The Conformation of Non-Aromatic Ring Compounds. LXXXVIII. The Crystal and Molecular Structure of 3α,3β-Dimethoxy-5α-oestran-17β-ol Toluene-*p*-sulphonate at −170°C

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The steroid 3α,3β-dimethoxy-5α-oestran-17β-ol toluene-*p*-sulphonate crystallizes in the space group $P2_1$. The lattice constants are $a=16\cdot563$, $b=9\cdot813$, $c=7\cdot889$ Å and $\beta=90\cdot56°$. At −170°C the intensities of 2329 significant reflexions were measured with Mo $K\alpha$ radiation: the structure was solved by a combination of Patterson and direct methods. The final R_w value is 6·01%. Rings *A*, *B* and *C* are normal chairs, ring *D* is a C(13) envelope.

Introduction

In the preceding paper (de Graaff & Romers, 1974) we discussed the structure of 3-oxo-5α-androstan-17β-ol toluene-*p*-sulphonate (AOT). The present publication deals with the structure of 3α,3β-dimethoxy-5α-oestran-17β-ol toluene-*p*-sulphonate (hereinafter EMT, Fig. 1). EMT differs at two positions (10 and 3) from AOT. The methyl group C(19) is absent and the ketonic oxygen atom at position 3 is replaced by two methoxyl groups.

During the initial stages of this investigation we believed we were dealing with the compound 3-oxo-5α-oestran-17β-ol toluene-*p*-sulphonate. However, during recrystallization from methanol the oxo group at position 3 was converted into a dimethoxy moiety.

This reaction was probably catalysed by small traces of toluene-*p*-sulphonic acid originating from hydrolysis of the parent compound. The preparation of suitable crystals of the oxo compound is still in progress.

Experimental

EMT was recrystallized from methanol as relatively large needles elongated along [001]. The lattice constants were measured on a three-circle diffractometer at room temperature and −170°C with Cu $K\alpha$ radiation ($\lambda=1\cdot54178$ Å) and Mo $K\alpha$ radiation ($\lambda=0\cdot71069$ Å) respectively.

Reflexions 0k0 with $k=2n+1$ were systematically absent. An inversion centre cannot be present in the structure. From these two considerations the space group $P2_1$ follows directly. Some relevant crystallographic data on EMT are listed in Table 1. The observed density indicates the presence of two molecules in the unit cell.

Reflexion intensities of a crystal of dimensions $0\cdot52 \times 0\cdot39 \times 0\cdot13$ mm were recorded at −170°C using a Nonius three-circle diffractometer. Mo $K\alpha$ radiation

Table 1. *Crystallographic data for EMT
at 20 and* −170°C (*quoted errors are e.s.d.'s*)

3α, 3β-Dimethoxy-5α-oestran-17β-ol toluene-*p*-sulphonate
$C_{27}H_{39}O_5S$

$M=475\cdot7$. Space group $P2_1$, $Z=2$

20°C	−170°C
$a=16\cdot66$ (1) Å	$a=16\cdot563$ Å
$b=\ 9\cdot909$ (2)	$b=\ 9\cdot8126$ (3)
$c=\ 7\cdot930$ (1)	$c=\ 7\cdot8890$ (5)
$\beta=90\cdot45$ (5)°	$\beta=90\cdot56$ (1)°
$\mu(Cu\ K\alpha)=12\cdot6$ cm^{-1}.	Total number of reflexions 3094
$\mu(Mo\ K\alpha)=1\cdot50$ cm^{-1}.	Not significant 765
$d_{obs}=1\cdot203$ g cm^{-3}	$|E|=0\cdot888$
$d_x\ =1\cdot204$ g cm^{-3}	$|E^2-1|=0\cdot767$

and a graphite monochromator were used. The recording technique has been described previously (Verschoor & Keulen, 1971; Portheine, Romers & Rutten, 1972). In all, 3094 symmetry-independent reflexions were recorded. From this data set 2329 reflexions had a count equal to or larger than twice the estimated standard deviation (from counting statistics only). The remainder, 765 reflexions, having a count smaller than twice their e.s.d., were labelled not significant. The maximum glancing angle during the measurements was 27·5°.

