

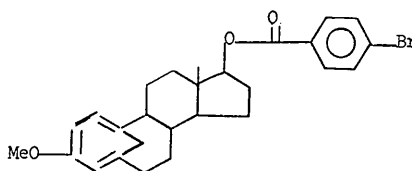
The Structure of 3-Methoxy-5 β ,19-cyclo-5,10-secoandrosta-1(10),2,4-trien-17 β -ol *p*-Bromobenzoate

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(Received 9 June 1967)

The structure of 3-methoxy-5 β ,19-cyclo-5,10-secoandrosta-1(10),2,4-trien-17 β -ol *p*-bromobenzoate has been determined by three-dimensional Fourier and least-squares methods using intensity data collected with an automatic diffractometer. The substance crystallizes in the orthorhombic system, space group $P2_12_12_1$, $a = 37.220$ ($\sigma \sim 0.008$), $b = 10.086$ ($\sigma \sim 0.020$), $c = 6.419$ ($\sigma \sim 0.013$) Å, with four molecules in the unit cell. The structure corresponds to the formula



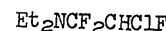
The *A* ring is a 'tub', the *D* ring is nearly a β -envelope. The molecules are held together in chains by $\text{Br} \cdots \text{O}(\text{methoxy})$ links of 2.93 Å. R for 1870 observed reflections is 0.050.

Introduction

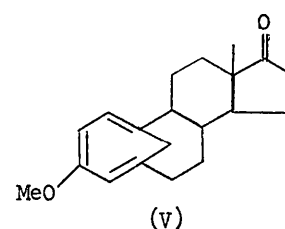
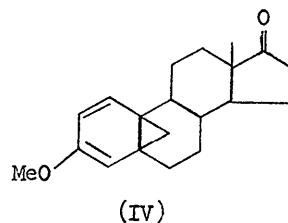
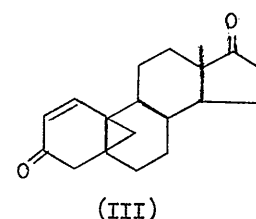
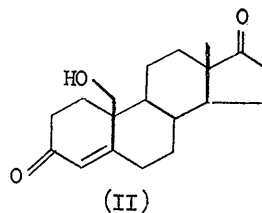
Reactions of steroidal alcohols with diethyl-(2-chloro-1,1,2-trifluoroethyl)amine (I) were studied by Knox and co-workers (Knox, Velarde, Berger, Cuadriello & Cross, 1962; Knox, Velarde & Cross, 1963). It was reported that 19-hydroxyandrost-4-ene-3,17-dione (II) reacted with the amine (I) to yield a mixture of 5 β ,19-cycloandrost-1-ene-3,17-dione (III) and a fluoro derivative (Knox *et al.*, 1963). Treatment of (III) with methanol-toluene-*p*-sulfonic acid gave a 3-enol methyl ether. Although molecular models suggested that the norcaradiene form (IV) might be less strained than the cycloheptatriene form (V) the nuclear magnetic resonance spectra obtained indicated that (V) was the only form present in solution.

Since it appeared to be of interest both to confirm the molecular structure of the solid and to investigate the geometry of the unusual bicyclo[4.4.1]undeca-1,3,5-triene configuration it was decided to carry out a crystal structure determination of a suitable derivative of (V).

Crystals of the compound 3-methoxy-5 β ,19-cyclo-5,10-secoandrosta-1(10),2,4-trien-17 β -ol *p*-bromobenzoate (Fig. 1), prepared by H. Hanni, had properties such as chemical stability, a heavy atom in the molecule and a reasonable space group, which made it seem well suited for an X-ray study.



(I)



Experimental

Preliminary examination of crystals of 3-methoxy-5 β ,19-cyclo-5(10)-secoandrosta-1(10),2,4-trien-17 β -ol *p*-bromobenzoate by precession methods indicated orthorhombic symmetry. The systematically absent reflections were $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd, uniquely determining the space group to be $P2_12_12_1$.

