Crystal Structure of 2α,3α-Epithio-5α-androst-6-en-17β-yl *p*-Bromobenzoate

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The crystal structure of the title compound (II) has been determined by three-dimensional *X*-ray analysis from diffractometer data. Crystals are orthorhombic, $a = 18.796 \pm 0.003$, $b = 9.657 \pm 0.002$, $c = 12.773 \pm 0.003$ Å, $Z = 4$, space group $P2_12_12_1$. The structure was solved by the program SEARCHER, for automatic heavy-atom analysis, and refined by full-matrix least-squares calculations to a final R of 0.083 for 1 273 independently observed reflections. Hydrogen atoms were located from a difference-Fourier synthesis. The absolute configuration was determined by the anomalous dispersion method. All the ring junctions are *trans,trans*. Rings A and B of the steroid skeleton have a half-chair, and ring C a chair conformation. The cyclopentane ring D has a distorted C(13) envelope conformation.

As thiosteroid derivatives have many interesting physiological and biological properties, Takeda [1,2] and his coworkers have studied the structure and conformational properties of these compounds on the basis of chemical evidence. In conjunction with a chemical study of thiosteroid derivatives, we have recently determined [3] the structure of 2α,3α-epithio-5α-androstan-17β-yl *p*-bromobenzoate (I), and found that introduction of the thiiran ring has some influence on the conformation of ring A. The present *X*-ray crystal structure analysis was undertaken in order to obtain detailed information of the molecular conformation of 2α,3α-epithio-5α-androst-6-en-17β-yl *p*-bromobenzoate (II).

EXPERIMENTAL

Crystals of (II) were prepared [4] and recrystallized from ethyl acetate as colourless prisms, m.p. 180—181 °C, elongated along *b*. Preliminary space-group data were

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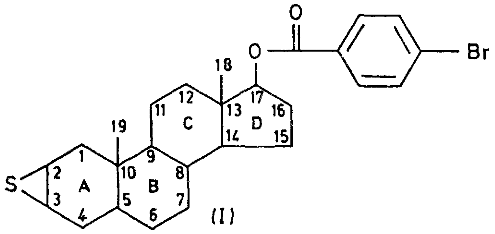
[1] K. Takeda, T. Komeno, J. Kawanami, S. Ishihara, H. Kadokawa, H. Tokura, and H. Itani, *Tetrahedron*, 1965, **21**, 329.

[2] K. Takeda, T. Komeno, S. Hayashi, S. Ishihara, H. Itani, H. Iwakura, A. Tanaka, and T. Miyake, *Ann. Report Shionogi Research Laboratory*, 1969, **19**, 1.

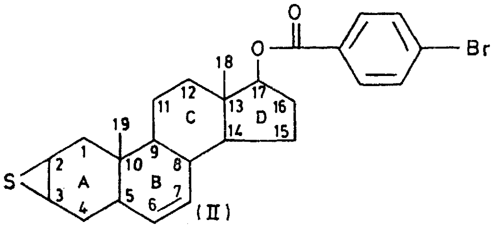
[3] K. Utsumi-Oda and H. Koyama, *J.C.S. Perkin II*, **1973**, 1866.

[4] T. Komeno, ref. 2.

determined from Weissenberg and precession photographs by use of Cu-K_α (λ = 1.5418 Å) radiation, and accurate unit-cell dimensions were obtained by least squares refinement of



(I)



(II)

the setting angles of 20 reflections measured on the automatic diffractometer.

Crystal Data.—$C_{26}H_{31}O_2SBr$, $M = 487.5$, Orthorhombic, $a = 18.796 \pm 0.003$, $b = 9.657 \pm 0.002$, $c = 12.773 \pm 0.003$ Å, $U = 2\,318$ Å^3, $D_m = 1.392$ (by flotation), $Z = 4$, $D_c = 1.396$, $F(000) = 1\,016$. Space group $P2_12_12_1$ (D_2^4, No. 19), from systematic absences: $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 19.88 cm^{-1}.

Three-dimensional intensity data were collected on a Hilger and Watts automatic four-circle Y 290 diffractometer controlled by a PDP 8 computer. Integrated intensities were measured for $\theta < 27.5°$ by the θ—2θ scan technique with Mo-K_α radiation and a scintillation counter (with a Zirconium filter and pulse-height analyser). Each reflection was integrated in 80 steps of 0.01°. A standard reflection was monitored every 10 reflections. Scan counts (P) and background counts (B_1,B_2) were combined to yield the integrated intensities $I = P - 2(B_1 + B_2)$.