The difference between maximum and minimum transmission for this particular crystal being well within the range of the experimental errors, no correction for absorption was applied. The intensities were reduced to structure factors in the usual way. Normalized structure factors E were calculated using the value $B=2\cdot4$ Å^2 derived from a Wilson plot.

Structure determination and refinement

The structure was solved by a combination of Patterson and direct methods. The first attempts were made using the set of programs described in the preceding paper. The phases of 224 E's > 1·5 were refined. Table 2 contains the starting set and the associated phases.

Table 2. *The starting set*

	h	k	l	E	Phase
Origin-	1	4	9	3·90	0
defining	4	5	9	3·03	$\pi/4$
reflexions	13	0	$\bar{4}$	2·21	0
Symbolic	9	5	4	2·82	$n\pi/4, n=1,3,5,7$
reflexions	11	-8	-6	3·38	$n\pi/4, n=1,3,5,7$

The best solution, according to the criteria described in the previous paper, yielded a possible position for sulphur surrounded by two tetrahedra, related by a mirror plane. Next a sharpened Patterson function was calculated following the procedure of Jacobson, Wunderlich & Lipscomb (1961). The possible positions of the S–O tetrahedra were in accordance with this Patterson function. A shift over two independent S–O vectors and their symmetry-related vectors yielded partial deconvolution. In the resulting map rings *A*, *B* and *D*, and *C* (11) together with the S–O tetrahedron could be recognized. A structure-factor calculation based on this model showed an R_w of 43·7%. [For a definition of R_w see Knobler, Romers, Braun & Hornstra (1972).] A subsequent Fourier map showed the rest of the molecule except for one carbon atom. Moreover, the position assumed for C(6) was shown to be wrong.

A renewed structure-factor calculation yielded an R_w ratio of 33·3%. Inspection of the calculated Fourier map indicated the presence of two extra carbon atoms and one extra oxygen atom near C(3) (see *Introduction*). The missing methyl group attached to the benzene ring could also be located. Only now did we discover our compound to be a $3\alpha,3\beta$-dimethoxy analogue instead of the expected 3-oxo derivative.

In subsequent least-squares cycles, refining with isotropic *B*'s, the R_w ratio dropped to 14%. Weights were calculated from $W_{hkl}=\sigma^{-2}(hkl)$ and $\sigma^2(hkl)=\sigma^2(\text{counting statistics})+0·03F^2(hkl)$.

The hydrogen atoms were located from difference Fourier maps in the usual way. Anisotropic refinement, keeping the H positions fixed, with *B* values equal to those of the parent carbon atoms resulted in an R_w of 7·4%. Subsequent isotropic refinement of the H atoms while constraining the parameters of the heavy atoms to their incidental values gave an R_w of 6·7%. Repetition of this procedure (necessary because of slow convergence) and finally refinement during two cycles
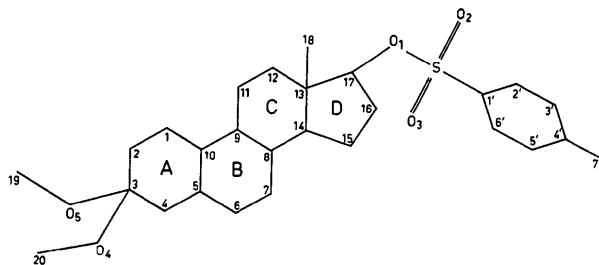
including the not significant reflexions yielded a final R_w value of 6·0%. The conventional *R* based on the final cycle was 8·1%.

A listing of observed and calculated structure factors is available on request.* The positional and thermal parameters of the non-hydrogen atoms are listed in Tables 3 and 4. The coordinates of the hydrogen atoms, together with their isotropic *B* values are given in Table 5.

