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The Crystal Structure of the Steroid 6β,7β-Methylene-17β-Hydroxyandrost-4-en-3-one 17-Acetate

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The crystal structure is reported of a steroid crystallizing in space group $P2_12_12_1$, with $a=21{\cdot}33$, $b=5{\cdot}91$ and $c=15{\cdot}20$ Å. Three-dimensional intensity data were collected with an automatic single-crystal diffractometer. The structure was solved by an automated Patterson search method, assuming the conformation of a part of the molecule to be known. The structure was refined by the method of least squares to a final R value of 4·0%. Bond distances, bond angles and dihedral angles are similar to those in other steroids. The extra carbon atom involved in the cyclopropane ring is proved to be in a β position. The plane of the acetate group is approximately normal to the plane of the D ring.

Introduction

The structure determination recorded in this paper is part of a series of investigations in the field of steroid structures. In an earlier paper (Braun, Hornstra & Leenhouts, 1969*b*) we have reported on the crystal structures of seven retro-steroids. Two reasons prompted us to undertake these investigations. Research in steroid chemistry at N.V. Philips–Duphar Research Labs, Weesp, The Netherlands, could be supported by structural information regarding the compounds being studied there. In addition, it would help to meet our own demands for test cases in the development of computer-programmed automatic Patterson-search methods (Braun, Hornstra & Leenhouts, 1969*a*). In this phase of investigation it was interesting to analyse a steroid from the normal series (9α, 10β). For this purpose we received the compound 6,7-methylene-17β-hydroxyandrost-4-en-3-one 17-acetate (m. p. 176–177·5 °C), described by Dyson, Edwards & Fried (1966). Dyson *et al.* (1966) assigned the α-position to the 6,7-methylene bridge. Van Kamp, Nissen & van Vliet (1967) synthesized corresponding compounds in the 9β,10α series. Comparison of the nuclear magnetic resonance data of the compounds from the two series, however, suggested a β-position of the methylene bridge in the above mentioned compound of the normal series. Our structure determination confirms this β-position. The same conclusion was drawn by Pfister, Wehrli & Schaffner (1967) from chemical evidence.

Experimental

The single crystal, a small irregular block, was ground to an almost spherical shape. Lattice constants and X-ray intensities were measured at room temperature, using the Philips automatic single-crystal diffractometer PAILRED, with crystal-monochromatized Cu $K\alpha$ radiation ($\lambda=1{\cdot}54178$ Å). Corrections for Lorentz, polarization and absorption effects were applied to the 3136 intensities, measured in 5 levels labelled 0 through 4, around [010]. The measurements were confined within a sphere corresponding to a d value of 0·98 Å, because reflexions of any appreciable intensity were hardly ever found outside that region. The data used in the structure determination and subsequent least-squares refinement contained 1296 independent reflexions, derived from the total number of measurements. The crystals are orthorhombic with space group $P2_12_12_1$ and $Z=4$; $a=21{\cdot}33\pm0{\cdot}01$, $b=5{\cdot}91\pm0{\cdot}005$ and $c=15{\cdot}20\pm0{\cdot}01$ Å.

Structure determination

The Patterson-search method applied has been described in detail, so only a short survey will be given here. Assuming the configuration of the C and D rings (see Fig. 1) to be equal to those in Duphaston (Braun, Hornstra & Leenhouts, 1969*b*) we used these nine atoms as a rigid search model.

A first Patterson search yields a list of probable orientations of this known part. For each of these orientations a small number of probable positions with respect to the symmetry elements are selected by a second search. The correct set of orientation and position parameters emerges after each selected set has been refined in Patterson space. The atoms not belonging to the model are now located one after the other by a third automated Patterson search. All positions in the neighbourhood of the located model, possibly occupied by new atoms, are calculated from stereochemical knowledge. That position which gives the best value of a decision function is taken as the site of a new atom. Consequently this atom and its three symmetry-related ones are added to the known part of the structure. This process is repeated until the molecule is complete. Without human intervention the structure was solved in under thirty minutes computing time using a CD

3600 computer. The parameters of the structure at this stage showed deviations of the order of 0·1 Å or less from the final parameters.

The programs, written in FORTRAN 63, may be obtained from the authors on request.