3 009 Independent reflections were recorded, of which 1 273 having intensities $I > 3\sigma(I)$ were considered observed. All intensities were corrected for Lorentz and polarization factors, and structure amplitudes were derived. No absorption corrections were applied since the specimen was considered to be sufficiently small (0.32 × 0.30 × 0.30 mm).

Structure Analysis.—The structure was solved by the SEARCHER programme for automatic heavy-atom analysis, written [5,6] for the CDC 3600 computer (later modified for CDC 6600 computer). Initial co-ordinates for the bromine atom were easily derived from a three-dimensional Patterson synthesis. The atomic co-ordinates of 29 light atoms, which were treated as carbon atoms, were found from the first cycle of the SEARCHER programme (CDC 6600 computer).

The co-ordinates of the 30 atoms from the first SEARCHER cycle were refined [7] by full-matrix least-

TABLE 1

Final fractional atomic co-ordinates and anisotropic thermal parameters (× 10^4) *, with estimated standard deviations in parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	11 300(1)	−1 200(2)	924(2)	36(0)	272(4)	124(2)	−3(1)	10(1)	−48(3)
S	2 849(2)	−1 568(5)	−557(4)	44(1)	172(8)	115(5)	−2(3)	4(2)	−18(5)
O(1)	7 828(6)	−491(11)	2 259(9)	40(4)	93(15)	77(9)	1(7)	7(5)	14(10)
O(2)	8 132(6)	−2 062(15)	3 438(9)	44(4)	206(22)	64(9)	−10(9)	−12(5)	50(13)
C(1)	4 249(7)	−376(18)	−512(13)	24(5)	142(24)	55(11)	14(9)	−4(6)	−25(15)
C(2)	3 484(9)	−181(23)	−898(16)	43(7)	213(34)	88(15)	2(13)	−0(10)	−2(24)
C(3)	2 934(10)	216(25)	−194(19)	34(6)	272(44)	137(23)	46(15)	12(11)	148(28)
C(4)	3 104(9)	617(20)	937(17)	44(7)	168(29)	95(17)	−25(12)	30(10)	−12(22)
C(5)	3 817(6)	135(18)	1 283(14)	5(3)	144(24)	114(17)	5(8)	−0(6)	−19(17)
C(6)	4 008(9)	604(19)	2 365(16)	34(6)	130(27)	102(17)	−11(11)	8(9)	−19(19)
C(7)	4 629(9)	880(17)	2 693(12)	45(6)	81(21)	52(12)	−7(11)	−6(7)	29(14)
C(8)	5 267(9)	820(18)	1 991(11)	41(6)	133(26)	21(9)	23(11)	15(6)	−28(14)
C(9)	5 119(7)	−038(13)	1 003(14)	26(4)	26(14)	114(16)	16(7)	49(8)	13(15)
C(10)	4 424(10)	420(16)	499(16)	42(7)	64(20)	112(19)	25(10)	29(10)	7(17)
C(11)	5 771(9)	−70(19)	285(12)	45(7)	139(26)	51(13)	−27(12)	9(7)	2(16)
C(12)	6 443(6)	−641(17)	836(14)	17(4)	143(24)	94(14)	−22(8)	−12(7)	−7(18)
C(13)	6 580(7)	170(14)	1 816(12)	23(4)	49(18)	54(11)	2(7)	22(6)	−12(12)
C(14)	5 916(9)	173(19)	2 516(11)	50(7)	158(28)	24(10)	−35(12)	−16(7)	−25(15)
C(15)	6 199(11)	747(22)	3 576(14)	56(8)	196(34)	76(14)	−23(16)	8(10)	−3(19)
C(16)	6 966(10)	194(24)	3 620(16)	47(8)	194(34)	88(17)	−13(15)	4(9)	20(21)
C(17)	7 088(8)	−547(18)	2 559(14)	24(5)	146(26)	74(14)	11(10)	19(7)	−14(17)
C(18)	6 852(8)	1 624(26)	1 556(16)	20(5)	297(47)	110(18)	0(13)	0(8)	3(26)
C(19)	4 406(8)	1 963(20)	241(14)	22(5)	191(32)	79(16)	17(11)	−6(7)	11(18)
C(1′)	9 012(8)	−1 261(20)	2 250(11)	27(4)	143(25)	35(10)	−29(11)	−22(6)	−8(17)
C(2′)	9 179(8)	−380(16)	1 428(13)	31(5)	90(22)	60(12)	38(9)	−7(7)	−1(14)
C(3′)	9 897(11)	−473(24)	1 094(15)	48(8)	230(41)	86(18)	20(15)	−22(11)	19(23)
C(4′)	10 376(8)	−1 184(20)	1 434(15)	27(5)	99(22)	102(15)	13(11)	−21(8)	−21(18)
C(5′)	10 171(8)	−2 167(19)	2 264(17)	25(5)	131(26)	120(20)	−18(11)	−20(9)	05(21)
C(6′)	9 496(9)	−2 196(19)	2 622(13)	37(6)	153(26)	50(13)	−6(12)	−4(8)	33(16)
C(7′)	8 258(9)	−1 345(18)	2 723(14)	44(7)	72(21)	76(15)	8(12)	−6(9)	24(17)

* In the form: $T = \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$.

