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

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The steroid 3-oxo-5α-androstan-17β-ol toluene-*p*-sulphonate crystallizes in the space group $P2_12_12_1$. The lattice constants are $a=17·748$, $b=21·711$, $c=5·969$ Å. With Mo $K\alpha$ radiation at −170°C, 2286 significant reflexions weıe measured. The final R_w value was 3·6%. Rings B and C are normal chairs; ring D is a C(13) envelope. Ring A has a low degree of puckering; no transmission of this effect to rings C and D is observed.

Introduction

This paper is a member of a series on the structure determination of steroids (*e.g.* Portheine, Romers & Rutten, 1971; Knobler, Romers, Braun & Hornstra, 1972). The knowledge of the geometry of 3-oxo-5α-androstan-17β-ol toluene-*p*-sulphonate (hereinafter AOT, Fig. 1) is of importance to the understanding of the Cotton effect in 3-oxo-steroids. It has been noted by Djerassi and Klyne (Kirk, Klyne & Wallis, 1970) that 5α-steroids containing a C(19) methyl group show a slightly smaller Cotton effect than the corresponding 19-nor steroids. Consequently, the conformations of rings A and B should differ slightly, the methyl group being present or absent.

The related compounds 3-oxo-5α-oestran-17β-ol toluene-*p*-sulphonate and 3α,3β-dimethoxy-5α-oestran-17β-ol toluene-*p*-sulphonate (hereinafter EMT) are also under investigation in our laboratory. The synthesis of the former is still in progress, while a description of the structure of the latter is presented in the paper following this one (de Graaff, van der Ende & Romers, 1974).

Experimental

The steroid AOT was recrystallized as needles, the longest direction being [001]. The lattice constants (Table 1) were measured with a three-circle diffractometer at room temperature and at −170°C using Cu $K\alpha$ radiation ($\lambda=1·54178$).
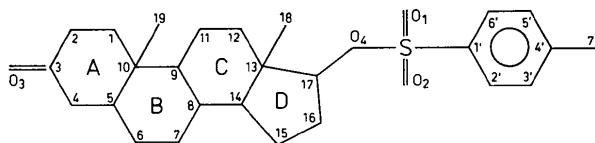
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Fig. 1. Numbering of atoms in AOT.

Table 1. Crystallographic data on AOT at 20 and −170°C

Quoted errors are e.s.d.'s.

3-Oxo-5α-androstan-17β-ol toluene-*p*-sulphonate
$C_{26}H_{36}O_4S$
$M=444·7$, m.p. 182°C
Space group $P2_12_12_1$, $Z=4$

20°C	−170°C
$a=17·954$ (4) Å	$a=17·748$ (3) Å
$b=22·067$ (5)	$b=21·711$ (3)
$c=6·032$ (3)	$c=5·969$ (2)
μ(Cu $K\alpha$)$=14·6$ cm^{-1}	Total number of reflexions 3029
μ(Mo $K\alpha$)$=1·7$ cm^{-1}	Unobserved reflexions 743
$d_{obs}=1·27$ g cm^{-3}	$|E|=0·88$
$d_x=1·282$ g cm^{-3}	$|E^2-1|=0·78$

From the systematic absence of reflexions $h00$, $0k0$, $00l$ for $h,k,l=2n+1$ the space group $P2_12_12_1$ follows directly. The observed density indicates the presence of four molecules in the unit cell.

The reflexion intensities of a crystal of dimensions $0·5\times0·3\times0·15$ mm were collected with a three-circle diffractometer at −170°C using Mo $K\alpha$ radiation ($\lambda=0·71069$ Å) and a graphite monochromator. The recording technique has been described previously (Verschoor & Keulen, 1971; Portheine *et al.*, 1972). In total, 2286 reflexions were observed with a count of at least twice the standard deviation (based on counting statistics only). 743 reflexions not satisfying this criterion were labelled as not significant. The maximum glancing angle used was 27·5°. The difference between minimum and maximum transmission for the largest and smallest path lengths being well within the experimental error (95 and 97·4% respectively), no correction for absorption was applied. The intensities were reduced to structure factors in the usual way. Subsequently, normalized structure factors E were calculated using the value $B=1·46$ Å^2 derived from a Wilson plot.

