Acta Cryst. (1976). B**32**, 397

The Crystal and Molecular Structure of 7a-Methyl-4,7-dioxocyclopenta[*b*]thiopyran 1,1-Dioxide

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(*Received* 9 *June* 1975; *accepted* 14 *June* 1975)

$C_9H_{12}O_4S$ is monoclinic, space group $P2_1/n$, with $a=14{\cdot}304$ (5), $b=9{\cdot}966$ (6), $c=6{\cdot}968$ (4) Å, $\beta=95{\cdot}02$ (2)°, $Z=4$. The structure was solved by the heavy-atom method, and refined to an R of 0·071 for 1325 visual reflexions. The S–O lengths are 1·446 (5) and 1·435 (5), the S–C lengths 1·761 (6) and 1·812 (5), and the C–O lengths 1·207 (7) and 1·208 (7) Å. The $C(sp^3)$–$C(sp^3)$ lengths vary between 1·524 (8) and 1·567 (7), and the $C(sp^2)$–$C(sp^3)$ lengths between 1·503 (8) and 1·547 (7) Å. The structure is held together by van der Waals forces. The six-membered ring has a chair, and the five-membered ring an almost perfect half-chair conformation. The C(7a) methyl is in an axial position and is *cis* to the C(4a) hydrogen.

Introduction

Heterocyclic steroids are drawing attention because of their interesting pharmacological properties (Huisman, 1968). The title compound (Fig. 1) was synthesized in our Bio-Organic Division (Jogdeo & Bhide, 1974) during the course of work on the total synthesis of thia analogues of steroids, particularly of oestrone. The molecule is intended to constitute the *C*/*D* rings of the complete steroid. Since the *C*/*D* ring fusion is normally *trans* in steroids (Klyne, 1965), it was necessary to ascertain that the C(7a) methyl is indeed *trans* to the C(4a) hydrogen before the total synthesis could proceed further. As the chemical and spectroscopic data did not provide an answer, the present X-ray study was undertaken to settle the question and also to obtain detailed stereochemical information about this new heterocycle.

Experimental

Colourless, transparent crystals were obtained from a warm solution in chloroform–hexane. The lattice parameters at room termpertaure were determined from zero-layer Weissenberg data by least-squares refinement with the program *CELPAR* (Wadhawan, 1972). The refinement included a correction for film shrinkage and radius error.

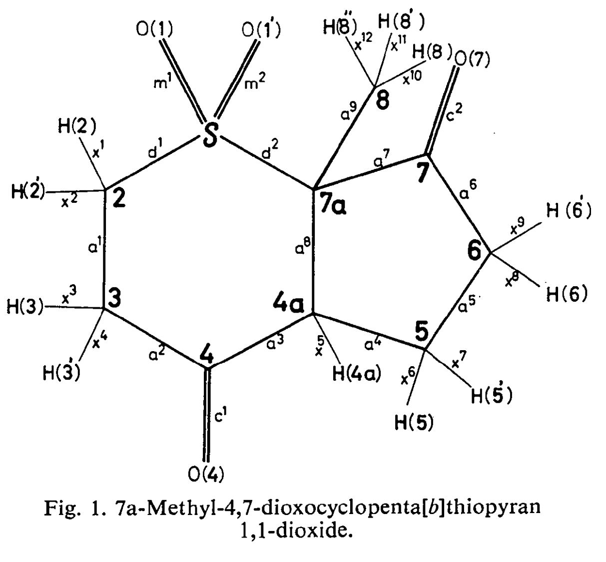

Fig. 1. 7a-Methyl-4,7-dioxocyclopenta[*b*]thiopyran 1,1-dioxide.

Crystal data

$C_9H_{12}O_4S$, $M=216{\cdot}2$, $a=14{\cdot}304$ (5), $b=9{\cdot}966$ (6), $c=6{\cdot}968$ (4) Å, $\beta=95{\cdot}02$ (2)°, $V=989{\cdot}6$ (9) Å^3, $D_x=1{\cdot}452$ (2) g cm^{-3}, $Z=4$, $F(000)=456$. Systematic absences: $0k0$, k odd; $h0l$, $h+l$ odd. Space group: $P2_1/n$. $\mu(\text{Cu } K\alpha)=27{\cdot}5$ cm^{-1}.

Multiple-film equi-inclination Weissenberg photographs were taken with Ni-filtered Cu $K\alpha$ radiation, along **c** for the zero to the fifth layer, and along **b** for the zero, first, and second layers. Nearly cylindrical specimens were used, with effective radii 0·11 mm and 0·20 mm respectively. 1914 unique reflexions were recorded and estimated visually by comparison with a calibrated film strip. Corrections for absorption, spot size and Lp factor were applied (*VALPS*, Wadhawan, 1970).

Structure determination

The S position was determined from a Patterson synthesis, and the remaining non-hydrogen atoms from two successive Fourier syntheses (*FORDAP*, Zalkin, 1962). A full-matrix least-squares refinement of the atomic parameters was then carried out (*ORFLS*, Busing, Martin & Levy, 1962). The quantity minimized was $\sum w(|F_o|-K|F_c|^2)$. Scattering factors for the non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1968). Zero weights were assigned to unobserved reflexions. For observed reflexions, unit weights were taken initially, but in the later stages weights based on error-analysis plots were used. A variable parameter for isotropic extinction was included. With isotropic temperature factors, a value of 0·134 was obtained for R for 1325 observed reflexions. WR at this stage was 0·138 $[WR=\{\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2\}^{1/2}]$.