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Cell dimensions were obtained from angles measured on a Picker diffractometer with a full-circle goniostat. A least-squares procedure was used to adjust cell dimensions and crystal orientation parameters to measured χ , ϕ , 2θ values. During our first attempts to measure the cell dimensions we were unable to obtain consistent results. We therefore remeasured some angles, whereby we detected discrepancies of such magnitude that we were led to the conclusion that they were caused by actual changes in cell dimensions resulting from X-ray exposure. The observed 2θ values (Cu $K\alpha_1$) for (44,00) serve to illustrate the effect. Our first measurement gave $2\theta = 130.73^\circ$ while measurement after about 150 hours exposure gave $2\theta = 131.16^\circ$.

The dimensions given here were obtained from measurements after a fairly stable state appeared to have been attained (about 150 hours exposure). They are (e.s.d. in parentheses):

$$a = 37.220 (0.008), b = 10.086 (0.020), c = 6.419 (0.013) \text{ \AA} \\ (\lambda \text{ Cu } K\alpha_1 = 1.54051 \text{ \AA}).$$

The intensity data were collected with a Picker automatic diffractometer using Ni filtered Cu $K\alpha$ radiation with a NaI(Tl) scintillation detector and pulse height discrimination.

A total of 2865 unique reflections with $\sin \theta/\lambda$ below 0.64 \AA^{-1} was scanned by use of the 2θ - θ technique at a scan speed of 2° min^{-1} , with the scan range given by $(2\theta(\alpha_1) - 1^\circ) - (2\theta(\alpha_2) + 1^\circ)$. Background counts were taken at both ends of the scan range. To keep counting losses low the automatic attenuator mechanism was set to add an attenuation filter when the count rate exceeded 10000 cps.

An estimated standard deviation for a recorded number of counts was obtained from the expression $s(N) = N^{1/2} + 0.005N$, the second term being intended to account for variations due to electronic instability. From the $s(N)$ for scan and background counts the e.s.d. for the net intensity was derived. Altogether 1870 reflections for which the net intensity exceeded three times its e.s.d. were recorded as observed; other reflections were not included in subsequent calculations. The intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption correction was applied.

Solution and refinement of the structure

The solution of the structure followed a straightforward application of the heavy atom method. The position of the Br atom was determined from a sharpened Patterson function, computed with the coefficients $F_0^2/(\sum f_j)^2$ (Patterson, 1935). A subsequent Fourier synthesis based on the phase angles due to the Br atom clearly revealed the positions of all C and O atoms in the structure, with exception of the methoxy C. Very few false maxima appeared, and they were easily identified as such by assuming that the molecule conformed with usual concepts of the structure of organic molecules. The methoxy C atom was located from a Fourier synthesis with phases determined by the atomic positions already found.

The positional parameters thus obtained, together with isotropic temperature factors, initially set to 4 \AA^2 , were used as starting parameters for two cycles of least-squares refinement, at the end of which the R index was about 0.15. At this stage anisotropic temperature factors were introduced. Owing to limitations of the computer a maximum of 163 parameters could be refined at a time. The atoms were divided into two groups of 18 and 13 atoms (atoms 1-17 and 19, and 18 and 20-31 respectively) and the refinement was carried out by adjusting the parameters of one group at a time alternately. A total of six cycles was calculated this way. In the last few cycles the H atoms (except those on the methyl groups) were included in the structure factor calculations, but none of their parameters was refined. The H positions were calculated from the C positions, assuming a C-H distance of 1.08 \AA , and all H atoms were assigned a temperature factor $B = 4.5 \text{ \AA}^2$.

A total difference Fourier synthesis calculated during the course of refinement indicated that no gross features of the structure had been overlooked. The R index at the end of the refinement was 0.050 for all observed reflections. The shifts in the last least-squares cycle were all well below 10% of the corresponding e.s.d.