Structure determination

The structure was determined by direct methods using a multiple-solution program (Kennard, Isaacs, Motherwell, Coppola, Wampler, Larson & Watson, 1971). The starting set of reflexions and their associated phases are listed in Table 2. No less than five reflexions could be phased by applying the Σ_1 relation (Hauptman & Karle, 1953). Phases $n\pi/4$, $n = 1, 3, 5, 7$ were assigned to the reflexions 993 and 884. The reflexion 13,10,1 was given the values $\pi/4$ and $3\pi/4$ only, since the values $5\pi/4$ and $7\pi/4$ resulted in solutions enantiomorphic with those obtained with $3\pi/4$ and $\pi/4$, respectively.

Table 2. *Starting set of reflexions*

h	k	l	E	Phase
Origin-defining reflexions				
9	17	0	2·80	$-\pi/2$
0	7	2	2·45	$\pi/2$
0	17	1	2·38	$\pi/2$
Σ_1 reflexions				
0	0	6	4·13	0
16	0	0	3·04	0
0	18	0	2·86	0
0	14	0	2·76	0
0	6	0	2·49	0
Symbolic reflexions				
9	9	3	2·49	$n\pi/4, n = 1,3,5,7$
8	8	4	3·27	$n\pi/4, n = 1,3,5,7$
13	10	1	2·44	$n\pi/4, n = 1,3$

The 32 starting sets were extended by using the tangent formula (Karle & Karle, 1969). The solutions obtained were checked by a number of criteria: minimum value of R (Karle), maximum of Σ_2 relations used, maximum value of the reliability parameter α, maximum internal consistency and maximum number of phases obtained.

Since a few groups of starting sets had converged to essentially the same solution, only the best of each group was considered.

From the remaining solutions an E map was calculated, in a sequence suggested by the aforementioned criteria.

The E maps were scanned with two programs. The first lists all peaks above a certain minimum value together with their respective heights; the second calculates distances and 'valency angles' in the fully generated unit cell (Motherwell, de Graaff & Verschoor, unpublished). The E map first selected proved to be the correct one. In this map the carbon atoms belonging to rings A and B, C(19), the sulphur atom, three oxygen atoms attached to sulphur and three carbon atoms of the benzene ring could be identified.

A structure-factor calculation resulted in an R_w value of 35%. [For the definition of R and R_w, see Knobler *et al.* (1972).]

After the refinement we returned to the E map. The positions of the sulphur and two oxygen atoms were

used to calculate a minimum function (Buerger, 1951) based on a modified E^2 map. In the resulting map all heavy atoms could be located. The sharpening of the Patterson function according to Jacobsen, Wunderlich & Lipscomb (1961) was essential. Only a few atoms could be recognized in the corresponding unsharpened function.

As will be shown in the next paper (de Graaff *et al.*, 1974) the combination of direct and Patterson methods is particularly favourable in the case of the former yielding a partial solution and the latter not producing recognizable Harker interactions. A similar procedure has been suggested by Schenk (1972).

Refinement

The Fourier map based on the model described in the previous section showed all heavy atoms except C(12) and C(7): $R_w = 29\%$. Using unitary weights the positional parameters and individual isotropic B values of all atoms were refined by the block-diagonal least-squares method: $R_w = 13\%$. At this point the individual reflexions were weighted according to the formula $w(hkl) = 1/\sigma^2(hkl)$. The variance $\sigma^2(hkl)$ was calculated from $\sigma^2(hkl) = \sigma^2(\text{counting statistics}) + 0.03F^2(hkl)$, $F(hkl)$ denoting the observed structure factor.

The hydrogen atoms were located in a difference Fourier map. Next, all heavy atoms were refined anisotropically, keeping the hydrogens at fixed positions with fixed values for the isotropic B's, equal to the B's of the parent atoms: $R_w = 4\%$. The hydrogen atoms were then refined isotropically, while constraining the parameters of the heavy atoms to their current values: $R_w = 3.7\%$. Finally, the heavy atoms were once more refined during two cycles. The final R and R_w values (observed reflexions only) are 5·8 and 3·6%. A list of observed and calculated structure factors is available on request.* The positional parameters and their estimated standard deviations are listed in Table 3. The thermal parameters may be found in Table 4. The coordinates of the hydrogen atoms and their isotropic temperature factors are given in Table 5.

Discussion of the structure

The bond lengths, valency and endocyclic torsion angles of AOT are given in Fig. 2.