Introduction of anisotropic temperature factors gave $R=0{\cdot}096$ and $WR=0{\cdot}109$.

A difference synthesis served to locate the 12 H atoms. The refinement was then repeated, treating the H atom coordinates as variable parameters, with a single, variable, isotropic temperature factor. Scattering

Table 1. *Observed and calculated structure factors*

Successive columns contain *h*, 10|*F*(obs)| and 10*F*(calc). An asterisk before the value of |*F*(obs)| means 'less than'.

*****H 0 0*****		
2	189	-198
4	553	-597
6	71	-71
8	61	-57
10	256	265
12	154	146
14	142	-130
16	83	-80
18	81	81
*****H 1 0*****		
1	39	15
2	832	-833
3	48	48
4	623	-671
5	119	-116
6	381	416
7	131	137
8	76	-51
9	95	91
10	84	64
11	*44	-31
12	223	-244
13	47	27
14	*46	45
15	75	-74
16	75	47
17	*40	27
18	*27	22
*****H 2 0*****		
0	919	-879
1	64	102
2	284	306
3	508	-521
4	314	-508
5	88	-75
6	247	-245
7	275	275
8	98	-101
9	123	128
10	96	-94
11	124	-137
12	*47	56
13	58	-52
14	92	72
15	*52	0
16	*46	20
17	66	60
*****H 3 0*****		
1	390	-411
2	1216	-967
3	222	-222
4	284	294
5	501	516
6	71	77
7	178	180
8	197	174
9	331	-314
10	82	74
11	98	-94
12	*47	21
13	*47	-37
14	*55	-46
15	101	91
16	44	38
17	*35	-44
*****H 4 0*****		
0	147	-163
1	141	-125
2	102	-107
3	164	154
4	517	530
5	124	101
6	213	208
7	227	-224
8	137	-147
9	145	-145
10	155	-148
11	238	258
12	*47	31
13	*44	9
14	135	118
15	*48	-34
16	*40	-15
17	*29	11
*****H 5 0*****		
1	157	-155
2	313	327
3	35	25
4	67	59
5	59	32
6	176	-182
7	190	190
8	283	-282
9	142	137
10	*47	48
11	*47	-18
12	165	156
13	*44	44
14	*50	6
15	*43	-18
16	70	-79
*****H 6 0*****		
0	44	44
1	53	-28
2	93	92
3	190	138
4	140	-141
5	110	101
6	138	-196
7	109	-106
8	97	100
9	*47	0
10	194	143
11	*44	[illegible]
12	*44	[illegible]
13	51	52
14	78	-75
15	44	-51
16	*25	4
*H 7 0*****		
1	59	57
2	*42	43
3	43	-48
4	88	75
5	152	-153
6	*44	24
7	81	-78
8	*47	-28
9	163	166
10	*46	-15
11	*44	31
12	*50	-4
13	285	-185
14	*38	-35
15	79	-76
*****H 8 0*****		
0	106	104
1	172	-174
2	91	68
3	225	-221
4	99	-74
5	115	111
6	157	-167
7	156	142
8	*46	6
9	*45	27
10	75	60
11	103	-96
12	*44	-44
13	112	-111
14	*27	-11
*****H 9 0*****		
1	185	-188
2	97	-86
3	164	172
4	76	-65
5	114	106
6	98	97
7	*45	34
8	86	86
9	*41	-41
10	65	-34
11	41	-55
12	59	-59
*****H 10 0*****		
0	*46	-26
1	72	68
2	*45	[illegible]
3	*45	34
4	99	107
5	61	-48
6	108	105
7	76	61
8	128	-124
9	*41	-7
10	*36	-37
11	*28	-21
*****H 11 0*****		
1	86	-92
2	63	65
3	78	72
4	87	65
5	94	78
6	118	-112
7	*38	-23
8	67	-62
9	45	-45
*****H 12 0*****		
0	*39	-6
1	137	125
2	*37	14
3	92	92
4	*34	-17
5	68	-74
6	103	-126
**************		
*****H 0 1*****		
-17	45	48
-15	*48	-2
-13	133	-146
-11	98	97
-9	205	211
-7	145	137
-5	647	578
-3	182	-170
-1	43	57
1	1592	1392
3	30	44
5	269	-263
7	*38	-3
9	*45	-22
11	354	369
13	112	-100
15	89	-89
17	*40	-37
*****H 1 1*****		
-18	67	58
-17	*44	-20
-16	*53	9
-15	84	-70
-14	47	-45
-13	179	179
-12	115	-124
-11	320	129
-10	46	32
-9	121	120
-8	466	465
-7	176	163
-6	323	328
-5	572	-588
-4	810	-825
-3	86	-76
-2	461	-453
-1	958	962
0	41	-29
1	402	-371
2	609	576
3	301	-312
4	413	386
5	301	-306
6	35	35
7	141	144
8	42	-50
9	55	46
10	155	-138
11	72	75
12	79	78
13	164	-169
14	51	56
15	43	34
16	57	-50
17	153	154
*****H 2 1*****		
-18	*28	13
-17	*42	-18
-16	73	-73
-15	*47	-40
-14	51	-65
-13	119	132
-12	*51	-6
-11	70	-21
-10	384	386
-9	338	-354
-8	58	39
-7	70	-53
-6	620	-632
-5	166	-160
-4	239	-242
-3	400	-391
-2	440	453
-1	322	317
0	777	800
1	609	-557
2	112	-94
3	447	-482
4	31	21
5	*34	-7
6	160	-153
7	80	95
8	53	37
9	98	92
10	98	88
11	131	-124
12	*52	25
13	*52	50
14	133	-137
15	46	-52
16	*49	-16
17	*39	18
*****H 3 1*****		
-17	*39	-26
-16	85	-75
-15	*56	-42
-14	*49	12
-13	*51	8
-12	179	189
-11	*50	-36
-10	*48	-48
-9	46	-27
-8	307	-306
-7	166	-164
-6	69	-68
-5	212	-215
-4	419	446
-3	177	-169
-2	412	-390
-1	483	476