The final positional parameters (with their e.s.d.) are given in Table 1, the thermal parameters in Table 2, and the assumed hydrogen positions in Table 3. Structure factors and phase angles calculated from the final

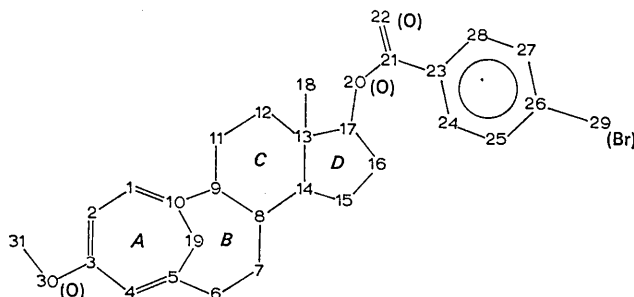


Fig. 1. Conventional structure formula with indication of the numbering system adopted. All unlabeled atoms are C.

parameters are listed in Table 4 together with the observed structure factors.

Table 1. *Final positional parameters and their standard deviations*

The e.s.d. (in parentheses) apply to the least significant digits.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.65097 (18)	0.2014 (9)	0.4018 (14)
C(2)	0.68682 (18)	0.1679 (9)	0.3353 (13)
C(3)	0.71709 (16)	0.2246 (9)	0.4138 (15)
C(4)	0.71688 (16)	0.3221 (10)	0.5843 (16)
C(5)	0.69237 (17)	0.3198 (10)	0.7383 (14)
C(6)	0.68334 (20)	0.4376 (9)	0.8720 (16)
C(7)	0.64559 (18)	0.4957 (8)	0.8194 (17)
C(8)	0.61378 (16)	0.3994 (7)	0.8503 (13)
C(9)	0.60789 (16)	0.3077 (8)	0.6606 (12)
C(10)	0.64174 (17)	0.2320 (7)	0.6013 (13)
C(11)	0.57531 (18)	0.2131 (7)	0.6987 (12)
C(12)	0.54142 (17)	0.2883 (7)	0.7416 (13)
C(13)	0.54624 (15)	0.3819 (6)	0.9279 (12)
C(14)	0.57814 (16)	0.4735 (7)	0.8858 (14)
C(15)	0.57537 (19)	0.5767 (8)	1.0532 (18)
C(16)	0.53485 (19)	0.5939 (7)	1.0884 (17)
C(17)	0.51740 (16)	0.4882 (7)	0.9542 (13)
C(18)	0.55000 (20)	0.3033 (8)	1.1329 (12)
C(19)	0.66845 (20)	0.2026 (9)	0.7657 (13)
O(20)	0.48471 (11)	0.4467 (5)	1.0598 (9)
C(21)	0.45758 (16)	0.4006 (7)	0.9438 (14)
O(22)	0.45981 (13)	0.3803 (6)	0.7593 (9)
C(23)	0.42459 (16)	0.3808 (7)	1.0680 (14)
C(24)	0.42109 (18)	0.4253 (7)	1.2741 (13)

Table 1 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>
C(25)	0.38860 (19)	0.4111 (7)	1.3771 (13)
C(26)	0.36049 (17)	0.3468 (7)	1.2792 (14)
C(27)	0.36329 (18)	0.2996 (8)	1.0835 (15)
C(28)	0.39535 (19)	0.3185 (9)	0.9724 (13)
Br(29)	0.31682 (2)	0.3205 (1)	1.4250 (2)
O(30)	0.75044 (12)	0.2071 (6)	0.3322 (10)
C(31)	0.75386 (21)	0.1284 (11)	0.1472 (16)

Computing procedures

The least-squares routine for calculation of cell dimensions and crystal orientation was written by A.T. Christensen. The program seeks a best fit of \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* , and their directional cosines (relative to a diffractometer coordinate system) to measured angular coordinates.

The diffractometer setting program was a revised version (H.Hope) of the program written by Prewitt (1965); the revisions include a change to full circle geometry and a sorting procedure to optimize the setting sequence for high angle reflections. The Lp program and a number of other small programs (H positions, distance-angle, *etc.*) were written by H.Hope.