Adding 40% to the calculated standard deviations – thereby allowing for the optimistic estimates of our L.S. program – we arrive at values of 0·004, 0·005, 0·006, 0·007 and 0·04 Å for the average standard deviations for S–O, S–C, C–O, C–C and C–H bond lengths, respectively. The corresponding errors for valency and

Table 3. *Fractional coordinates of AOT chosen in conformity with the accepted absolute configuration and with respect to a right-handed reference system*

The estimated standard deviations are given in parentheses.

	x	y	z
C(1)	0·0623 (34)	0·6325 (33)	1·0029 (40)
C(2)	−0·0223 (34)	0·6394 (36)	0·9429 (43)
C(3)	−0·0403 (30)	0·6985 (34)	0·8252 (41)
C(4)	0·0177 (31)	0·7219 (34)	0·6596 (43)
C(5)	0·0995 (34)	0·7129 (35)	0·7315 (37)
C(6)	0·1536 (33)	0·7359 (33)	0·5505 (40)
C(7)	0·2353 (32)	0·7319 (32)	0·6264 (39)
C(8)	0·2560 (32)	0·6683 (33)	0·7138 (36)
C(9)	0·1992 (31)	0·6454 (33)	0·8916 (35)
C(10)	0·1165 (31)	0·6460 (34)	0·8090 (39)
C(11)	0·2239 (31)	0·5830 (32)	0·9898 (42)
C(12)	0·3050 (32)	0·5822 (33)	1·0762 (39)
C(13)	0·3593 (32)	0·6030 (34)	0·8951 (37)
C(14)	0·3342 (31)	0·6673 (33)	0·8131 (38)
C(15)	0·4012 (34)	0·6913 (35)	0·6776 (42)
C(16)	0·4719 (32)	0·6629 (33)	0·7947 (41)
C(17)	0·4383 (34)	0·6203 (32)	0·9757 (38)
C(18)	0·3651 (32)	0·5561 (35)	0·7051 (38)
C(19)	0·1038 (32)	0·5986 (36)	0·6207 (40)
O(3)	−0·0998 (22)	0·7250 (23)	0·8532 (29)
O(1)	0·5646 (24)	0·5030 (24)	1·2336 (25)
O(2)	0·5537 (23)	0·6148 (22)	1·3089 (25)
O(4)	0·4819 (20)	0·5631 (22)	1·0101 (27)
S	0·55643 (9)	0·56483 (9)	1·1518 (11)
C(1')	0·6288 (31)	0·5786 (33)	0·9562 (39)
C(2')	0·6799 (34)	0·6254 (34)	0·9974 (43)
C(3')	0·7398 (34)	0·6350 (34)	0·8534 (44)
C(4')	0·7481 (32)	0·5984 (35)	0·6615 (43)
C(5')	0·6952 (32)	0·5522 (35)	0·6231 (39)
C(6')	0·6360 (33)	0·5425 (36)	0·7660 (39)
C(7')	0·8136 (34)	0·6083 (38)	0·5048 (46)

torsion angles not involving hydrogen are 0·4 and 0·6°, those involving hydrogen about 4°.

Accepting equivalence of all C–H distances, C–C–H angles and H–C–H angles (excepting hydrogen atoms attached to the phenyl ring) we calculate mean values of 0·98 Å, 109 and 107°, respectively. These values are in good agreement with the results obtained by Braun, Hornstra & Leenhouts (1969). Estimated standard errors of 0·04 Å, 3·8 and 4·4° were obtained. These results agree nicely with the estimates from our L.S. program.

With the exception of bonds C(1)–C(2) and C(15)–C(16) no abnormally large or small bond lengths are noted. The observed length of the bond C(1)–C(2) (1·551 Å) is exceptionally long. As yet no reasonable explanation can be offered for this anomaly. The mean length of this bond calculated from 15 saturated 5α-steroids (Romers, Altona, Jacobs & De Graaff, 1974) is 1·537 Å. The difference of 0·014 Å from the observation in this study must be considered significant on a 95% confidence level. The bond C(15)–C(16) (1·563 Å) is also exceptionally long. This is caused by the partial eclipsing of the hydrogen atoms due to the small endocyclic torsion angle about the bond C(15)–C(16) (4·8°).

The overall shape of the molecule is elongated and slightly curved towards the α-side, causing the vectors C(10)–C(9) and C(13)–C(18) to diverge. Some Newman projections at salient points in the molecule are shown in Fig. 3.

