4 - dimethylandrostan - 3 - on - 17β - yl iodoacetate **2e** was published in 1970 as a preliminary communication,[11] and reported that ring A assumed a chair conformation. The presence of the iodine atom, as well as the incomplete refinement (R = 0.14), leaves some question as to the precision of the molecular geometry in this case.

In the present work, molecular mechanics calculations have been carried out on several structures related to the problem. In addition, the crystal structure of the title compound has been solved and is reported here. We will consider the molecular mechanics calculations first.

The structures of androstan-3-one **1b** and androstan-17-one **1c** were first calculated using the 1973 force field.[10,12] These are unexceptional. They can be compared with analogous structures in the literature,[9,11] as studied by X-ray crystallography, and the agreement is very good. The bond lengths can all be regarded as within experimental error of those reported in the literature, while a



1a: X = H_2; Y = H_2
b: X = O; Y = H_2
c: X = H_2; Y = O
d: X = O; Y = O



2a: Y = H_2
b: Y = O
c: Y = HOH
d: Y = HOBz
e: Y = $HOCOCH_2I$

few bond angles differ somewhat. Bond angles not involving hydrogens are in agreement with experiment to perhaps the extent of 90% of the cases, the remainder being perhaps 1° or so beyond the limits of experimental error, and 2 or 3 angles being more seriously in error (by up to 3° or so, when the experimental error is less than 1°). It is uncertain at the present time to what extent these deviations are due to crystal packing forces, and to what extent they are due to imperfections in the force field.

It seemed to us that androstan-3,17-dione **1d** would unquestionably have ring A in a chair conformation, and the dipole moment should be calculable by molecular mechanics. In fact, the calculated value (3.58 D) differs significantly, but not alarmingly, from the experimental values (2.94–3.28 D[14]), by being 0.30–0.64 D too high. There are many reasons why dipole moments cannot in general be very accurately calculated from group moments. These include, for example, the uncertainty of how to deal with atomic polarization, the effect of solvation, and uncertainty in the exact relative orientations of the component dipoles. There are three reported structures of androstan-3,17-dione from X-ray studies.[16] From the relative atomic coordinates obtained by these studies, dipole moments can be calculated and they are 2.59, 2.69 and 3.03 D. Note from the last values that there is a difference of 0.44 D in the dipole moment expected from the molecule due solely to the distortions which occur in one crystal packing compared to another. These values are again lower than the experimental values.[8] An examination of the calculated and experimental structures shows why this is so. Experimentally the molecule is more flat, and there is less z component (perpendicular to the general plane of the ring system) to the dipole moment. The calculated structure is more folded so that the middle bulges up, and the ends (with the dipoles) hang down. The discrepancies between calculated and experimental bond angles are individually small in general (tenths of degrees), but the cumulative effect across the length of the steroid molecule leads to an effect of the size noted.

4,4-Dimethylandrostan-3,17-dione **2b** was then examined. The two stable conformations of ring A, a somewhat distorted chair and a twisted boat, have very similar calculated energies, the chair being more stable by 0.2 kcal/mole. The calculated dipole moments are 3.96 D for the chair and 2.75 D for the boat. Obviously, no possible mixture of these conformations can lead to the experimental value[8] of 2.28 D. As found to be the case with the parent androstane-3,17-dione **1d**, the calculated value is clearly too large. If the same kind of distortion is found in the 4,4-dimethyl ring system as was found with the parent dione **1d**, the experimental value of the dipole moment would be expected to fall in the range 3.3–3.7 D if the chair form predominated. There is no way to judge the magnitude of a similar correction for the boat form. Clearly, though, the experimental value is too low to be attributed to the chair form alone. The best interpretation of the dipole moment data is that the boat conformation is the major contributor to the boat-chair equilibrium. This is consistent with the molecular mechanics calculations, which indicate that the boat and chair are similar in energy. We do not regard this point as firmly established, however.