The structure factors and all Fourier summations were calculated by use of programs written by K.N. Trueblood, P.K. Gantzel and H.Hope. The least-

Table 2. *Final thermal parameters (\AA^2) and their standard deviations*

The relation between the B 's given below and the β 's in the anisotropic temperature factor expression is given by

$$B_{11} = 4a^2\beta_{11}, B_{12} = 2ab\beta_{12} \text{ etc.}$$

The e.s.d. (in parentheses) apply to the least significant digits.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3.65 (25)	6.92 (45)	6.03 (45)	0.32 (29)	-0.44 (30)	-1.75 (44)
C(2)	4.22 (29)	7.19 (42)	5.37 (36)	1.04 (34)	-0.41 (29)	-1.08 (38)
C(3)	3.06 (25)	8.33 (51)	6.26 (44)	1.04 (28)	-0.37 (32)	0.17 (50)
C(4)	3.27 (25)	8.00 (47)	7.69 (50)	0.65 (32)	-0.76 (34)	-2.59 (58)
C(5)	3.94 (28)	7.74 (46)	6.59 (44)	0.32 (34)	-1.25 (31)	-2.14 (47)
C(6)	4.03 (28)	7.96 (47)	8.68 (61)	-0.52 (35)	-0.85 (41)	-2.77 (47)
C(7)	3.93 (28)	5.56 (39)	10.10 (67)	-0.99 (28)	0.55 (38)	-1.48 (46)
C(8)	3.47 (25)	4.53 (32)	6.08 (42)	-0.31 (24)	-0.30 (28)	0.13 (33)
C(9)	3.97 (25)	4.99 (33)	4.90 (34)	0.91 (27)	-0.39 (25)	-0.28 (33)
C(10)	3.72 (25)	4.70 (32)	5.28 (41)	-0.02 (23)	-0.30 (28)	0.07 (34)
C(11)	4.39 (27)	4.46 (34)	5.02 (37)	-0.47 (24)	-0.14 (27)	-0.91 (31)
C(12)	3.88 (25)	4.42 (33)	5.58 (39)	-0.15 (24)	0.15 (28)	-0.76 (33)
C(13)	3.43 (22)	3.74 (25)	4.45 (32)	-0.15 (20)	-0.41 (27)	0.21 (32)
C(14)	3.93 (25)	3.64 (28)	6.27 (46)	0.09 (22)	-0.10 (30)	-0.29 (32)
C(15)	4.45 (30)	5.67 (39)	9.20 (60)	-0.47 (28)	0.23 (40)	-1.27 (50)
C(16)	4.87 (31)	4.95 (34)	7.69 (52)	0.39 (27)	0.65 (39)	-1.48 (45)
C(17)	3.59 (24)	4.53 (30)	5.36 (40)	0.16 (23)	0.19 (29)	-0.22 (35)
C(18)	4.87 (22)	6.25 (37)	4.97 (37)	0.07 (31)	-0.01 (29)	1.29 (36)
C(19)	5.02 (31)	6.88 (48)	4.97 (38)	1.05 (35)	-0.57 (32)	0.41 (40)
O(20)	3.78 (17)	6.10 (23)	5.27 (23)	-0.07 (17)	-0.37 (22)	-0.50 (27)
C(21)	3.59 (22)	5.51 (32)	5.68 (37)	0.78 (25)	-0.61 (30)	0.06 (40)
O(22)	5.05 (22)	9.86 (33)	5.03 (27)	-0.12 (24)	-0.01 (22)	-0.96 (30)
C(23)	3.58 (22)	4.57 (28)	5.77 (37)	0.51 (23)	-0.23 (31)	-0.38 (38)
C(24)	4.24 (28)	4.67 (32)	5.28 (37)	0.28 (26)	0.01 (30)	-0.20 (35)
C(25)	5.15 (28)	4.61 (32)	5.77 (43)	0.08 (28)	0.70 (32)	0.36 (35)
C(26)	3.92 (22)	4.46 (32)	7.27 (44)	0.64 (24)	0.52 (31)	1.31 (36)
C(27)	3.82 (22)	7.01 (39)	7.30 (42)	-0.23 (29)	-0.52 (34)	-1.40 (47)
C(28)	3.99 (28)	7.69 (39)	5.54 (40)	0.20 (33)	-0.61 (28)	-0.08 (43)
Br(29)	4.61 (6)	7.00 (4)	9.92 (5)	0.32 (4)	1.52 (4)	1.67 (5)
O(30)	3.66 (17)	10.15 (35)	7.77 (32)	0.88 (23)	-0.17 (22)	-1.72 (32)
C(31)	4.89 (33)	12.30 (54)	6.54 (48)	1.60 (38)	0.79 (36)	-0.75 (49)