Refinement

The least-squares refinement was carried out with our own programs, written in FORTRAN. The atomic scattering factors were from *International Tables for X-ray Crystallography* (1962). The weighting scheme used in the refinement was derived in the following way. To the $\sigma^2(F^2)$ derived from counting statistics we added $(0\cdot04\ F^2)^2$ to avoid giving undue weights to strong reflexions. On averaging equivalent reflexions a weighted average was calculated. For $\sigma^2(F^2)$ the larger of $1/\sum_i^n\{1/\sigma^2(F_i^2)\}$ and $\sum_i^n\{(F_i^2-F^2)^2/\sigma^2(F_i^2)\}/[(n-1)\sum_i^n\{1/\sigma^2(F_i^2)\}]$ was taken. For the weight of F we used $w(F)=\frac{w'}{1+0\cdot1\,w'}$ instead of $w'=4F^2/\sigma^2(F^2)$, in order to reduce the maximum value of w.

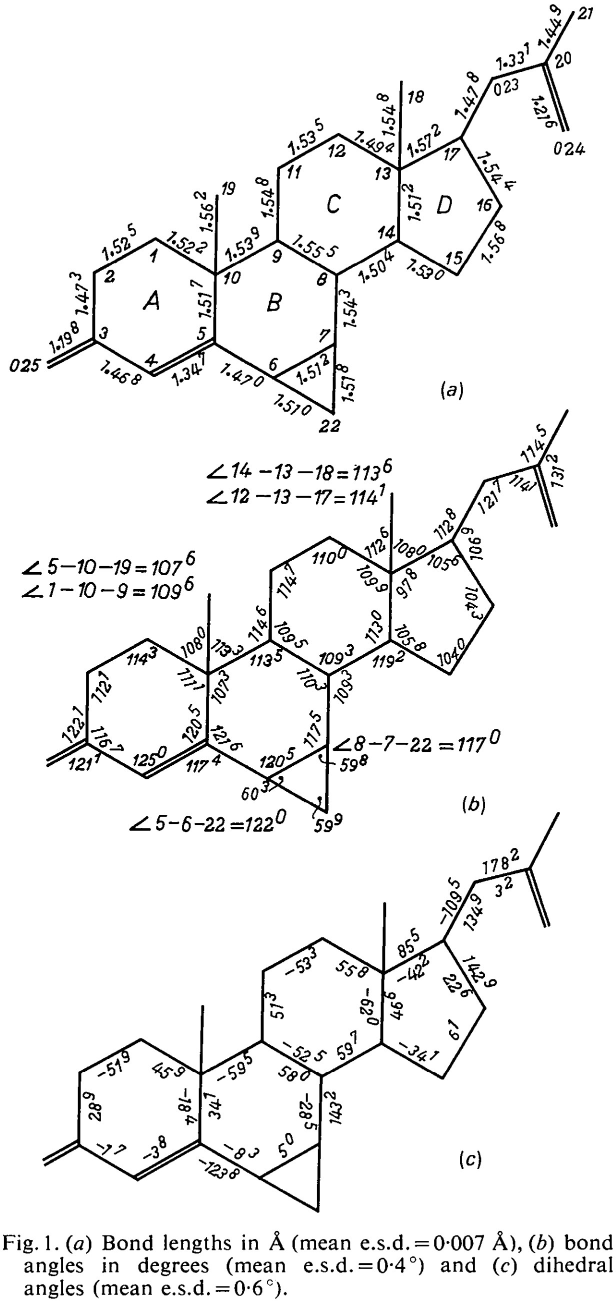

Fig. 1. (*a*) Bond lengths in Å (mean e.s.d. = 0·007 Å), (*b*) bond angles in degrees (mean e.s.d. = 0·4°) and (*c*) dihedral angles (mean e.s.d. = 0·6°).

Before the introduction of the hydrogen atoms and of anisotropy in the thermal vibration the factor R_w defined as $R_w=\sum w||F_o|-k|F_c||/\sum w|F_o|$ had dropped to 13·8%. The quantity minimized $\sum w\Delta^2=\sum w(|F_o|-k|F_c|)^2$ was at that stage 56885, including all reflexions within the limiting sphere. All non-hydrogen parameters were refined simultaneously, in the case of isotropic vibration in full matrix, but with anisotropic coefficients in a 9×9 block-diagonal approximation. The positions of most hydrogen atoms were computed with a simple program using standard bond lengths and angles. In a later stage a difference Fourier synthesis revealed the positions of the hydrogen atoms of the methyl groups. To ensure reasonable positions of the hydrogen atoms whilst treating C and O atoms, the shifts calculated for the latter were added to the related hydrogen atoms. The thermal parameters of the hydrogen atoms were kept identical with those of the carbon atoms to which they are bonded. After the introduction of the H positions the reliability indices became $R_w=10\cdot6\%$ and $\sum w\Delta^2=30571$. Allowance for anisotropic vibration resulted in $R_w=5\cdot5\%$ and $\sum w\Delta^2=8997$. Now all hydrogen position parameters were refined in one matrix, giving rise to $R_w=5\cdot0\%$ and $\sum w\Delta^2=6994$. Final refinement cycles with C and O in 9×9 and H in 3×3 blocks yielded the final values $R_w=4\cdot0\%$ and $\sum w\Delta^2=4614$. Preceding the refinement of the hydrogen positions the F_o values were corrected for extinction according to Gomes de Mesquita (1967). This had only a small effect. The final difference Fourier synthesis showed no significant features. The list of observed and calculated structure factors may be obtained on request.