To further investigate this problem, it seemed desirable to have available a precise crystal structure for a molecule which contains *gem*-dimethyl substitution at C-4. In order to establish bond lengths and angles to the greatest possible precision, we chose to examine a molecule containing only first-row atoms. Accordingly, we looked at 4,4-dimethylandrostan-3-on-17β-ol **2c**. While a suitable crystal was readily available, there proved to be 3 non-equivalent molecules in the unit cell, and it seemed that this might be a rather formidable crystallographic problem. We therefore converted the alcohol to the benzoate **2d**, and found the crystal was much more amenable to an X-ray study. The crystal structure was solved by direct methods, and refined by least-squares. Ring A is clearly seen to be in a deformed chair conformation (Fig. 1). An ORTEP drawing[17] of the molecule from the crystal is shown in Fig. 1. Plots of the calculated **2b** and experimental **2d** structures look to be essentially superimposable in rings A and B.[†] The structural details are in good agreement with the chair conformation predicted by molecular mechanics (Table 1). The bond lengths are seen to be within two esd of the X-ray value with one exception (C-2—C-3). The bond angles are mostly in agreement to within about 1°, but there are two angles which differ by as much as 3°. Thus the agreement for this quite distorted structure is as good

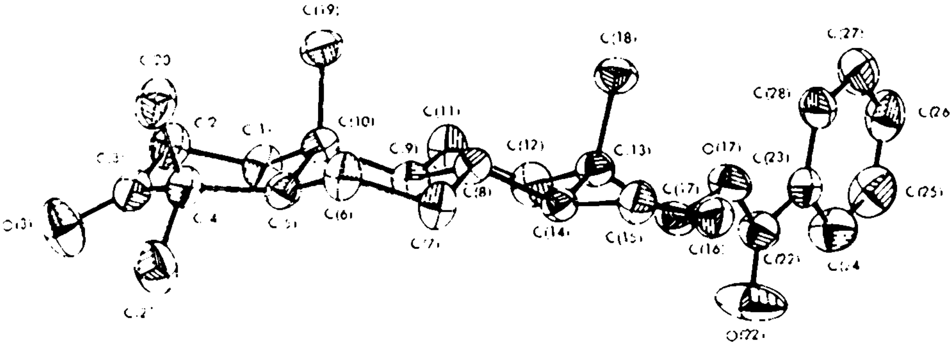


Fig. 1. A perspective drawing of the molecule of 4,4-dimethylandrostan-3-on-17β-yl benzoate, with hydrogen atoms omitted for clarity. The absolute configuration shown corresponds to that accepted for androstane steroids, and is reversed from that implied by the coordinates of Table 2. The thermal ellipsoids are drawn at 40% probability.

[†] It is not possible to carry out the molecular mechanics calculations on the benzoate moiety at this time, so no comparison of that portion of the molecule is possible at present.

Table 1. Comparison of the calculated and experimental structures of ring A for compound 2[†]

Bond lengths	Calcd.	Exper.	Bond angles	Calcd	Exper.	Torsional angles	Calcd.	Exper.
1-2	1.528	1.533(4)	1-2-3	110.8	112.3(2)	1-2-3-4	-50.8	-47.8(3)
2-3	1.509	1.487(4)	2-3-4	117.7	118.1(2)	2-3-4-5	38.1	37.6(3)
3-4	1.528	1.526(4)	3-4-5	110.8	111.3(4)	3-4-5-10	-35.7	-39.2(3)
4-5	1.552	1.566(3)	4-5-10	121.5	118.4(2)	4-5-10-1	43.2	48.7(3)
5-10	1.557	1.552(4)	5-10-1	107.2	107.5(2)	5-10-1-2	-53.4	56.3(3)
10-1	1.546	1.545(4)	10-1-2	113.8	112.6(2)	10-1-2-3	59.2	57.5(3)
3-O	1.210	1.214(4)	3-4-20	107.4	107.0(2)			
4-20	1.539	1.540(4)	3-4-21	106.2	107.8(4)			
4-21	1.555	1.547(4)	5-4-20	114.3	113.7(2)			
10-19	1.544	1.542(4)	5-4-21	111.8	108.8(2)			
			20-4-21	105.9	108.0(2)			
			1-10-19	107.9	108.8(2)			
			5-10-19	113.5	114.0(2)			
			9-10-19	108.7	110.3(2)			