squares refinement was carried out with a program which is essentially the same as ACA computer program 317, by P.K. Gantzel, R.A. Sparks and K.N. Trueblood. This program minimizes the weighted sum of the squares of $(K \cdot F_o - G \cdot |F_c|)$ by a full-matrix routine. The scale factor G is one of the adjustable parameters. The weighting scheme used was that of Hughes (1941), with $4F_o(\text{min}) = 18$.

The atomic form factors were those given by Hanson, Herman, Lea & Skillman (1964). The isotropic temperature factors are of the form $\exp(-B \sin^2\theta/\lambda^2)$, the anisotropic of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. The R index is defined by $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, including observed reflections only. The standard deviations were estimated from the diagonal elements of the inverse matrix of the normal equations.

Analysis of the thermal motion and some of the molecular geometry calculations were done with a set of programs written by K.N. Trueblood.

The structure

Projections of the structure along c and b are shown in Fig. 2(a) and (b) respectively. The heavily outlined

molecule corresponds to the positional parameters given in Table 1.

Table 3. Assumed hydrogen positions

Hydrogen at	x	y	z
C(1)	0.6300	0.2022	0.2851
C(2)	0.6898	0.0930	0.2157
C(4)	0.7371	0.3986	0.5860
C(6)	0.7032	0.5138	0.8470
	0.6836	0.4073	1.0336
C(7)	0.6457	0.5264	0.6579
	0.6412	0.5810	0.9182
C(8)	0.6209	0.3416	0.9860
C(9)	0.6015	0.3697	0.5282
C(11)	0.5811	0.1501	0.8309
	0.5714	0.1523	0.5615
C(12)	0.5201	0.2185	0.7756
	0.5343	0.3459	0.6054
C(14)	0.5776	0.5235	0.7367
C(15)	0.5873	0.6689	1.0026
	0.5883	0.5431	1.1943
C(16)	0.5262	0.6918	1.0403
	0.5282	0.5790	1.2508
C(17)	0.5089	0.5184	0.8002
C(19)	0.6564	0.2001	0.9190
	0.6823	0.1102	0.7370
C(24)	0.4436	0.4704	1.3526
C(25)	0.3852	0.4501	1.5329
C(27)	0.3410	0.2477	1.0124
C(28)	0.3974	0.2849	0.8128