Table 3. *Fractional coordinates of the non-hydrogen atoms*

Standard deviations are given in parentheses.

	x	y	z
S	8850 (1)	10025 (1)	4589 (1)
C(1)	4319 (2)	9105 (4)	10360 (5)
C(2)	3592 (3)	8610 (5)	11337 (5)
C(3)	2848 (3)	8342 (4)	10202 (5)
C(4)	3060 (2)	7428 (5)	8753 (5)
C(5)	3769 (2)	7963 (4)	7738 (5)
C(6)	3931 (2)	7009 (5)	6266 (5)
C(7)	4658 (2)	7482 (5)	5246 (5)
C(8)	5406 (2)	7669 (4)	6371 (5)
C(9)	5242 (2)	8668 (4)	7840 (5)
C(10)	4528 (2)	8173 (4)	8883 (5)
C(11)	6001 (3)	8975 (5)	8884 (5)
C(12)	6718 (2)	9451 (5)	7810 (5)
C(13)	6887 (2)	8431 (4)	6417 (5)
C(14)	6105 (3)	8202 (4)	5355 (5)
C(15)	6379 (3)	7418 (5)	3779 (5)
C(16)	7239 (3)	8014 (5)	3467 (5)
C(17)	7402 (2)	8983 (5)	4977 (5)
C(18)	7257 (2)	7122 (5)	7142 (5)
C(1')	9075 (2)	9177 (4)	2703 (5)
C(2')	9544 (2)	7992 (5)	2793 (5)
C(3')	9725 (2)	7328 (5)	1307 (5)
C(4')	9455 (2)	7811 (5)	-251 (5)
C(5')	8986 (2)	8999 (5)	-317 (5)
C(6')	8792 (2)	9681 (5)	1165 (5)
C(7')	9654 (3)	7076 (6)	-1851 (5)
C(19)	1931 (3)	8326 (5)	12518 (6)
C(20)	1911 (3)	9669 (6)	8534 (6)
O(1)	8260 (2)	9009 (3)	5520 (3)
O(2)	9541 (2)	10070 (4)	5693 (3)
O(3)	8420 (2)	11265 (3)	4159 (4)
O(4)	2594 (2)	9666 (3)	9669 (4)
O(5)	2236 (2)	7658 (3)	11064 (4)

Discussion of the structure

The geometrical entities of EMT are shown in Fig. 2. Adding 40% to the calculated standard deviations (thereby allowing for the overestimated accuracy by our L.S. program) we arrive at values of 0·005, 0·006, 0·008, 0·009 and 0·09 Å for the average standard deviations of S–O, S–C, C–O, C–C and C–H bond lengths respectively. The corresponding errors for valency and torsion angles not involving hydrogen are 0·5 and 0·7°. The angles involving hydrogen have an average stan-

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Fig. 1. Numbering of atoms in EMT.

Table 4. *Thermal parameters*
of the non-hydrogen atoms in 10^{-3} $Å^2$

Standard deviations are given in parentheses.