Table 4. *Vibrational parameters U_{ij} of AOT and their estimated standard deviations ($\times 10^4$ Å^2)*

The temperature factor is defined as $\exp[-2\pi^2\Sigma_{ij}h_ih_ja_i^*a_j^*U_{ij}]$, $i,j=1,2,3$.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	165 (16)	178 (19)	207 (22)	76 (34)	−23 (40)	34 (41)
C(2)	194 (17)	249 (21)	227 (25)	−14 (37)	125 (43)	−41 (40)
C(3)	178 (17)	231 (20)	183 (22)	−23 (30)	245 (44)	167 (38)
C(4)	183 (16)	218 (20)	231 (24)	4 (34)	92 (47)	−20 (43)
C(5)	201 (16)	158 (19)	143 (22)	37 (33)	94 (37)	25 (37)
C(6)	212 (17)	142 (20)	198 (26)	−4 (33)	−10 (40)	95 (40)
C(7)	204 (17)	174 (20)	154 (24)	18 (32)	−34 (41)	41 (39)
C(8)	174 (16)	153 (19)	92 (22)	42 (32)	54 (37)	−9 (34)
C(9)	124 (15)	147 (18)	103 (22)	40 (30)	16 (37)	16 (33)
C(10)	186 (17)	154 (19)	137 (22)	72 (30)	−55 (39)	−11 (36)
C(11)	177 (16)	157 (20)	212 (23)	9 (30)	−103 (41)	70 (38)
C(12)	191 (17)	180 (20)	196 (24)	22 (32)	−26 (39)	−20 (37)
C(13)	200 (17)	180 (19)	107 (22)	−24 (32)	−16 (39)	5 (36)
C(14)	164 (16)	156 (19)	110 (21)	49 (31)	63 (41)	50 (36)
C(15)	209 (16)	187 (19)	205 (23)	9 (32)	−22 (43)	37 (42)
C(16)	151 (15)	161 (19)	258 (26)	−7 (32)	75 (42)	77 (38)
C(17)	191 (16)	154 (19)	157 (22)	−84 (33)	38 (37)	6 (41)
C(18)	224 (17)	179 (20)	213 (24)	−60 (35)	78 (42)	−25 (37)
C(19)	214 (17)	231 (21)	202 (25)	3 (33)	122 (42)	−15 (42)
O(3)	208 (11)	266 (15)	328 (18)	45 (24)	102 (34)	−55 (33)
O(1)	272 (12)	208 (13)	227 (16)	67 (26)	−77 (26)	52 (29)
O(2)	249 (11)	212 (13)	171 (16)	113 (25)	98 (27)	69 (30)
O(4)	150 (10)	160 (12)	222 (15)	−53 (24)	86 (31)	−76 (26)
S	177 (3)	193 (4)	188 (5)	26 (9)	−10 (11)	34 (11)
C(1')	144 (16)	235 (22)	173 (23)	63 (32)	−68 (40)	41 (37)
C(2')	238 (18)	211 (22)	225 (24)	61 (34)	80 (45)	25 (42)
C(3')	235 (18)	210 (21)	330 (27)	−125 (34)	114 (49)	16 (46)
C(4')	194 (16)	250 (21)	230 (24)	83 (34)	−72 (45)	−15 (42)
C(5')	242 (17)	250 (22)	196 (24)	88 (35)	30 (44)	15 (41)
C(6')	204 (17)	226 (21)	211 (25)	−50 (35)	26 (41)	98 (38)
C(7')	240 (19)	253 (22)	347 (28)	11 (37)	−50 (51)	−47 (45)

Table 5. *Fractional coordinates and isotropic B values*
(Å²) of hydrogen atoms of AOT

The estimated standard deviations are given in parentheses.