[†] The experimental work refers to **2d**, while the calculations were carried out on **2b**.

as with the relatively strainless steroid case discussed earlier. Such agreement suggests that errors in the force field are probably small, otherwise the strained structure would be expected to show a larger deviation between calculation and experiment. Since the chair and boat conformations are calculated to have such similar energies, packing forces could easily determine the conformation in the crystal, so the finding of a chair form in this case is not in itself compelling evidence that the chair form will be found in general for molecules having this kind of structure in ring A.

Returning to the question of which interactions are necessary to stabilize the boat conformation in Barton's compound, the answer seems to be probably all of them, although just barely. Without the axial halogen at C-2, the chair form approximately equals the boat in stability (present work), and without the axial methyl at C-4, the chair is more stable.[7]

EXPERIMENTAL

The synthesis of 4,4-dimethylandrostan-3-one-17β-ol **2c** has been reported.[18] Hydrogenation of the Δ^5 derivative proved to be very difficult, but was finally achieved using a pre-hydrogenated palladium (10%) on carbon catalyst and the cyclic ethylene ketal of the 3-ketone in dry methanol as solvent. Crystals (m.p. 147° from ethanol) were grown by slow evaporation of an ethanol solution which was seeded. Precession photographs showed the crystals to be monoclinic with the unit cell dimensions a = 18.731, b = 21.781, c = 6.795 Å, β = 92° 15′. The space group was determined as $P2$ from the lack of any systematically absent reflections. Based on the measured density (d_m = 1.151 g/cm^3 by flotation in hexane/CCl_4), Z was found to be 6 (d_c = 1.145 g/cm^3). Therefore, the unit cell contains 3 crystallographically independent molecules, and an X-ray analysis would thus be very difficult, although the possibility that the three molecules might exist in different conformations is very intriguing.

Derivatives of **2c** were prepared in an attempt to find one which crystallized in a more suitable space group. The benzoate **2d** was found to form large tabular crystals, m.p. 213.5° from ethanol. The unit cell dimensions (determined by a least-squares refinement of 15 precisely measured values in the 2θ range 9–40°) were found to be a = 17.096 (2), b = 22.136 (3), c = 6.217 (1) Å. The orthorhombic space group $P2_12_12_1$ was established from systematic absences. Density measurements by flotation in hexane/CCl_4 showed that there was only one molecule in the asymmetric unit (d_m = 1.181, d_c = 1.201 g/cm^3 for Z = 4).

Integrated intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (CuK_α radiation, graphite monochromator, λ = 1.5418 Å) using the ω-2θ scan technique. 2793 reflections were measured, 2168 (77.6%) of which were found to be observed at a 3σ level of significance. The data were corrected for crystal decompositon during data collection, as monitored by 3 standard reflections, and for Lorentz and polarization factors. Normalized structure factors were calculated and the structure was solved by the direct method using MULTAN[19] to determine phases for all reflections for which $|E| \geq 1.3$. The best set of phases (absolute figure of merit = 1.2422) was used to calculate an E-map, from which all carbon and oxygen atoms were located. Full matrix least-squares refinement minimizing $\Sigma(|F_o| - |F_c|)^2$ including only the C and O atoms with anisotropic temperature factors reduced the R value to 0.097. Attempts to locate hydrogen atoms from a ΔF map were unsuccessful. All hydrogen atoms except methyl hydrogens were calculated from the positions of the carbons assuming a bond length of 1.05 Å and bond angles of 109° and 120° for tetrahedral and trigonal carbons, respectively. After least-squares refinement varying all positional and anisotropic thermal parameters for C and O, and only positional parameters for H, a ΔF map showed the remainder of the hydrogen atoms.