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[5] H. Koyama and K. Okada, 1970, SEARCHER, A Fortran program for the automatic heavy-atom analysis of organic compounds, Shionogi Research Laboratory, Osaka, Japan.

[6] H. Koyama and K. Okada, *Acta Cryst.*, 1970, **B26**, 444.

[7] W. L. Busing, K. O. Martin, and H. A. Levy, ORFLS, A Fortran crystallographic least-squares program, Oak Ridge National Laboratory, Tennessee, Report ORNL TM 305, 1962.

squares calculations. After three cycles, with isotropic temperature factors, R was 0.118. At this stage, a three dimensional difference-Fourier synthesis was calculated and the positions of the **31** hydrogen atoms were found and their positions (only) were refined subsequently (B values were fixed at 2.43 Å^2). The final five cycles of full-matrix least-squares refinement, which were carried out on a CDC 6600 computer, decreased R to 0.083 for the 1 273 observed reflexions. In this refinement the function minimized was $\Sigma w(F_o - F_c)^2$ with unit weights.

TABLE 2

Final fractional hydrogen atomic co-ordinates ($\times 10^3$)

Atom	x	y	z
H(1a)	463	−041	−95
H(1b)	437	−145	−23
H(2)	357	−42	−166
H(3)	268	74	−54
H(4a)	266	5	128
H(4b)	310	146	88
H(5)	379	−114	118
H(6)	353	29	248
H(7)	473	144	336
H(8)	543	179	174
H(9)	503	−114	111
H(11a)	586	56	−1
H(11b)	570	−82	−35
H(12a)	622	−153	83
H(12b)	698	−71	54
H(14)	580	−98	270
H(15a)	595	29	391
H(15b)	616	173	331
H(16a)	733	99	376
H(16b)	689	−42	408
H(17)	694	−150	280
H(18a)	712	193	210
H(18b)	647	192	117
H(18c)	722	156	129
H(19a)	441	276	82
H(19b)	484	212	−4
H(19c)	387	243	−31
H(2′)	893	33	119
H(3′)	980	13	73
H(5′)	1 059	−222	246
H(6′)	939	−286	313

Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21258 (4 pp, 1 microfiche).* Atomic scattering factors used in all calculations were taken from ref. 8 for non-hydrogen and from ref. 9 for hydrogen atoms.

Final positional and thermal parameters, with their estimated standard deviations, are given in Tables 1 and 2.

Absolute Configuration.—In the final stage of the analysis the absolute configuration of the molecule was determined by the anomalous dispersion method.[10] The differences between $I_o(hkl)$ and $I_o(hkl)$ were measured visually from rotation photographs rotated around the c axis, taken with Cr-K_α radiation (λ = 2.290 9 Å). Structure factors were calculated for all the hkl and hkl reflections, with a scattering factor for the bromine atom of the form $f_{Br} = f_{Br} + \Delta f'_{Br} + i\Delta f''_{Br}$, where $\Delta f'_{Br} = -0.6$ and $\Delta f''_{Br} = 2.7$. The results (Table 3) indicate that the parameters of Tables 1 and 2 represent the true absolute configuration.

TABLE 3

Determination of the absolute configuration

h	k	l	$\lvert F_c(hkl)\rvert^2$	$\lvert F_c(hkl)\rvert^2$	$I_o(hkl) \lessgtr I_o(hkl)$
2	5	1	384	625	<
3	1	1	630	1 204	<
3	2	1	739	268	>
5	7	1	169	108	>
7	7	1	118	148	<
11	3	1	334	479	<
11	4	1	475	275	>
1	5	2	32	163	<
1	7	2	136	345	<
2	5	2	428	635	<
2	6	2	376	252	>
3	4	2	3 956	3 588	>
4	7	2	299	190	>
5	3	2	62	256	<
5	5	2	449	213	>

DISCUSSION

The configuration of the molecule is illustrated[11] in Figure 1. The steroid skeleton consists of the thiiran ring and the basic 5α-androstene moiety with rings A, B, C, and D *trans*-connected.