0	120	113
1	249	251
2	368	-384
3	120	-111
4	186	-171
5	208	187
6	406	422
7	119	-125
8	195	-126
9	161	160
10	214	-230
11	117	-117
12	112	-115
13	*52	-43
14	*60	6
15	*54	43
16	46	54
*****H 4 1*****		
-17	*34	-39
-16	*45	38
-15	*53	72
-14	*48	21
-13	109	97
-12	*52	-16
-11	53	-56
-10	160	-172
-9	69	-64
-8	99	101
-7	155	-173
-6	41	49
-5	122	132
-4	172	-163
-3	886	902
-2	76	-87
-1	113	113
0	230	-248
1	78	-92
2	142	142
3	378	-384
4	*37	14
5	*40	18
6	132	111
7	211	198
8	320	-320
9	*30	-37
10	52	-55
11	124	-130
12	139	140
13	*50	25
14	*47	58
15	129	122
16	42	-3
*****H 5 1*****		
-16	*39	-3
-15	123	145
-14	*45	6
-13	*49	-1
-12	104	77
-11	112	-109
-10	74	82
-9	81	-68
-8	*49	-32
-7	275	280
-6	*45	11
-5	74	86
-4	161	-158
-3	67	55
-2	301	294
-1	257	-273
0	97	-94
1	285	-284
2	110	105
3	232	239
4	215	209
5	191	195
6	178	-163
7	127	-120
8	112	94
9	295	-311
10	174	173
11	140	139
12	*51	-1
13	115	117
14	*55	3
15	*46	20
16	74	69
*****H 6 1*****		
-16	41	44
-15	*42	41
-14	136	126
-13	98	-106
-12	70	-71
-11	82	-92
-10	178	-188
-9	55	81
-8	52	54
-7	*50	-12
-6	253	254
-5	*47	-4
-4	46	30
-3	138	-127
-2	79	68
-1	96	91
0	100	-93
1	68	56
2	165	-163
3	147	151
4	328	333
5	283	-278
6	*49	1
7	134	-123
8	64	-60
9	75	74
10	*52	5
11	167	170
12	*48	-30
13	95	71
14	*48	29
15	86	-78
16	*18	-6
*****H 7 1*****		
-15	71	-89
-14	96	-75
-13	*41	2
-12	147	-159
-11	*49	15
-10	109	108
-9	118	136
-8	167	178
-7	91	-92
-6	*51	-31
-5	*50	2
-4	155	-140
-3	*48	-9
-2	255	-273
-1	101	90
0	116	109
1	48	35
2	235	233
3	169	-163
4	103	-91
5	*51	15
6	187	-175
7	*52	9
8	140	-131
9	*52	44
10	*51	28
11	48	38
12	*44	51
13	*48	13
14	84	-78
*****H 8 1*****		
-14	43	-47
-13	*41	-14
-12	85	72
-11	*54	-10
-10	68	62
-9	*50	-39
-8	*52	-24
-7	64	40
-6	130	-142
-5	75	-67
-4	*52	-18
-3	75	76
-2	121	125
-1	*51	-34
0	103	93
1	*51	-5
2	174	-163
3	*52	-9
4	246	-241
5	75	-43
6	*53	23
7	173	-172
8	189	189
9	116	119
10	*47	31
11	80	70
12	93	-78
13	94	-94
*****H 9 1*****		
-12	*38	18
-11	102	91
-10	*41	-8
-9	*45	55
-8	68	62
-7	50	-49
-6	103	-96
-5	130	-139
-4	95	75
-3	*52	14
-2	102	88
-1	112	102
0	217	-226
1	*53	31
2	*53	-20
3	99	-84
4	177	182
5	177	-170
6	95	85
7	105	115
8	82	90
9	128	127
10	*40	-52
11	*43	-16
12	77	-85
*****H 10 1*****		
-11	75	80
-10	*39	19
-9	*45	-49
-8	*41	-39
-7	177	-188
-6	*46	0
-5	144	156
-4	*49	21
-3	170	166
-2	*50	1
-1	*50	38
0	*51	-14
1	134	-132
2	*50	47
3	86	-79
4	*48	7
5	100	103
6	79	71
7	161	149
8	*48	-28
9	*43	-5
10	*37	-32
*****H 11 1*****		
-9	57	-60
-8	37	-50
-7	94	101
-6	*46	19
-5	109	109
-4	*51	27
-3	75	-59
-2	*44	28
-1	94	-98
0	80	-73
1	*44	-8
2	44	-59
3	74	67
4	94	79
5	102	99
6	77	60
7	75	-65
8	34	-38
*****H 12 1*****		
-5	83	-103
-4	110	107
-3	*39	-5
-2	131	-140
-1	*41	-7
0	93	-85
1	*41	-8
2	106	106
3	*38	14
4	79	78
5	*31	-40
6	*22	-37
**************		
*****H 0 2*****		
-18	*32	19
-16	131	125
-14	*55	24
-12	68	-80
-10	173	-174
-8	170	183
-6	696	732
-4	424	659
-2	63	-64
0	250	-249
2	118	-115
4	463	-461
6	499	472
8	105	-103
10	62	-55
12	229	241
14	*54	20
16	95	-79
*****H 1 2*****		
-18	119	125
-17	*46	20
-16	*56	40
-15	*51	23
-14	95	-82
-13	*56	15
-12	48	42
-11	108	-98
-10	189	192
-9	106	-112
-8	103	107
-7	344	331
-6	261	238
-5	63	69
-4	384	-457
-3	302	-383
-2	77	-92
-1	147	-145
0	201	-182
1	622	569
2	267	267
3	253	257
4	31	23
5	108	-102
6	168	-169
7	140	-139
8	192	191
9	64	-71
10	96	79
11	70	72
12	101	79
13	151	150
14	93	-62
15	*48	-9
16	71	-60
17	74	-67
*****H 2 2*****		
-17	*44	-7
-16	*54	-30
-15	*50	-1
-14	*54	-41
-13	182	-181
-12	*56	1
-11	*54	7
-10	127	-130
-9	373	386
-8	200	-218
-7	168	170
-6	*38	23
-5	299	-310
-4	28	27
-3	345	-364
-2	30	-29
-1	345	346
0	72	84
1	594	576
2	792	-726
3	135	-146
4	136	132
5	232	-233
6	107	97
7	81	81
8	174	165
9	115	103
10	97	66
11	153	157
12	148	-158
13	80	-90
14	53	-50
15	116	-102
16	*48	-3
17	*35	-27
*****H 3 2*****		
-17	70	-68