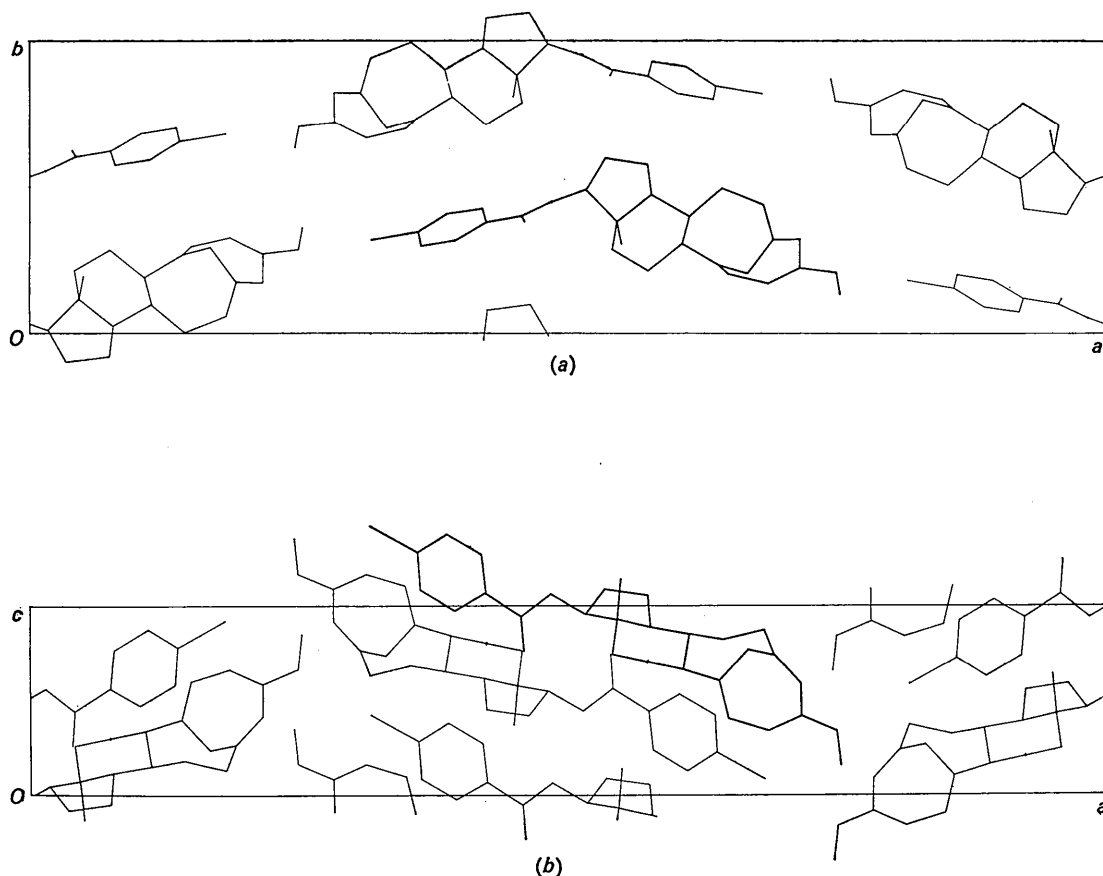


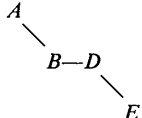
Fig. 2. (a) Projection of the structure along the c axis. (b) Projection of the structure along the b axis. The heavily outlined molecule corresponds to the positional parameters given in Table 1. For identification of the atoms compare with Fig. 1.

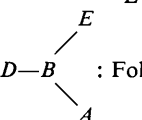
Table 4. Observed and calculated structure factors

The data are separated into groups having common k and l. The four columns in each group list h, 10F_o, 10F_c and the phase alpha (degrees).

Table with multiple columns containing numerical data for structure factors and phases, organized into groups by k and l values. The table includes observed (F_o) and calculated (F_c) values along with phase angles in degrees.

Table 7. *Torsion and fold angles*

Torsion angle (T):  : View along $B-D$, angle is rotation of $A-B$ to cover $D-E$, positive clockwise.

Fold angle (F):  : Fold along $D-B$, angle is positive for B below ADE when viewed as in diagram.

A	B	D	E	Angle	A	B	D	E	Angle
2	1	10	19	$-12.9^\circ T$	12	13	14	8	$-59.3^\circ T$
10	1	2	3	$-36.5 T$	12	13	14	15	$168.5 T$
30	3	2	4	$-9.4 F$	12	13	14	17	$59.1 F$
2	3	4	5	$32.3 T$	8	14	13	15	$47.8 F$
3	4	1	5	$29.2 F$	8	14	13	17	$179.9 T$
3	4	4	19	$11.8 T$	13	14	17	15	$47.7 F$
4	5	10	6	$-42.9 F$	14	15	16	17	$5.9 T$
4	5	10	19	$63.5 F$	13	17	14	16	$-43.8 F$
19	5	6	7	$-63.6 T$	17	20	21	22	$7.0 T$
7	8	9	10	$54.5 T$	22	21	23	24	$169.4 T$
19	10	9	8	$27.6 T$					

Table 8. *Least-squares planes*

The normal equations are given. Deviations are in Å. Planes are defined by atoms listed before slash (/).