|	U_{11}	U_{22}	U_{33}	$2U_{21}$	$2U_{23}$	$2U_{31}$
S	39 (1)	19 (0)	13 (0)	5 (1)	4 (1)	14 (1)
C(1)	36 (3)	23 (2)	19 (2)	−4 (4)	−5 (4)	3 (4)
C(2)	48 (3)	20 (2)	25 (2)	3 (5)	1 (4)	18 (4)
C(3)	45 (3)	10 (2)	29 (2)	−11 (4)	9 (4)	19 (4)
C(4)	38 (3)	24 (2)	22 (2)	−14 (5)	6 (4)	−4 (4)
C(5)	37 (3)	13 (2)	27 (2)	0 (4)	0 (4)	8 (4)
C(6)	40 (3)	26 (3)	23 (2)	−5 (5)	−18 (4)	−3 (4)
C(7)	42 (3)	27 (2)	19 (2)	−7 (5)	−18 (4)	6 (4)
C(8)	40 (3)	12 (2)	14 (2)	−6 (4)	0 (3)	7 (4)
C(9)	35 (3)	12 (2)	17 (2)	−7 (4)	−11 (3)	8 (4)
C(10)	38 (3)	19 (2)	19 (2)	−1 (4)	−11 (4)	14 (4)
C(11)	43 (3)	30 (3)	21 (2)	−15 (5)	−9 (4)	16 (4)
C(12)	37 (3)	26 (2)	15 (2)	−15 (4)	−20 (4)	11 (4)
C(13)	37 (3)	16 (2)	13 (2)	0 (4)	−4 (3)	3 (4)
C(14)	50 (3)	16 (2)	12 (2)	4 (4)	0 (4)	8 (4)
C(15)	46 (3)	40 (3)	14 (2)	−8 (5)	−18 (4)	7 (4)
C(16)	50 (3)	44 (3)	22 (2)	−22 (5)	−16 (5)	29 (4)
C(17)	27 (2)	23 (2)	14 (2)	−2 (4)	2 (4)	3 (3)
C(18)	39 (3)	26 (2)	30 (2)	1 (5)	26 (4)	24 (4)
C(1')	33 (3)	19 (2)	15 (2)	−8 (4)	−5 (3)	12 (3)
C(2')	30 (3)	25 (3)	21 (2)	3 (4)	5 (4)	6 (4)
C(3')	30 (3)	27 (3)	26 (2)	5 (4)	−2 (4)	6 (4)
C(4')	40 (3)	24 (2)	17 (2)	5 (5)	−2 (4)	14 (4)
C(5')	38 (3)	28 (2)	15 (2)	6 (5)	2 (4)	12 (4)
C(6')	34 (3)	19 (2)	20 (2)	7 (4)	−1 (4)	17 (4)
C(7')	52 (3)	47 (3)	21 (2)	29 (6)	−17 (5)	16 (4)
C(19)	47 (3)	37 (3)	36 (3)	−3 (5)	12 (5)	40 (5)
C(20)	62 (4)	42 (3)	51 (3)	35 (6)	45 (6)	15 (5)
O(1)	30 (2)	21 (2)	13 (1)	3 (3)	3 (3)	14 (2)
O(2)	46 (2)	37 (2)	12 (1)	−10 (4)	−14 (3)	5 (2)
O(3)	53 (2)	18 (2)	22 (2)	0 (3)	−4 (3)	23 (3)
O(4)	39 (2)	17 (2)	34 (2)	9 (3)	11 (3)	18 (3)
O(5)	34 (2)	26 (2)	34 (2)	0 (3)	13 (3)	27 (3)
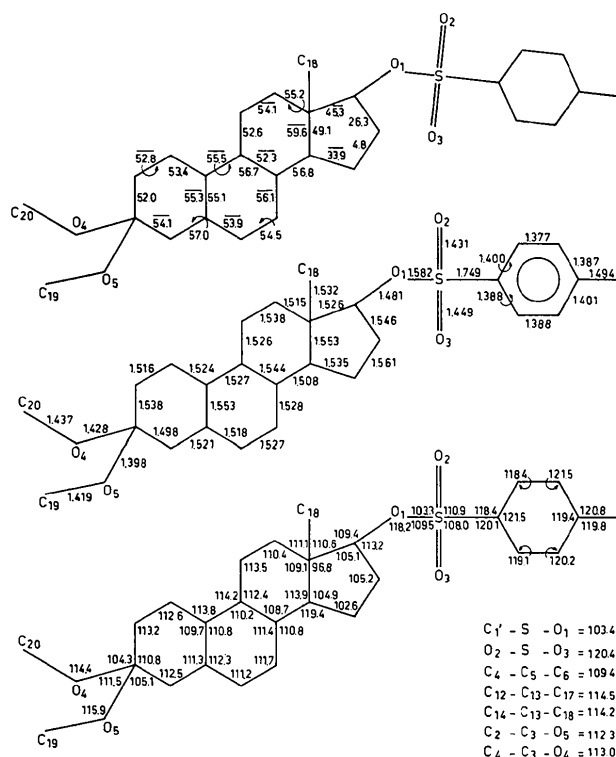
Fig. 2. Geometrical entities of EMT.