-16	*51	-43
-15	60	-67
-14	53	-45
-13	88	80
-12	80	-69
-11	179	177
-10	131	-126
-9	143	147
-8	217	218
-7	468	-635
-6	*41	36
-5	277	-280
-4	170	-161
-3	143	134
-2	125	118
-1	250	230
0	211	-187
1	*34	-11
2	212	-202
3	308	-301
4	344	340
5	314	-286
6	113	96
7	214	202
8	184	-183
9	*55	-35
10	137	129
11	130	-131
12	82	-95
13	111	-97
14	81	-81
15	*55	6
16	*44	27
*****H 4 2*****		
-17	*33	-8
-16	89	-97
-15	*57	-3
-14	*52	31
-13	74	74
-12	77	71
-11	92	-93
-10	128	131
-9	123	-128
-8	*52	20
-7	87	66
-6	*47	26
-5	81	-68
-4	60	44
-3	*41	-30
-2	112	123
-1	68	-55
0	126	-106
1	387	-378
2	106	80
3	140	-134
4	232	-224
5	272	278
6	92	79
7	*52	37
8	241	243
9	127	-137
10	108	-115
11	58	-46
12	69	-63
13	45	68
14	*59	-31
15	*50	-13
16	72	47
*****H 5 2*****		
-16	*40	1
-15	*51	-28
-14	162	167
-13	*53	4
-12	*56	41
-11	186	177
-10	101	-90
-9	111	-105
-8	111	-105
-7	*53	-17
-6	*51	1
-5	139	-129
-4	186	185
-3	165	-155
-2	*45	-20
-1	385	364
0	137	-146
1	105	104
2	311	-307
3	57	47
4	219	229
5	349	332
6	192	199
7	95	-90
8	*56	5
9	*58	-21
10	216	-224
11	95	68
12	*54	22
13	*41	4
14	101	100
15	*44	38
*****H 6 2*****		
-15	*44	46
-14	*53	-17
-13	78	78
-12	132	-147
-11	*56	-26
-10	123	-124
-9	71	-81
-8	192	196
-7	*56	-2
-6	*55	18
-5	214	192
-4	52	54
-3	204	207
-2	306	-312
-1	69	30
0	181	-170
1	161	-149
2	282	291
3	112	105
4	232	224
5	218	218
6	112	-98
7	99	-79
8	130	-151
9	116	-97
10	*57	54
11	*56	-50
12	*62	23
13	*55	4
14	99	97
15	75	82
*****H 7 2*****		
-14	*44	-49
-13	*53	-31
-12	*60	22
-11	130	-139
-10	*56	75
-9	129	133
-8	*58	23
-7	*58	30
-6	58	-50
-5	*56	-31
-4	164	-167
-3	*55	4
-2	119	126
-1	332	-349
0	201	213
1	109	117
2	145	145
3	287	298
4	247	-259
5	181	-177
6	*58	16
7	258	-257
8	58	-60
9	113	-95
10	54	44
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6	*36	21
7	*33	26
8	56	-51
*****H 9 5*****		
-8	63	62
-7	30	-33
-6	*33	17
-5	116	109
-4	57	44
-3	*38	3
-2	31	-14
-1	39	-48
0	84	-72
1	85	-83
2	98	82
3	*35	15
4	*33	3
5	31	36
6	60	-63
*****H 10 5*****		
-4	*26	18
-3	85	-85
-2	*29	-21
-1	*29	-8
0	*29	23
1	*28	21
2	*27	-14
3	49	38
4	*20	-21
**************		
*****H 0 6*****		
-14	67	-64
-12	*48	-11
-10	46	48
-8	132	-137
-6	*50	34
-4	124	-131
-2	*50	-55
0	471	426
2	101	-113
4	102	-99
6	*49	-25
8	56	68
10	39	33
12	*32	28
*****H 1 6*****		
-14	31	26
-13	*39	16
-12	74	77
-11	41	50
-10	44	-28
-9	56	68
-8	47	45
-7	68	-73
-6	79	-81
-5	100	-100
-4	189	172
-3	*48	26
-2	108	113
-1	48	52
0	102	90
1	*48	19
2	146	-128
3	*48	-2
4	*48	-19
5	59	-70
6	67	78
7	*45	43
8	43	25
9	*40	20
10	*45	-11
11	*38	-27
12	51	-57
*****H 2 6*****		
-13	*38	37
-12	44	33
-11	*49	43
-10	62	-53
-9	103	-103
-8	67	70
-7	103	-109
-6	*49	-8
-5	159	149
-4	70	63
-3	110	115
-2	69	75
-1	49	-45
0	148	-155
1	*49	-47
2	49	71
3	69	-83
4	60	-71
5	97	86
6	*47	-33
7	85	89
8	*43	-22
9	*49	-6
10	*43	20
11	74	-64
**************		
*****H 0 7*****		
-11	*40	15
-9	76	69
-7	*45	2
-5	*48	8
-3	*49	-55
-1	*49	-53
1	138	142
3	*47	31
5	*54	-53
7	*47	-45
9	*36	32
*****H 1 7*****		
-12	*30	-14
-11	75	52
-10	*42	12
-9	*47	8
-8	*41	33
-7	*45	30
-6	*44	-26
-5	45	-66
-4	65	-72
-3	46	60
-2	*46	3
-1	115	115
0	*46	24
1	46	-24
2	*45	51
3	*45	-48
4	44	-47
5	*42	-49
6	*39	-14
7	45	52
8	*40	25
9	*34	18
10	*23	-3
*****H 2 7*****		
-11	*36	13
-10	93	76
-9	56	-43
-8	*49	-34
-7	63	59
-6	66	-60
-5	*55	16
-4	*46	-4
-3	*46	-39
-2	57	57
-1	*47	13
0	*47	40
1	98	-97
2	*45	-49
3	*44	3
4	*53	9
5	*50	34
6	*47	52
7	*44	13
8	*39	15
9	*32	4
10	*16	-26
**************		
*****H 0 8*****		
-8	81	79
-6	*43	8
-4	*47	-51
-2	*40	-52
0	*39	29
2	*46	39
4	*41	-28
6	*31	-21
*****H 1 8*****		
-9	27	-26
-8	34	-11
-7	58	14
-6	41	-5
-5	35	35
-4	36	-25
-3	37	-15
-2	58	58
-1	58	-39
0	*37	-10
1	*44	29
2	*43	13
3	*41	32
4	54	-64
5	*34	-16
*****H 2 8*****		
-5	*42	-38
-4	*43	-29
-3	56	-49
-2	*45	-5
-1	*45	31
0	*44	30
1	97	87
2	42	-41
3	49	-38
4	37	34
5	*32	-30