- $11.4355x - 9.1594y + 1.8258z = 6.3240$.
Deviations: 1, 0.009; 4, -0.009; 5, 0.012; 10, -0.012.
- $1.6967x - 7.4013y + 4.3509z = 1.3685$.
Deviations: 1, -0.006; 2, 0.013; 3, -0.013; 4, 0.006.
- $5.2913x - 8.1672x + 3.6542z = 3.4833$.
Deviations: 2, 0.005; 3, -0.011; 30, 0.010; 31, -0.005.
- $3.8911x + 5.9772y - 5.1266z = 0.8109$.
Deviations: 5, 0.010; 6, -0.007; 9, 0.007; 10, -0.010/
7, 0.463; 8, -0.396.
- $12.0074x - 8.8831y + 2.2258z = 4.0960$.
Deviations: 23, -0.003; 24, 0.018; 25, -0.017; 26, -0.001;
27, 0.016; 28, -0.014/ 17, -0.096; 20, 0.115; 21, -0.060;
22, -0.263; 29, 0.033.

Treating the steroid skeleton as a rigid body an analysis of its thermal motion was carried out (Schomaker & Trueblood, 1968). Its translational motion was indicated to be fairly isotropic, the r.m.s. amplitude varying between 0.21 Å and 0.26 Å. The libration was much more anisotropic with the largest r.m.s. amplitude ($\sim 6^\circ$) about the long axis of the molecule, and the two other principal axes of libration being about 1° or 2° .

It should be noted, however, that the rigid body model does not seem to be quite satisfactory; the r.m.s. difference between 'observed' and 'calculated' amplitude parameters was 0.005 Å². We also find it appropriate to point out that while all the B_{11} have values within the commonly encountered range of 3–5 Å², some of the B_{22} and B_{33} are quite large. In particular, atoms 7, 15, 22, 29, 30, and 31 show a somewhat unusual behavior. We have not investigated this aspect further, but it appears tempting to link it to the irregularities experienced in connection with the determination of the cell dimensions, assuming that a slight change in molecular packing takes place. It is also possible, e.g. for C(31), that a slight degree of disorder manifests itself in this manner.

Based on the rigid body model corrected distances and angles were computed (Cruickshank, 1961), but most changes were small, the largest being 0.008 Å and with the e.s.d. of the interatomic distances in mind, we did not find it justified to give a full listing of the results.

From the observed distances and angles it is clear that the structure is in agreement with the already assigned bicyclo[4.4.1]undecatriene structure represented by Fig. 1.

Although the overall shape of the A ring is quite similar to that of the rings in bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene as observed in its 2-carboxylic acid (Dobler & Dunitz, 1965) there is no indication of the delocalization of single and double bonds displayed by that compound. The three double bonds have the same length, within our limits of error (average 1.355 Å, corrected 1.360 Å), also the single bonds 1–2 and 3–4, (1.441 and 1.471 Å respectively) may not be different. The single and double bond distances are about the same as in cyclooctatetraene where they are 1.476 and 1.340 Å (Trætterberg, 1966), the indicated differences between corresponding distances in the two compounds possibly being real.

The conformation of the A ring may be described as that of a 'tub' with the coplanar atoms 1,4,5,10 (plane no. 1) making up the 'bottom'. Other planes in this region are defined by atoms 1,2,3,4, (plane no. 2) and atoms 2,3,30,31 (plane no. 3). One might think that planes no. 2 and 3 would be little different, but this does not turn out to be the case. The angles between the various planes are shown in Fig. 4, where it is seen that the angle between planes 2 and 3 is 170.6° . This highly significant deviation from planarity at the 2–3 double bond deserves some comment. It seems that the following qualitative argument can be applied. The apparent torsion angle at the 4–5 double bond is 12° , and since the double bond offers strong resistance to twisting the strain is transferred to the 3–4 single bond,

resulting in this bond being bent up and outwards (with reference to Fig. 4). A similar situation exists on the opposite side of the ring, and if atoms 2 and 3 are to retain a planar hybridization this can only be achieved by moving O(30) and the hydrogen at 2 downwards. However, since it would involve the precise location of a H atom, no attempt was made to confirm the effect in the latter case.