dard deviation of about 5°. Averaging all C–H distances, C–H–C and H–C–H angles (disregarding the hydrogens attached to the phenyl ring) we arrive at values of 0·98 Å, 109 and 108°. These values are in good agreement with those quoted in the literature (Braun, Hornstra & Leenhouts, 1969). The estimated standard errors were 0·09 Å, 4° and 6° respectively, in good agreement with the corrected estimates of our L.S. program.

Table 5. *Fractional coordinates and isotropic B values*
($Å^2$) *of the hydrogen atoms*

Standard deviations are given in parentheses.

|	x	y	z	B_{iso}
H(11)	418 (2)	993 (5)	991 (4)	19 (8)
H(12)	476 (2)	931 (4)	1115 (4)	9 (7)
H(21)	353 (2)	914 (5)	1225 (5)	29 (10)
H(22)	375 (2)	773 (4)	1177 (4)	14 (8)
H(41)	269 (2)	744 (3)	799 (3)	−5 (5)
H(42)	323 (2)	647 (4)	928 (4)	8 (7)
H(5)	361 (2)	890 (4)	732 (4)	10 (7)
H(61)	407 (2)	606 (4)	682 (5)	26 (9)
H(62)	355 (2)	701 (4)	547 (4)	6 (7)
H(71)	478 (2)	679 (4)	416 (5)	25 (9)
H(72)	456 (2)	829 (4)	471 (4)	18 (8)
H(8)	555 (2)	677 (3)	688 (4)	0 (6)
H(9)	513 (2)	960 (4)	738 (4)	9 (7)
H(10)	463 (2)	734 (5)	930 (5)	31 (10)
H(111)	590 (2)	966 (4)	997 (4)	18 (8)
H(112)	615 (2)	821 (4)	943 (4)	18 (8)
H(121)	710 (2)	964 (4)	849 (4)	12 (7)
H(122)	656 (2)	1040 (4)	716 (4)	6 (7)
H(14)	595 (2)	917 (4)	493 (4)	16 (8)
H(151)	601 (2)	762 (4)	272 (4)	19 (8)
H(152)	651 (2)	644 (4)	408 (4)	13 (7)
H(161)	722 (2)	851 (5)	237 (5)	29 (9)
H(162)	768 (2)	716 (5)	334 (5)	38 (10)
H(17)	725 (2)	1013 (5)	474 (5)	24 (8)
H(181)	693 (2)	680 (5)	792 (5)	36 (11)
H(182)	735 (3)	648 (6)	632 (6)	48 (12)
H(183)	781 (3)	736 (7)	789 (6)	68 (14)
H(2')	977 (2)	777 (5)	383 (5)	20 (9)
H(3')	1003 (2)	662 (4)	133 (4)	18 (8)
H(5')	879 (2)	928 (4)	−143 (5)	16 (8)
H(6')	850 (2)	1056 (5)	123 (5)	30 (10)
H(7'1)	1004 (3)	734 (6)	−238 (6)	47 (12)
H(7'2)	928 (2)	742 (4)	−284 (4)	16 (8)
H(7'3)	961 (3)	595 (6)	−179 (6)	56 (13)
H(191)	179 (3)	924 (8)	1228 (8)	99 (20)
H(192)	224 (2)	823 (4)	1352 (4)	6 (7)
H(193)	142 (2)	787 (4)	1297 (4)	17 (8)
H(201)	194 (3)	936 (5)	708 (6)	56 (13)
H(202)	157 (2)	912 (5)	896 (5)	38 (11)
H(203)	173 (2)	1047 (5)	874 (5)	30 (10)
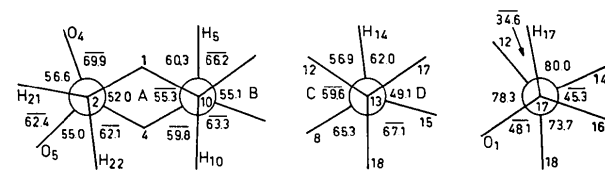
Fig. 3. Newman projections at some salient points in the molecule EMT.