factors for H were taken from Stewart, Davidson & Simpson (1965). The weighting scheme was

$$w^{-1/2}=0{\cdot}82 \text{ for } F_o<25{\cdot}0$$

$$w^{-1/2}=0{\cdot}82+0{\cdot}0465\ (F_o-25{\cdot}0) \text{ for } F_o\geq 25{\cdot}0.$$

The final values for R and WR are 0·071 and 0·087 respectively. The extinction constant g' (Coppens & Hamilton, 1970) refined to 0·28 (6). This corresponds to an average* value of 20·8″ for the equivalent mosaic spread parameter η.

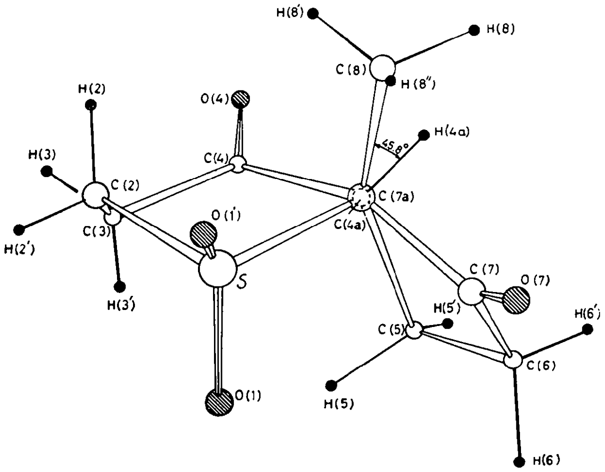

Fig. 2. View of the molecule along the ring fusion bond [C(7a) → C(4a)].