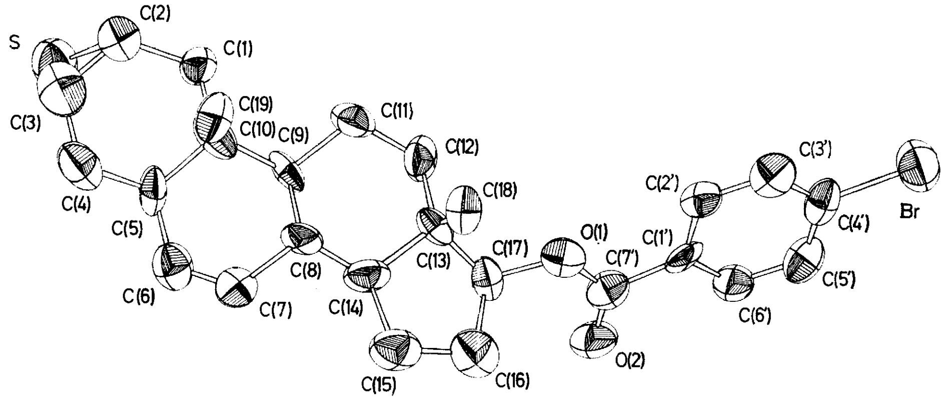

FIGURE 1 A view of molecule (II)

Intramolecular bond distances and angles are given in Table 4, together with their estimated standard deviations computed from the least-squares residuals. Mean

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

[8] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[10] J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, 1951, **168**, 271.

[11] C. K. Johnson, ORTEP, A Fortran thermal-ellipsoid plot program, Oak Ridge, National Laboratory, Tennessee, Report ORNL 3794, 1965.

TABLE 4

Interatomic distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Bond distances

Br–C(4′)	1.853(16)	C(9)–C(11)	1.530(23)
S–C(2)	1.845(21)	C(10)–C(19)	1.526(25)
S–C(3)	1.792(25)	C(11)–C(12)	1.546(23)
O(1)–C(17)	1.444(19)	C(12)–C(13)	1.500(23)
O(1)–C(7′)	1.296(21)	C(13)–C(14)	1.535(22)
O(2)–C(7′)	1.170(22)	C(13)–C(17)	1.513(22)
C(1)–C(2)	1.532(23)	C(13)–C(18)	1.531(28)
C(1)–C(10)	1.540(26)	C(14)–C(15)	1.557(25)
C(2)–C(3)	1.422(29)	C(15)–C(16)	1.538(30)
C(3)–C(4)	1.531(33)	C(16)–C(17)	1.549(28)
C(4)–C(5)	1.485(23)	C(1′)–C(2′)	1.387(23)
C(5)–C(6)	1.498(27)	C(1′)–C(6′)	1.367(24)
C(5)–C(10)	1.542(25)	C(1′)–C(7′)	1.543(23)
C(6)–C(7)	1.267(26)	C(2′)–C(3′)	1.419(26)
C(7)–C(8)	1.499(23)	C(3′)–C(4′)	1.212(28)
C(8)–C(9)	1.535(22)	C(4′)–C(5′)	1.473(28)
C(8)–C(14)	1.525(24)	C(5′)–C(6′)	1.350(24)
C(9)–C(10)	1.523(24)		