Results and accuracy

The final list of atomic coordinates with their corresponding estimated standard deviation values are presented in Tables 1 and 2. These e.s.d. values have been derived from the elements of the inverse 9×9 and 3×3 matrices with $m-n=1296-(25\times9+28\times3+1)=986$. Probably both these estimates and the e.s.d.'s for distances and angles are somewhat optimistic, as usual. Bond distances, bond angles and dihedral angles (Bucourt, 1964) not corrected for libration, with their mean e.s.d. values, may be read from Fig. 1 as far as non-hydrogen atoms are concerned. Intermolecular distances below 4 Å, excluding hydrogen atoms, are shown in Table 3. The reference molecule is in contact with 12 neighbours. In these complicated types of molecules the individual values of C–H bonds and related angles as detected by X-ray diffraction are considered not to have a high accuracy. For this reason only their means with calculated errors are given in Table 4.

Table 1. *Positional coordinates, chosen in conformity with the normally accepted absolute configuration*

Estimated standard deviations are given in brackets

	x	y	z
C(1)	0·09625 (19)	0·16690 (93)	0·13432 (30)
C(2)	0·12103 (22)	0·16844 (103)	0·04023 (34)
C(3)	0·17992 (21)	0·29697 (104)	0·03217 (32)
C(4)	0·22022 (19)	0·30482 (90)	0·11039 (31)
C(5)	0·20657 (18)	0·20884 (75)	0·18843 (30)
C(6)	0·25090 (19)	0·24554 (99)	0·26109 (32)
C(7)	0·23179 (17)	0·19688 (104)	0·35499 (31)
C(8)	0·16673 (17)	0·08963 (82)	0·37007 (30)
C(9)	0·12094 (17)	0·15950 (79)	0·29523 (30)
C(10)	0·14402 (17)	0·09273 (75)	0·20285 (31)
C(11)	0·05401 (17)	0·07676 (89)	0·31778 (31)
C(12)	0·03086 (17)	0·14344 (90)	0·40983 (29)
C(13)	0·07736 (18)	0·07056 (75)	0·47769 (29)
C(14)	0·14104 (17)	0·16906 (75)	0·45688 (29)
C(15)	0·18036 (19)	0·13767 (99)	0·54019 (33)
C(16)	0·13195 (21)	0·16605 (115)	0·61702 (33)
C(17)	0·06797 (19)	0·18483 (89)	0·57015 (30)
C(18)	0·07813 (20)	−0·18896 (85)	0·49110 (31)
C(19)	0·15472 (21)	−0·16715 (80)	0·19202 (33)
C(20)	−0·03407 (20)	0·15199 (108)	0·64363 (33)
C(21)	−0·07407 (21)	0·00812 (135)	0·69663 (35)
C(22)	0·28089 (18)	0·05126 (117)	0·31002 (36)
O(23)	0·02191 (13)	0·06423 (63)	0·62561 (21)
O(24)	−0·04430 (16)	0·33165 (96)	0·60743 (30)
O(25)	0·19662 (16)	0·37775 (84)	−0·03623 (23)
H(1)	0·0861 (16)	0·3473 (81)	0·1349 (24)
H(1)	0·0565 (15)	0·0451 (87)	0·1494 (24)
H(2)	0·0807 (17)	0·2473 (97)	−0·0065 (25)
H(2)	0·1328 (17)	−0·0057 (100)	0·0113 (25)
H(4)	0·2640 (15)	0·4213 (77)	0·0973 (24)
H(6)	0·2875 (14)	0·4041 (84)	0·2708 (25)
H(7)	0·2510 (15)	0·3117 (91)	0·3995 (24)
H(8)	0·1701 (14)	−0·1075 (71)	0·3735 (23)
H(9)	0·1186 (14)	0·3490 (69)	0·3022 (24)
H(11)	0·0245 (14)	0·1479 (74)	0·2708 (25)
H(11)	0·0531 (14)	−0·0877 (78)	0·3052 (25)
H(12)	0·0266 (14)	0·3402 (79)	0·4077 (23)
H(12)	−0·0145 (15)	0·0520 (80)	0·4220 (24)
H(14)	0·1361 (14)	0·3221 (69)	0·4568 (23)
H(15)	0·2211 (15)	0·2842 (88)	0·5468 (25)
H(15)	0·1968 (14)	0·0038 (91)	0·5360 (25)
H(16)	0·1391 (16)	0·3178 (92)	0·6261 (25)
H(16)	0·1340 (16)	0·0313 (98)	0·6724 (25)
H(17)	0·0503 (14)	0·3454 (78)	0·5672 (25)
H(22)	0·3242 (19)	0·0853 (102)	0·3375 (26)
H(22)	0·2585 (19)	−0·1357 (101)	0·2777 (27)
H(19)	0·1756 (16)	−0·2365 (76)	0·2427 (25)
H(19)	0·1817 (17)	−0·1976 (75)	0·1416 (25)
H(19)	0·1150 (17)	−0·2326 (74)	0·1920 (26)
H(18)	0·0778 (16)	−0·2244 (79)	0·4311 (26)
H(18)	0·0310 (15)	−0·2323 (81)	0·5220 (25)
H(18)	0·1088 (15)	−0·2609 (83)	0·5281 (25)
H(21)	−0·0458 (14)	−0·1589 (84)	0·7292 (27)
H(21)	−0·1045 (16)	0·1282 (86)	0·7267 (26)
H(21)	−0·1065 (16)	−0·1139 (86)	0·6456 (25)