Table 1 compares observed and calculated structure factors. Table 2 lists the coordinates and temperature factors, and Table 3 the bond distances and angles (*ORFFE*, Busing, Martin & Levy, 1964). Fig. 2 shows a view of the molecule along the ring fusion bond, and Fig. 3 the Newman projections (*TORANG*, Ramanadham, 1970). Intermolecular distances less than 3·0 Å are given in Table 4.

Discussion

This study shows that the methyl group, which occupies an axial position, is *cis* to the C(4a)–hydrogen [Fig. 3(x)]. The *cis* configuration was further confirmed in a way which does not require knowledge of the C(4a) hydrogen coordinates: Substitution of the coordinates of C(8) (the methyl C) and C(4a) in the equation of the plane defined by C(7a), C(4) and C(5) gave 0·886 and 0·444 Å as the distances from this plane. That these two numbers have the same sign shows that C(8) and C(4a) are on the same side of the plane. Construction of Dreiding models shows that if this is so, C(8) must be *cis* to the C(4a) hydrogen.

Since the *C*/*D* ring fusion is normally *trans* in steroids, the compound has thus to be isomerized before it can form part of the complete steroidal molecule.

The six-membered ring in the molecule has a chair conformation [*cf.* Fig. 3 (iii) and (x)]. O(1′) is equatorial, and O(1) *trans*-diaxial to the methyl group.

For the five membered ring, $\Delta=-0{\cdot}3°$ and φ_m[C(4a) → C(5)] = 35·0° [Δ is the phase angle of pseudorotation and φ_m the angle of maximum puckering (Altona, Geise & Romers, 1968)]. That $\Delta=0$ within the error of experiment means that, so far as the torsional angles

Table 2. *Fractional coordinates and thermal parameters with their standard deviations in parentheses*

The thermal parameters for non-hydrogen atoms are defined by $T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$. For hydrogen atoms a common isotropic temperature factor (B) was refined. All values except B [=4·5 (4) Å^2] are multiplied by 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	1055 (1)	1505 (1)	−1535 (2)	37 (5)	49 (10)	251 (23)	−7 (1)	0 (2)	−10 (2)
O(1)	1575 (3)	616 (4)	−193 (7)	52 (6)	68 (11)	415 (26)	7 (3)	7 (5)	60 (6)
O(1′)	765 (4)	1012 (5)	−3429 (7)	76 (6)	118 (12)	334 (27)	−17 (4)	−13 (5)	−105 (8)
O(4)	808 (3)	5017 (4)	2080 (6)	66 (6)	110 (11)	237 (25)	32 (3)	18 (4)	−27 (6)
O(7)	3017 (3)	2079 (5)	−3354 (6)	55 (6)	125 (12)	249 (25)	15 (3)	40 (4)	−43 (6)
C(2)	63 (4)	2085 (6)	−453 (10)	33 (6)	82 (12)	327 (31)	−7 (4)	17 (6)	29 (9)
C(3)	344 (4)	2765 (7)	1487 (10)	42 (6)	131 (13)	217 (28)	0 (4)	30 (6)	18 (10)
C(4)	972 (4)	3974 (6)	1297 (8)	39 (6)	98 (12)	159 (26)	17 (4)	0 (5)	12 (8)
C(4a)	1831 (3)	3837 (5)	197 (7)	37 (6)	57 (11)	158 (26)	0 (3)	1 (4)	−15 (6)
C(5)	2675 (4)	3196 (7)	1437 (9)	40 (6)	123 (13)	185 (27)	−4 (4)	−12 (5)	−27·(9)
C(6)	3353 (4)	2797 (6)	−35 (9)	32 (6)	112 (12)	220 (28)	−1 (4)	−3 (5)	−3 (9)
C(7)	2759 (4)	2539 (5)	−1886 (9)	37 (6)	57 (12)	222 (27)	4 (3)	15 (5)	3 (7)
C(7a)	1740 (3)	3020 (6)	−1733 (7)	38 (6)	49 (11)	149 (26)	−5 (3)	5 (4)	4 (6)
C(8)	1359 (4)	3819 (6)	−3496 (8)	47 (6)	105 (13)	179 (26)	6 (4)	4 (6)	15 (8)

	x	y	z		x	y	z
H(2)	−302 (40)	2747 (62)	−1170 (85)	H(5′)	2916 (41)	3813 (61)	2289 (84)
H(2′)	−302 (41)	1310 (61)	−366 (82)	H(6)	3749 (40)	1875 (61)	378 (83)
H(3)	−211 (41)	3191 (59)	2176 (82)	H(6′)	3740 (41)	3419 (62)	−316 (84)
H(3′)	661 (43)	2336 (65)	2211 (87)	H(8)	1815 (41)	4634 (60)	−3785 (81)
H(4a)	2015 (42)	4748 (60)	−136 (85)	H(8′)	746 (41)	4132 (63)	−3250 (82)
H(5)	2351 (42)	2367 (60)	2034 (82)	H(8″)	1412 (42)	3263 (62)	−4629 (85)

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* Strictly speaking, separate extinction parameters should be refined for each crystal specimen. However, since both crystals were from the same batch, and most of the data (94%) were from one crystal only, it was not thought necessary to modify the least-squares program to allow for individual extinction parameter refinement.