(*b*) Valency angles

C(2)–S–C(3)	46.0(9)	C(11)–C(12)–C(13)	109.5(12)
C(17)–O(1)–C(7′)	117.0(13)	C(12)–C(13)–C(14)	110.2(12)
C(2)–C(1)–C(10)	114.0(14)	C(12)–C(13)–C(17)	113.0(12)
S–C(2)–C(1)	116.1(14)	C(12)–C(13)–C(18)	110.8(14)
S–C(2)–C(3)	65.0(12)	C(14)–C(13)–C(17)	98.5(12)
C(1)–C(2)–C(3)	120.8(17)	C(14)–C(13)–C(18)	113.3(13)
S–C(3)–C(2)	69.0(13)	C(17)–C(13)–C(18)	110.2(12)
S–C(3)–C(4)	120.4(17)	C(8)–C(14)–C(13)	113.2(12)
C(2)–C(3)–C(4)	120.8(17)	C(8)–C(14)–C(15)	120.6(15)
C(3)–C(4)–C(5)	112.9(16)	C(13)–C(14)–C(15)	103.2(14)
C(4)–C(5)–C(6)	113.3(15)	C(14)–C(15)–C(16)	103.1(16)
C(4)–C(5)–C(10)	114.7(16)	C(15)–C(16)–C(17)	105.5(15)
C(6)–C(5)–C(10)	111.5(13)	O(1)–C(17)–C(13)	115.0(13)
C(5)–C(6)–C(7)	126.0(17)	O(1)–C(17)–C(16)	110.9(13)
C(6)–C(7)–C(8)	122.0(16)	C(13)–C(17)–C(16)	104.0(13)
C(7)–C(8)–C(9)	111.5(13)	C(2′)–C(1′)–C(6′)	121.1(14)
C(7)–C(8)–C(14)	113.1(12)	C(2′)–C(1′)–C(7′)	122.4(14)
C(9)–C(8)–C(14)	106.5(13)	C(6′)–C(1′)–C(7′)	116.1(15)
C(8)–C(9)–C(10)	110.2(12)	C(1′)–C(2′)–C(3′)	113.8(15)
C(8)–C(9)–C(11)	110.9(12)	C(2′)–C(3′)–C(4′)	129.4(20)
C(10)–C(9)–C(11)	116.1(15)	Br–C(4′)–C(3′)	125.0(16)
C(1)–C(10)–C(5)	107.3(14)	Br–C(4′)–C(5′)	119.4(12)
C(1)–C(10)–C(9)	113.0(14)	C(3′)–C(4′)–C(5′)	115.3(16)
C(1)–C(10)–C(19)	107.5(15)	C(4′)–C(5′)–C(6′)	120.2(16)
C(5)–C(10)–C(9)	108.0(15)	C(1′)–C(6′)–C(5′)	119.6(16)
C(5)–C(10)–C(19)	107.3(14)	O(1)–C(7′)–O(2)	127.3(17)
C(9)–C(10)–C(19)	113.1(14)	O(1)–C(7′)–C(1′)	111.0(15)
C(9)–C(11)–C(12)	112.8(13)	O(2)–C(7′)–C(1′)	121.4(16)

(*c*) Bond distances (Å) associated with hydrogen positions

C(1)–H(1a)	0·92	C(15)–H(15a)	0.76
C(1)–H(1b)	1.12	C(15)–H(15b)	1.01
C(2)–H(2)	1.02	C(16)–H(16a)	1.05
C(3)–H(3)	0.82	C(16)–H(16b)	0.84
C(4)–H(4a)	1.08	C(17)–H(17)	1.01
C(4)–H(4b)	0.81	C(18)–H(18a)	0.92
C(5)–H(5)	1.24	C(18)–H(18b)	0.90
C(6)–H(6)	0.94	C(18)–H(18c)	0.77
C(7)–H(7)	1.03	C(19)–H(19a)	1.07
C(8)–H(8)	1.04	C(19)–H(19b)	0.90
C(9)–H(9)	1.09	C(19)–H(19c)	1.30
C(11)–H(11a)	0.74	C(2′)–H(2′)	0.88
C(11)–H(11b)	1.10	C(3′)–H(3′)	0.76
C(12)–H(12a)	0.96	C(5′)–H(5′)	0.84
C(12)–H(12b)	1.09	C(6′)–H(6′)	0.93
C(14)–H(14)	1.16		

estimated standard deviations are *ca.* 0.024 Å and 1.4°. Most observed bond distances and angles are comparable to those found in other androstene-type steroids.[12–16] The geometry of molecule (II) is somewhat different from that of the previously reported 2α,3α-epithio-5α-androstan-17β-yl *p*-bromobenzoate (I). A major difference between the stereochemistry of the steroid nucleus in the two structures, being due to the presence of the double bond C(6)=C(7) in (II). Two or three differences which appear to be significant in terms of the estimated standard

TABLE 5

Comparison of bond distances, bond angles, and torsion angles in (I) [a] and (II) [b]

(*a*) Bond distances (Å)

	(I)	(II)		(I)	(II)
(i) Epithio-ring					
S–C(2)	1.788	1.845	C(2)–C(3)	1.474	1.422
S–C(3)	1.775	1.792			
(ii) Ring A					
C(1)–C(2)	1.519	1.532	C(4)–C(5)	1.548	1.485
C(2)–C(3)	1.474	1.422	C(5)–C(10)	1.565	1.542
C(3)–C(4)	1.488	1.531	C(10)–C(1)	1.488	1.540
(iii) Ring B					
C(5)–C(6)	1.482	1.498	C(8)–C(9)	1.581	1.535
C(6)–C(7)	1.591	1.267	C(9)–C(10)	1.554	1.523
C(7)–C(8)	1.510	1.499	C(10)–C(5)	1.565	1.542
(iv) Ring C					
C(8)–C(9)	1.581	1.535	C(12)–C(13)	1.486	1.500
C(9)–C(11)	1.480	1.530	C(13)–C(14)	1.584	1.535
C(11)–C(12)	1.534	1.546	C(14)–C(8)	1.503	1.525
(v) Ring D					
C(13)–C(14)	1.584	1.535	C(16)–C(17)	1.468	1.549
C(14)–C(15)	1.521	1.557	C(17)–C(13)	1.533	1.513
C(15)–C(16)	1.601	1.538			