|	x	y	z	B
H(11)	0·077 (26)	0·588 (25)	1·047 (31)	1·67 (71)
H(12)	0·076 (28)	0·662 (27)	1·132 (31)	1·42 (74)
H(21)	−0·030 (27)	0·610 (28)	0·854 (32)	2·36 (73)
H(22)	−0·060 (39)	0·639 (35)	1·080 (39)	5·35 (106)
H(41)	0·008 (24)	0·702 (25)	0·531 (32)	0·71 (61)
H(42)	0·008 (26)	0·768 (26)	0·632 (30)	0·94 (70)
H(5)	0·111 (25)	0·739 (26)	0·854 (31)	1·24 (66)
H(61)	0·149 (24)	0·709 (24)	0·416 (27)	0·00 (58)
H(62)	0·137 (25)	0·780 (25)	0·570 (31)	1·32 (64)
H(71)	0·242 (27)	0·764 (26)	0·756 (29)	0·54 (69)
H(72)	0·273 (26)	0·745 (27)	0·515 (34)	1·34 (69)
H(8)	0·254 (24)	0·642 (23)	0·595 (26)	0·23 (58)
H(9)	0·197 (26)	0·676 (24)	1·014 (32)	1·08 (64)
H(111)	0·194 (25)	0·567 (26)	1·084 (28)	1·24 (67)
H(112)	0·218 (22)	0·550 (24)	0·877 (26)	0·00 (59)
H(121)	0·321 (27)	0·539 (28)	1·126 (31)	1·20 (72)
H(122)	0·311 (31)	0·610 (32)	1·190 (35)	3·45 (86)
H(14)	0·333 (28)	0·693 (27)	0·950 (32)	2·41 (74)
H(151)	0·393 (24)	0·687 (23)	0·505 (31)	0·00 (61)
H(152)	0·400 (25)	0·735 (24)	0·667 (30)	0·11 (61)
H(161)	0·507 (27)	0·693 (27)	0·861 (32)	1·08 (75)
H(162)	0·499 (28)	0·642 (29)	0·686 (33)	1·58 (73)
H(17)	0·434 (23)	0·639 (22)	1·120 (25)	0·00 (52)
H(181)	0·317 (25)	0·550 (26)	0·645 (30)	0·54 (66)
H(182)	0·409 (28)	0·568 (28)	0·607 (31)	2·31 (76)
H(183)	0·384 (27)	0·518 (27)	0·765 (31)	1·41 (74)
H(191)	0·141 (29)	0·601 (30)	0·517 (36)	2·36 (80)
H(192)	0·055 (26)	0·607 (24)	0·564 (27)	0·66 (60)
H(193)	0·111 (28)	0·556 (30)	0·667 (34)	1·88 (77)
H(2'1)	0·673 (25)	0·651 (26)	1·127 (30)	0·89 (65)
H(3'1)	0·780 (33)	0·671 (31)	0·884 (35)	4·51 (96)
H(5'1)	0·698 (25)	0·526 (24)	0·489 (30)	0·95 (66)
H(6'1)	0·597 (27)	0·509 (27)	0·750 (29)	1·02 (69)
H(7'1)	0·864 (31)	0·578 (29)	0·532 (38)	3·54 (92)
H(7'2)	0·833 (30)	0·654 (30)	0·514 (37)	2·40 (85)
H(7'3)	0·797 (34)	0·588 (33)	0·368 (38)	4·48 (100)
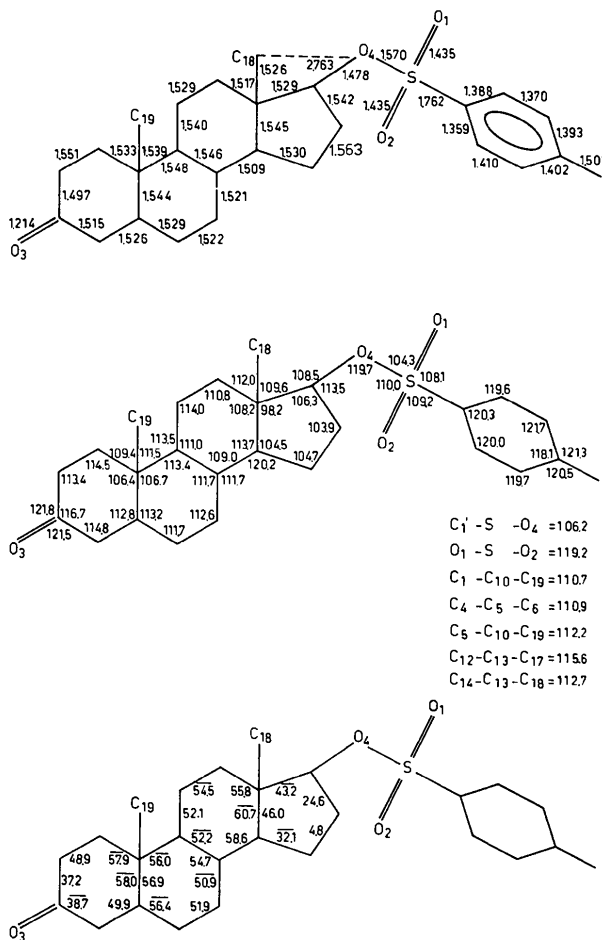
Fig. 2. Geometrical entities of AOT.