In sharp contrast to our findings in the preceding paper no irregularities of any kind can be observed in this structure. The conformation of rings A, B and C is a quite regular chair. The mean angles of puckering are 54·0, 55·1 and 55·0° respectively. Ring D is almost a C(13) envelope. The conformation of ring D is described by the phase angle $\Delta = 24\cdot3°$ and the angle of puckering $\varphi_m = 50\cdot4°$ (Altona, Geise & Romers, 1968). Some Newman projections at important points are shown in Fig. 3.

There is a striking resemblance between the geometry of rings C and D in AOT (preceding paper), EMT and the compound 2β-methyl-3-oxo-oestr-4-en-17β-ol p-bromobenzenesulphonate (Cody & Duax, 1972). A more detailed discussion of this phenomenon can be found in the preceding paper.

The packing of EMT is shown in Table 6. Each molecule is surrounded by 12 nearest neighbours. No remarkably short intermolecular distances were observed.

All calculations were carried out on the IBM 360/65 of the Central Computing Institute of the State University, Leiden.

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Table 6. *Packing of EMT*

I	x	y	z	VIII	$2-x$	$\frac{1}{2}+y$	$1-z$
II	x	y	$1-z$	IX	$2-x$	$\frac{1}{2}+y$	$-z$
III	x	y	$1+z$	X	$2-x$	$\frac{1}{2}-y$	$-z$
IV	$1+x$	y	$1-z$	XI	$2-x$	$\frac{1}{2}-y$	$1-z$
V	$1-x$	y	$1+z$	XII	$1-x$	$\frac{1}{2}-y$	$2-z$
VI	$1-x$	$\frac{1}{2}+y$	$2-z$	XIII	$1-x$	$\frac{1}{2}-y$	$1-z$
VII	$1-x$	$\frac{1}{2}+y$	$1-z$				

Crystal and Molecular Structure of a Dimer C42H28 from 1-Phenyl-3,3-biphenylene-allene

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A dimer from 1-phenyl-3,3-biphenylene-allene, chemical formula $C_{42}H_{28}$, was investigated by X-ray analysis. The space group is Cc with lattice parameters $a = 18\cdot546$, $b = 19\cdot924$, $c = 8\cdot688$ Å, $\beta = 110\cdot07°$ and $Z = 4$. The phase problem was solved by the multisolution method with two reflexions for origin definition and four unrestricted reflexions as variable. The final $R = 3\cdot6\%$, including an isotropic extinction factor in refinement. The compound was identified as 2-phenyl-3-fluorenylidene-4-benzylidene-spiro[cyclobutane-1,9'-fluorene] verifying a head-to-tail dimerization. The cyclobutane ring is nonplanar and shows a remarkable lengthening of one C–C bond to 1·61 Å. The orientation of the benzylidene group gives information about the mechanism of thermal allene dimerization.

Introduction

The stereochemical course of the thermal dimerization of allenes has been the subject of several investigations during the last few years (Dehmlow & Ezimora, 1972; Jacobs, Byrn, Maverick, Muscio & Trueblood, 1971; Baldwin & Fleming, 1970, and references cited therein).

In this connexion the structures of several allene dimers have been determined. However, the understanding of the stereochemistry and mechanism of the allene dimerization is still incomplete. Further progress requires more definitive information about the structure of allene dimers. In particular, in the case of the dimers of highly substituted aryl-allenes, the conclusive deter-