Table 3. *Bond distances and angles*

Bond labels are indicated in Fig. 1. The values here are uncorrected for thermal motion. The standard deviations of the lattice parameters were also included in estimating the standard deviations listed here.

Bond distances and angles not involving H atoms

a^1	1·534 (9) Å	a^1a^2	112·7 (5)°	a^7a^8	102·2 (4)°
a^2	1·516 (9)	a^1d^1	111·3 (4)	a^7a^9	112·3 (4)
a^3	1·510 (9)	a^2a^3	119·1 (5)	a^7c^2	122·4 (5)
a^4	1·558 (7)	a^2c^1	120·3 (5)	a^7d^2	105·4 (3)
a^5	1·525 (8)	a^3a^4	112·4 (4)	a^8a^9	114·7 (4)
a^6	1·503 (8)	a^3a^8	118·2 (4)	a^8d^2	111·8 (3)
a^7	1·547 (7)	a^3c^1	120·5 (5)	a^9d^2	109·8 (3)
a^8	1·567 (7)	a^4a^5	104·0 (5)	d^1d^2	102·7 (3)
a^9	1·524 (8)	a^4a^8	105·4 (5)	d^1m^1	108·2 (3)
c^1	1·207 (7)	a^5a^6	106·1 (4)	d^1m^2	109·1 (3)
c^2	1·208 (7)	a^6a^7	110·7 (5)	d^2m^1	108·0 (2)
d^1	1·761 (6)	a^6c^2	126·8 (5)	d^2m^2	109·3 (3)
d^2	1·812 (5)			m^1m^2	118·4 (3)
m^1	1·446 (5)				
m^2	1·435 (5)				

Bond distances and angles involving H atoms

x^1	0·96 (6)	a^1x^1	104 (4)	a^6x^9	105 (4)
x^2	0·94 (6)	a^1x^2	114 (4)	a^8x^5	106 (3)
x^3	1·05 (6)	a^1x^3	115 (3)	a^9x^{10}	112 (3)
x^4	0·78 (6)	a^1x^4	115 (5)	a^9x^{11}	107 (3)
x^5	0·98 (6)	a^2x^3	101 (3)	a^9x^{12}	108 (4)
x^6	1·05 (6)	a^2x^4	100 (5)	d^1x^1	115 (4)
x^7	0·90 (6)	a^3x^5	106 (4)	d^1x^2	103 (4)
x^8	1·10 (6)	a^4x^5	107 (3)	x^1x^2	109 (5)
x^9	0·86 (6)	a^4x^6	101 (3)	x^3x^4	110 (6)
x^{10}	1·07 (6)	a^4x^7	109 (4)	x^6x^7	116 (5)
x^{11}	0·96 (6)	a^5x^6	113 (3)	x^8x^9	109 (5)
x^{12}	0·97 (6)	a^5x^7	113 (4)	$x^{10}x^{11}$	112 (5)
		a^5x^8	113 (3)	$x^{10}x^{12}$	101 (5)
		a^5x^9	115 (4)	$x^{11}x^{12}$	118 (5)
		a^6x^8	109 (3)		

Table 4. *Intermolecular distances less than* 3·0 Å

(I)	x	y	z	(V)	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$-\frac{1}{2}-z$
(II)	$\bar{x}$	$\bar{y}$	$\bar{z}$	(VI)	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
(III)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(VII)	$\bar{x}$	$1-y$	$\bar{z}$
(IV)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	(VIII)	x	y	$1+z$
				(IX)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$

O(1)–H(8)$^{\text{V}}$	2·66 (6)	O(7)–H(3)$^{\text{IX}}$	2·54
–H(2′)$^{\text{II}}$	2·70	–H(4a)$^{\text{V}}$	2·55
–H(5′)$^{\text{VI}}$	2·76	–H(8)$^{\text{V}}$	2·86
O(1′)–H(6′)$^{\text{V}}$	2·84	C(4)–H(8″)$^{\text{VIII}}$	2·94
O(4)–H(2)$^{\text{VII}}$	2·41	C(7)–H(8)$^{\text{V}}$	2·99
–H(8′)$^{\text{VII}}$	2·58		
–H(6)$^{\text{IV}}$	2·60		
–H(8″)$^{\text{VIII}}$	2·95		

are concerned, the five-membered ring has an almost perfect half-chair form with C_2 symmetry. In a survey of 14 steroid structures (Altona *et al.*, 1968), the nearest a *D* ring came to having a perfect half-chair form was in the structure of duphaston (Romers, Hesper, van Heijkoop & Geise, 1966), for which $\Delta = 2{\cdot}1°$. For steroids, of course, the *C*/*D* ring fusion is *trans*, whereas it is *cis* in the present molecule. The various factors which determine the conformation of a substituted five-membered ring are not fully understood (Altona *et al.*, 1968), and a quantitative explanation of steroid conformations may have to await more data, not only for steroid structures but also for *cis*-fused compounds of the type described here.