The refinement was then continued minimizing $\Sigma w(|F_o| - |F_c|)^2$ with $w^2 = 1/(1 + ((F_o - 17.0)/11.5))^2$, thus giving both very small and very large structure amplitudes a reduced weight. Individual isotropic temperature factors were assigned to each of the hydrogen atoms, and a correction for isotropic extinction was included in the last 2 cycles of least-squares refinement. The final agreement residuals are R = 0.039 and R_w = 0.038, based on the observed reflections only.[†] The difference electron density map based on the final atomic parameters showed no maxima greater than 0.22 e/Å^3. In the final cycle of refinement, the average parameter shift was 0.5 × the esd. The final atomic positional and thermal parameters are listed in Table 2. The numbering scheme is shown in Fig. 1.

The refinement was carried out using the programs of the

[†] A table of calculated and observed structure factors is available from the authors.

Table 2. Positional coordinates and thermal parameters for **2c**. The anisotropic temperature factor is of the form $\exp[2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	1886(2)	2288(1)	8474(4)	59(2)	52(1)	49(2)	5(1)	-7(1)	-12(1)
C(2)	1130(2)	2634(1)	7979(5)	65(2)	52(2)	60(2)	10(1)	-3(2)	-14(2)
C(3)	0476(2)	2225(1)	7386(5)	58(2)	55(2)	51(2)	13(1)	-2(1)	-1(1)
C(4)	0633(1)	1732(1)	5727(4)	44(1)	50(1)	50(1)	7(1)	-7(1)	-3(1)
C(5)	1472(1)	1457(1)	6006(4)	41(1)	39(1)	44(1)	1(1)	-5(1)	-1(1)
C(6)	1700(1)	1034(1)	4164(4)	44(1)	49(1)	59(2)	3(1)	-12(1)	-15(1)
C(7)	2410(1)	0654(1)	4783(5)	45(1)	42(1)	69(2)	2(1)	-12(1)	-15(1)
C(8)	3102(1)	1034(1)	5530(4)	42(1)	40(1)	43(1)	-3(1)	-5(1)	-1(1)
C(9)	2849(1)	1483(1)	7306(4)	44(1)	45(1)	41(1)	-5(1)	-5(1)	-1(1)
C(10)	2156(1)	1890(1)	6575(4)	47(1)	36(1)	38(1)	-2(1)	-3(1)	-2(1)
C(11)	3551(1)	1832(1)	8235(5)	49(1)	56(2)	67(2)	-5(1)	-13(2)	-19(2)
C(12)	4210(2)	1413(1)	8990(5)	50(1)	70(2)	58(2)	-7(1)	-16(1)	-9(2)
C(13)	4475(1)	0990(1)	7185(4)	39(1)	51(1)	49(1)	-8(1)	-5(1)	5(1)
C(14)	3763(1)	0634(1)	6400(4)	38(1)	43(1)	48(1)	-5(1)	-3(1)	5(1)
C(15)	4111(1)	0136(1)	4985(5)	49(1)	49(1)	65(2)	3(1)	-2(1)	-4(1)
C(16)	4916(1)	-0003(1)	6063(5)	46(1)	53(1)	75(2)	2(1)	0(1)	10(2)
C(17)	4988(1)	0461(1)	7873(5)	35(1)	68(2)	58(2)	-8(1)	0(1)	18(1)
C(18)	4881(2)	1341(1)	5377(5)	52(2)	57(2)	67(2)	-10(1)	1(1)	15(2)
C(19)	2411(2)	2302(1)	4704(5)	60(2)	51(1)	59(2)	-3(1)	-3(2)	13(1)
C(20)	0490(2)	2013(1)	3495(5)	63(2)	82(2)	54(2)	21(2)	-12(2)	-2(2)
C(21)	0022(2)	1226(1)	6071(6)	49(2)	72(2)	101(3)	-3(1)	2(2)	-13(2)
C(22)	6144(2)	0497(1)	10020(5)	54(2)	66(2)	52(2)	-2(1)	-5(1)	5(2)