Both the average C–C distance in the 5–19–10 bridge (1.485 Å, corrected 1.492 Å) and the angle 5–19–10 (99.1°) correspond closely to those in bicyclo[4.4.1]undecapentaene (Dobler & Dunitz, 1965) (1.477 Å and 99.5° respectively). The distance 5–10 is 2.26 Å, a rather close contact for nonbonded atoms but still much too long for a norcaradiene structure. We note that the atoms 5 and 10 are displaced about 0.05 Å towards the 'outside' of the planes defined by 4,6,19 and 1,9,19 respectively.

An impression of the general shape of the B ring may be obtained from Fig. 4. The atoms 5,6,9 and 10 are coplanar, while 7 and 8 are displaced in opposite directions from this plane, about 0.46 Å and 0.39 Å respectively. The angles at 6,7,8 and 9 are somewhat larger (average 113.1°) than is usual in unstrained ring compounds. This seems reasonable, since the 5–10 bond has been replaced by a bridge, thereby spreading out the ring.

Considering the estimated standard deviations, the regular C–C single bond distances within the B and C rings appear to be about normal. The average C–C–C angle in the C ring is 110.5°, but the angles 9–8–14 (106.6°) and 8–14–13 (113.7°) deviate significantly from the average. The overall flattening of the ring is in agreement with observations both in simple six-membered rings *e.g.* cyclohexane, dioxane and piperazine (Davis & Hassel, 1963) and in steroid skeletons, *e.g.* androsterone (High & Kraut, 1966) or cholestanes (Geise & Romers, 1966); in these steroids the 9–8–14 angle is also less than, and the 8–14–13 angle is greater than the average.

The largest deviations from the tetrahedral angle are found around the D ring, the largest angle being 8–14–15 (120.2°) and the smallest 14–13–17 (98.1°). The other external angle, 12–13–17, is also large (115.9°) while the remaining four inside angles are about 104–105°. This pattern seems to be the normal in such compounds; in androsterone the corresponding angles have essentially the same values that we find, and there is also a good correlation with the cholestanes.

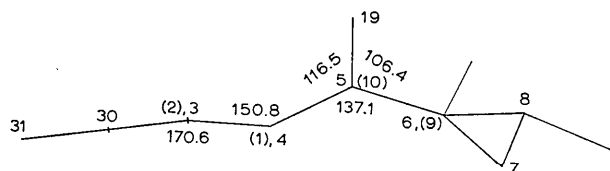


Fig. 4. Angles between planar portions of the A and B rings. The drawing represents a projection along the vector C(1)–C(4).

The torsion angle 14–15–16–17 is 6°, indicating that the D ring is a slightly distorted β -envelope, using the terminology of Brutcher & Leopold (1966). The fold angle about 14–17 (the angle between the 'flap' and the 'body' of the envelope) is near 45°. Another point of interest in connection with the conformation of the D ring is the observation that the torsion angle 8–14–13–17 is 180° while 12–13–14–15 is only 169°.

We note with interest that the conformation of the 17 β substituted D ring as predicted by Brutcher & Bauer (1962) is in good agreement with observation in the present case.

Other geometrical parameters in the molecule that are of interest are the magnitude of the two C–O–C angles, both 118°, and the near coplanarity of the ester group and the benzene ring, the torsion angle being only 11°.

The absolute configuration of the molecule was not determined directly; rather, we considered the configuration to be well established, and used the geometry around C(13) when we assigned the configuration.

The packing involving C–H...C–H contacts is normal. Inspection of Fig. 2 may give an impression of the efficiency of the packing. The only short intermolecular distance is the O(30)–Br(29') distance of 2.93 Å, well below the sum of van der Waals radii (3.35 Å). It appears that we have an example of a molecular complex of the same type as in *e.g.* oxalyl bromide (O–Br = 3.27 Å) (Groth & Hassel, 1961), the main difference being the much stronger bond indicated in the present case.

We wish to thank Dr H. Hanni for supplying the crystals used in this study, and the UC Davis Computer Center for valuable services rendered.

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