(*b*) Bond angles (°)

	(I)	(II)		(I)	(II)
(i) Epithio-ring					
C(2)–S–C(3)	48.8	46.0	C(2)–C(3)–S	66.0	69.0
C(3)–C(2)–S	65.1	65.0			
(ii) Ring A					
C(1)–C(2)–C(3)	118.2	120.8	C(4)–C(5)–C(10)	110.1	114.7
C(2)–C(3)–C(4)	120.2	120.8	C(5)–C(10)–C(1)	106.1	107.3
C(3)–C(4)–C(5)	113.1	112.9	C(10)–C(1)–C(2)	118.0	114.0
(iii) Ring B					
C(5)–C(6)–C(7)	110.9	126.0	C(8)–C(9)–C(10)	111.7	110.2
C(6)–C(7)–C(8)	109.6	122.0	C(9)–C(10)–C(5)	105.8	108.0
C(7)–C(8)–C(9)	109.0	111.5	C(10)–C(5)–C(6)	112.4	111.5
(iv) Ring C					
C(8)–C(9)–C(10)	111.7	110.2	C(12)–C(13)–C(14)	108.0	110.2
C(9)–C(11)–C(12)	114.1	112.8	C(13)–C(14)–C(8)	110.4	113.2
C(11)–C(12)–C(13)	111.2	109.5	C(14)–C(8)–C(9)	108.9	106.5
(v) Ring D					
C(13)–C(14)–C(15)	101.0	103.2	C(16)–C(17)–C(13)	105.8	104.0
C(14)–C(15)–C(16)	103.3	103.1	C(17)–C(13)–C(14)	99.3	98.5
C(15)–C(16)–C(17)	106.1	105.5			

(*c*) Torsion angles (°) between the steroid skeleton and *p*-bromobenzoate group

	(I)	(II)
C(13)–C(17)–O(1)–C(7′)	−164.679	−164.670
C(16)–C(17)–O(1)–C(7′)	73.642	78.249
C(17)–O(1)–C(7′)–C(1′)	−179,804	173.600
C(17)–O(1)–C(7′)–O(2)	−22.066	−8.774
O(2)–C(7′)–C(1′)–C(2′)	169.589	−177.914
O(2)–C(7′)–C(1′)–C(6′)	−11.218	7.083
O(1)–C(7′)–C(1′)–C(2′)	−23.078	−0.185
O(1)–C(7′)–C(1′)–C(6′)	156.113	−175.189

[a] From ref. 3. [b] Present work.

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[12] C. M. Weeks, A. Cooper, and D. A. Norton, *Acta Cryst.*, 1971, **B27**, 531.

[13] E. Thom and A. T. Christensen, *Acta Cryst.*, 1971, **B27**, 794.

[14] C. M. Weeks, H. Hauptman, D. A. Norton, *Cryst. Struct. Comm.*, 1972, **1**, 79.

[15] H. C. Mez and G. Rihs, *Helv. Chim. Acta*, 1972, **55**, 375.

[16] D. L. Ward, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1973, **B29**, 2016.

deviations are more likely to indicate a slight underestimation of errors. Table 5 summarizes the bond distances and angles of the steroid skeleton in the two molecules. The mean C–C single bond distances in the steroid skeleton are 1.525 Å. The C–S bonds (1.792 and 1.845 Å) in the thiiran ring are slightly different from a C–S single bond distance (1.817 Å), but similar distances were observed in the recently determined structures of sulphur-containing heterocyclic compounds.[17-20] The bond distances in the *p*-bromobenzoate group are as expected and in good agreement with those reported previously.[21-23] C–H distances range from 0.74 to 1.30 Å, the mean (0.97 Å) being shorter than the internuclear separations (1.08 Å) obtained spectroscopically.[24]

The bond angles in the thiiran ring are as expected. The mean interbond angle in rings A, B, and C is 110.9°, except for the angles at C(2), C(3), C(6), and C(7) atoms, which are slightly, but not significantly, greater than the normal tetrahedral angle of 109.4°. The angles in the five-membered ring D are similar to corresponding angles in other steroids.[25-27] It may be that introduction of the double bond C(6)=C(7) in ring B has no influence on the conformation of ring D. Maximum distortion of bond angles occurs at C(13) in ring D. The angle C(14)–C(13)–C(17) of *ca.* 99° is an indication of strain imposed at the C/D junction. The various torsion angles between the steroid skeleton and *p*-bromobenzoate group were calculated and are listed in Table 5(*c*).