C(23)	6934(1)	0764(1)	10237(5)	44(1)	57(2)	58(2)	7(1)	-3(1)	-2(1)
C(24)	7342(2)	0658(2)	12143(6)	69(2)	92(2)	73(2)	-7(2)	-21(2)	12(2)
C(25)	8080(2)	0909(2)	12390(6)	68(2)	104(3)	98(3)	2(2)	-37(2)	2(2)
C(26)	8410(2)	1258(2)	10836(7)	47(2)	84(2)	124(3)	3(2)	-15(2)	-8(2)
C(27)	8009(2)	1367(2)	8966(7)	47(2)	84(2)	102(3)	-2(2)	0(2)	7(2)
C(28)	7271(1)	1117(1)	8664(5)	42(1)	76(2)	72(2)	3(1)	-2(2)	5(2)
O(3)	-0170(1)	2288(1)	8168(4)	66(1)	95(2)	102(2)	10(1)	21(1)	-30(2)
O(17)	5792(1)	0650(1)	8211(3)	36(1)	92(1)	60(1)	-8(1)	-7(1)	25(1)
O(22)	5855(1)	0161(1)	11305(4)	90(2)	169(3)	81(2)	-58(2)	-30(1)	63(2)
H(1A)	1820(13)	2015(10)	9699(40)	60(7)					
H(1B)	2316(14)	2597(11)	8780(43)	71(8)					
H(2A)	0967(15)	2884(11)	9274(46)	77(9)					
H(2B)	1236(14)	2946(11)	6871(42)	66(8)					
H(5)	1419(13)	1171(10)	7368(40)	49(7)					
H(6A)	1258(13)	0766(10)	3889(39)	51(7)					
H(6B)	1819(15)	1273(10)	2856(42)	61(8)					
H(7A)	2263(15)	0385(12)	5992(46)	76(9)					
H(7B)	2583(15)	0396(11)	3598(44)	71(8)					
H(8)	3328(13)	1276(10)	4282(39)	48(7)					
H(9)	2634(13)	1221(9)	8475(39)	47(7)					
H(11A)	3772(14)	2130(11)	7061(45)	71(8)					
H(11B)	3379(15)	2116(11)	9538(46)	78(9)					
H(12A)	4613(15)	1673(11)	9631(45)	66(8)					
H(12B)	4016(16)	1120(13)	10195(49)	85(9)					
H(14)	3565(13)	0445(10)	7611(39)	51(7)					
H(15A)	3744(14)	-0257(11)	4972(42)	67(8)					
H(15B)	4224(14)	0270(11)	3437(42)	65(8)					
H(16A)	4971(13)	-0464(10)	6609(41)	58(7)					
H(16B)	5379(13)	0044(10)	5000(40)	56(7)					
H(17)	4827(14)	0280(10)	9142(42)	62(8)					
H(18A)	5096(15)	1074(12)	4252(50)	84(9)					
H(18B)	4556(18)	1684(13)	4829(54)	95(10)					
H(18C)	5317(17)	1556(12)	5937(52)	84(9)					
H(19A)	2657(16)	2084(13)	3479(50)	85(9)					
H(19B)	2849(17)	2548(14)	5190(52)	87(9)					

Table 2 (*Contd.*)

Atom	x	y	z	U
H(19C)	1981(17)	2531(13)	4163(48)	96(10)
H(20A)	-0076(16)	2118(13)	3490(48)	82(9)
H(20B)	0524(15)	1699(12)	2378(46)	73(8)
H(20C)	0866(14)	2336(11)	3211(43)	64(8)
H(21A)	-0505(16)	1434(12)	5977(47)	76(9)
H(21B)	0098(17)	0868(13)	5076(53)	96(10)
H(21C)	0070(17)	1078(13)	7546(51)	90(9)
H(24)	7098(14)	0426(12)	13217(44)	74(8)
H(25)	8357(18)	0826(13)	13623(52)	106(11)
H(26)	8956(15)	1449(11)	10998(46)	75(9)
H(27)	8293(18)	1661(13)	7946(50)	95(10)
H(28)	6957(17)	1215(12)	7309(49)	92(10)

X-ray System.[20] The atomic scattering factors for C and O were calculated using analytic approximations to numerical Hartree-Fock wave functions,[21] and the values of Stewart, Davidson and Simpson were used for H.[22]

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