The conformation of ring A is a distorted chair. The mean angle of puckering is 48·4°, a low value compared with 55·9° for cyclohexane (Geise, Buys & Mijlhoff, 1971). A similar value (49·6°) was found by Ferguson, Macaulay, Midgley, Robertson & Whalley (1970) for 4,4-dimethyl-3-oxo-5α-androstan-17β-ol iodoacetate. These authors attribute the deformation to a rotation about the C(4)–C(5) bond due to interaction of the axial methyl groups on C(4) and C(10).
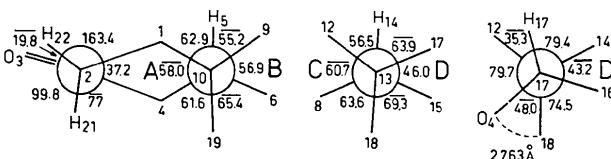

Fig. 3. Some Newman projections at important points in the molecule.

Table 6. *Bond lengths (Å) and valency angles (°) of rings C and D of AOT, EMT and MAB*

	AOT	EMT	MAB		AOT	EMT	MAB
13–14	1·545	1·554	1·545	17–13–14	98·2	96·9	96·6
14–15	1·530	1·536	1·546	13–14–15	104·5	104·6	104·0
15–16	1·563	1·561	1·526	14–15–16	104·7	102·6	104·3
16–17	1·542	1·543	1·527	15–16–17	103·9	105·3	104·7
13–17	1·529	1·527	1·530	16–17–13	106·3	105·0	105·2
13–12	1·517	1·517	1·518	12–13–18	112·0	111·0	111·4
13–18	1·526	1·527	1·557	17–13–18	109·6	110·8	111·1
17– 4	1·478	1·478	1·487	13–12–11	110·8	110·4	110·8
8–14	1·509	1·505	1·531	12–11– 9	114·0	113·6	113·3
12–11	1·529	1·539	1·544	11– 9– 8	111·0	112·4	113·2
11– 9	1·540	1·522	1·532	9– 8–14	109·0	108·7	109·4
9– 8	1·546	1·544	1·540	8–14–13	113·7	113·8	112·0
				12–13–14	108·2	109·1	108·6

In our case an explanation is less easily available. An attempt has been made to reproduce the geometry of AOT by a Westheimer type of computation, using the force-field of Altona (Altona & Hirschmann, 1970; Altona & Sundaralingam, 1970). The results, especially for ring *A*, were rather disappointing. Large discrepancies in the torsion angles in ring *A* (and to a certain extent in ring *B*) were obtained. However, the minimum of the potential energy curve is extremely flat for a ring of this particular type. A change of 10° in the endocyclic torsion angles about C(2)–C(3) and C(3)–C(4) resulted in an energy increase of no more than 0.20 kcal mol^{-1}. Therefore, crystal forces may be the cause of the observed abnormally low angle of puckering. No transmission of this distortion to the rings *C* and *D* is observed. By comparison of the geometrical entities of AOT, EMT (see next paper) and 2β-methyl-3-oxo-oestra-4-en-17β-ol p-bromobenzenesulphonate (Cody & Duax, 1972; hereafter MAB) a striking agreement between corresponding values in rings *C* and *D* is obvious (Tables 6 and 7). However, there is a slight effect in ring *B*. The torsional angle C(6)–C(7)–C(8)–C(9) is especially affected, being 50.6° in AOT compared with 55.8° in EMT and 61.7° in MAB. Ring *D* is described by the phase angle $\Delta = 24.6°$ and the angle of puckering $\varphi_m = 47.5°$ (Altona, Geise & Romers, 1968). The conformation tends to a C(13) envelope.

Table 7. *Torsion angles (°) of rings C and D of AOT, EMT and MAB*

	AOT	EMT	MAB
17–13–14–15	46.0	49.3	47.1
13–14–15–16	−32.1	−34.1	−30.9
14–15–16–17	4.8	5.1	1.1
15–16–17–13	24.6	26.1	29.5
16–17–13–14	−43.2	−45.3	−46.9
12–13–14– 8	−60.7	−59.6	−62.3
13–14– 8– 9	58.6	56.9	57.9
14– 8– 9–11	−52.2	−52.4	−50.8
8– 9–11–12	52.1	52.5	49.2
9–11–12–13	−54.5	−53.9	−52.7
11–12–13–14	55.8	55.0	57.7

The packing of AOT is shown in Table 8: each molecule is surrounded by 12 nearest neighbours. We observe no remarkably short intermolecular distances.

Table 8. *Packing of AOT*

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

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