TABLE 6

Equations of planes, and in square brackets, displacements (Å) of the atoms from mean planes; X, Y, Z are orthogonal co-ordinates (Å)

Plane (I): C(1)—(4)

$$0.1827X + 0.9473Y - 0.2629Z = 1.3021$$

[C(1) −0.01, C(2) 0.03, C(3) −0.03, C(4) 0.01, C(5) −0.29, C(10) 0.43]

Plane (II): C(5)—(8)

$$-0.1402X + 0.9538Y - 0.2654Z = -1.3116$$

[C(5) −0.00, C(6) 0.01, C(7) −0.01, C(8) 0.00, C(9) −0.41, C(10) 0.36]

Plane (III): C(8), C(11), C(12), C(14)

$$0.4779X + 0.8704Y - 0.1178Z = 5.1024$$

[C(8) 0.02, C(9) −0.68, C(11) −0.02, C(12) 0.02, C(13) 0.68, C(14) −0.02]

Plane (IV): C(15)—(17)

$$0.3321X + 0.8558Y - 0.3965Z = 2.6760$$

[C(13) 0.65, C(14) −0.11]

Plane (V): C(1′)—(6′)

$$0.2527X + 0.6878Y + 0.6804Z = 5.3625$$

[C(1′) 0.03, C(2′) −0.01, C(3′) −0.02, C(4′) 0.02, C(5′) −0.00, C(6′) −0.03, C(7′) 0.03, O(1) 0.00, O(2) 0.12, Br 0.01]

Deviations from the best plane through the various atom groups are in Table 6. The benzene ring is planar, and rings A and B of the steroid skeleton have the half-chair conformation. The atoms C(5)—C(8) are nearly coplanar and atoms C(9) and C(10) are displaced by −0.41 and 0.36 Å to opposite sides of this plane. Ring C is in the normal chair form, while ring D has a slightly distorted β envelope.

In order to obtain detailed information on the molecular shape and the conformational features we calculated the displacements from the planes through C(8), C(10), and C(13) in the steroid skeleton (Figure 2). Atoms C(18), C(19), and O(1) are on the β side of the ring system of the steroid skeleton, while the S atom is on the α side.

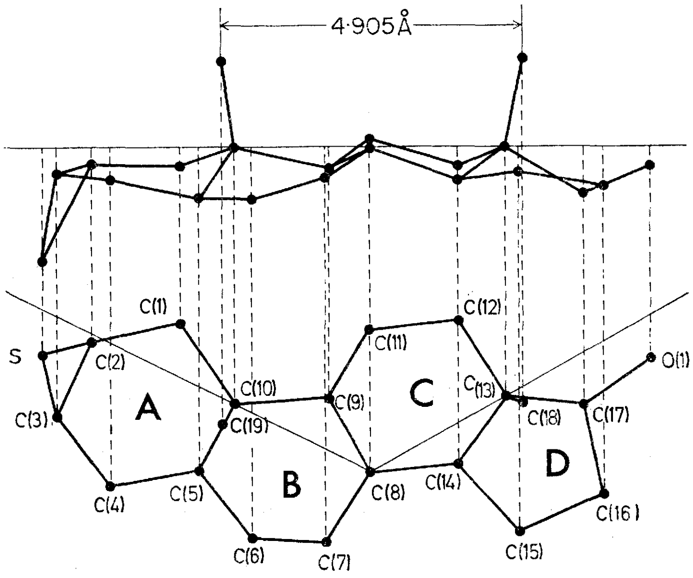

FIGURE 2 Projection of the steroid nucleus on the plane of C(10), C(8), and C(13)

TABLE 7

Intermolecular distances <3.60 Å

$Br\cdots S^{I}$	3.491	$S\cdots C(7'^{II})$	3·507
$S\cdots O(1^{II})$	3.576	$O(2)\cdots C(4^{III})$	3.324

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x + 1, y, z$ II $-\frac{1}{2} + x, -\frac{1}{2} - y, -z$
III $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$

The presence of the thiiran ring does not significantly affect the overall planarity of the steroid skeleton. Indeed, the distance of 4.905 Å between the C(18) and C(19) axial methyl groups is comparable to that found in other steroids. However, it may be concluded that introduction of the thiiran ring has some influence on the conformation of ring A. The dihedral angle between the thiiran ring and the least-squares plane through atoms

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[17] J. J. H. McDowell, *Acta Cryst.*, 1970, **B26**, 954.