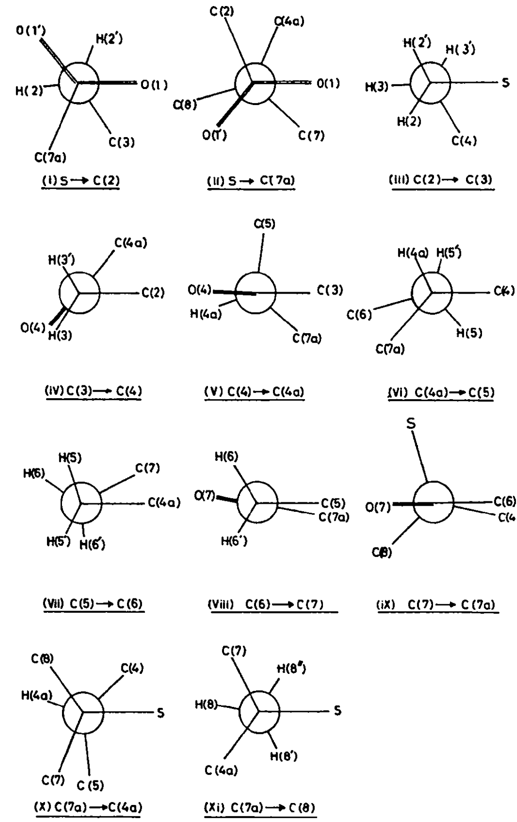

Fig. 3. Newman projections along various bonds in the molecule.

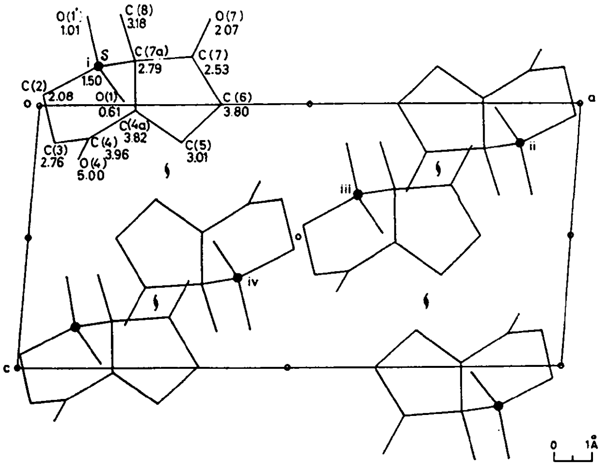

Fig. 4. Projection of the structure down **b**. H atoms are omitted. The numbers against each atom are y coordinates in Å.

Interatomic distances and angles

The S–O distances [1·446 (5) and 1·435 (5) Å] are shorter than the sum of Pauling covalent radii for double bonded atoms by about 0·05 Å. A similar situation exists in β-isoprene sulphone (Jeffrey, 1951), 2-(*o*-hydroxyphenyl)-1-phenylpropanesulphonic acid sultone (Bjåmer & Ferguson, 1967), saccharin (Okaya, 1969), and many other similar compounds. Another common feature in these compounds is the rather large O–S–O angle [118·4 (3)° in the present case]. Short S–O lengths and the correspondingly enlarged O–S–O angles are well correlated in terms of the hard-sphere model of non-bonded repulsion between the O atoms (Bartell, 1960; McDonald & Cruickshank, 1967).

The S–C(7a) length [1·812 (5) Å] compares well with the value 1·82 Å for a pure single S–C bond (Abrahams, 1956), but S–C(2) [1·761 (6) Å] is considerably shorter. The C–O double bond lengths are normal.

The average $C(sp^3)$–$C(sp^3)$ length in the molecule is 1·542 Å. Though this is somewhat larger than the normal value of 1·533 Å (Sutton, 1965), not much significance can be attached to it because the individual $C(sp^3)$–$C(sp^3)$ lengths show a large variation [between 1·524 (8) and 1·567 (7) Å].

$C(sp^2)$–$C(sp^3)$ lengths in the molecule range from 1·503 (8) to 1·547 (7) with an average of 1·519 Å.

Table 5. *Some short intramolecular contacts* (Å)

S···H(8′)	2·90 (6)	S······C(4)	3·163 (6)
S···H(8″)	2·86 (6)	O(4)···H(4a)	2·43 (6)

Some short intramolecular contacts are listed in Table 5. The methyl H(8′) and H(8″) make nearly equal short contacts with S of the same molecule. Apart from this, there are no other inter- or intramolecular short contacts with the methyl H atoms and the methyl group is fully staggered [Fig. 3 (xi)].

Fig. 4 shows a projection of the structure along **b**. As seen from Table 4, there are no short intermolecular contacts [except possibly for O(4)···H(2)$^{\text{vii}}$] and the structure is held together by van der Waals forces.

The author thanks Dr R. Chidambaram and Dr S. K. Sikka for useful discussions. Crystals were kindly supplied by Dr P.S. Jogdeo and Dr G. V. Bhide, who also synthesized the compound.

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