[18] M. Fehlaman, *Acta Cryst.*, 1970, **B26**, 1736.

[19] R. M. Schaffrin and J. Trotter, *J. Chem. Soc.* (*A*), 1970, 1561.

[20] W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Nagel, F. Wudl, and P. Coppens, *Chem. Comm.*, 1971, 889.

[21] J. C. Portheine and C. Romers, *Acta Cryst.*, 1970, **B26**, 1791.

[22] H. Koyama, M. Shiro, T. Sato, and Y. Tsukuda, *J. Chem. Soc.* (*B*), 1970, 443.

[23] J. C. Portheine, C. Romers, and E. W. M. Rutten, *Acta Cryst.*, 1972, **B28**, 849.

[24] L. E. Sutton, *Chem. Soc. Special Publ.*, No. 18, 1965.

[25] P. B. Braun, J. Hornstra, and J. I. Leenhouts, *Acta Cryst.*, 1970, **B26**, 352.

[26] C. M. Weeks and D. A. Norton, *J. Chem. Soc.* (*B*), 1970, 1494.

[27] D. R. Pollard and F. R. Ahmed, *Acta Cryst.*, 1971, **B27**, 1976.

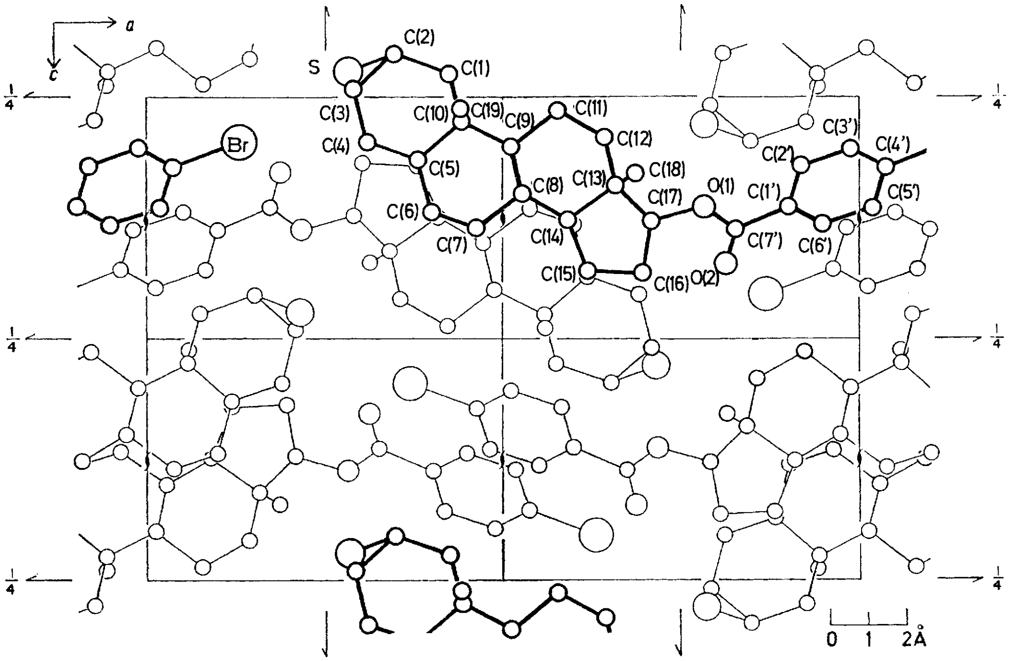

FIGURE 3 The structure viewed down the *b* axis

C(1)—(4) is *ca.* 69.7°. The torsion angle H(2)-C(2)-C(3)-H(3) is *ca.* −30°. The width of the steroid skeleton, calculated as the distance between C(3) and O(1), is 9.766 Å.

The packing of molecules in the unit-cell is illustrated in Figure 3. The mean plane of the steroid skeleton is nearly parallel to the *ac* plane of the cell. All intermolecular distances were calculated, and the most significant contacts (<3.60 Å) are given in Table 7. There is no hydrogen bonding in the crystal, the shortest contact being O(2) $\cdots$ C(4^{III}) 3.324 Å. Other intermolecular contacts are greater than the sum of the van der Waals radii.

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