Geometry of the molecule

As usual in steroids, bond angles and dihedral angles are significantly different from the ideal values (Geise, Altona & Romers, 1967; Braun, Hornstra & Leenhouts, 1969*b*). Bond angles are too large, whereas dihedral angles are below the ideal value. The rings *B*, *C* and *D* are all *trans* connected and the substituents to the steroid skeleton C(18), C(19), C(22) and O(23) are all on the same side of the molecule, *i.e.* the β side. The atoms C(2), C(3), O(25), C(4), C(5), C(10), C(6), C(7) and C(8) are, roughly speaking, coplanar. Deviations from coplanarity in the *B* ring are greater than those in the *A* ring. Both *A* and *B* rings are sofa shaped with the atoms C(1) and C(9) pointing out of the plane in the direction opposite to C(19). The *C* ring is a distorted chair. The *D* ring is a distorted envelope with C(13) out of the plane of the other members of the ring. Still roughly speaking, the plane of the acetate group is normal to that of the *D* ring with O(24) pointing to the hydrogen atom attached to C(17), a feature observed before (Mathieson, 1965; Jennings, Mose & Scopes, 1967; Braun, Hornstra & Leenhouts, 1969*b*). The hydrogen atoms of both methyl groups C(18) and C(19) are in a staggered configuration with respect to the steroid skeleton. A spatial impression of the molecule, as far as carbon and oxygen atoms are concerned, may be obtained from the computer-drawn Fig. 2 (Leenhouts, 1968).

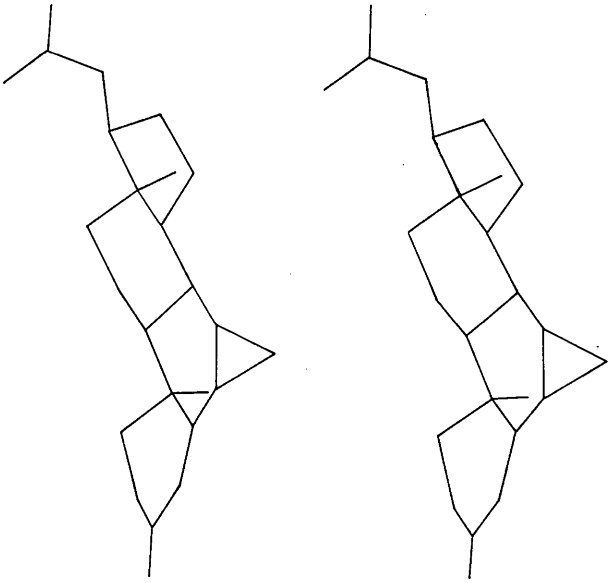

Fig. 2. Stereo pair of drawings of the molecule. The pictures should be viewed from a distance of about 40 cm, the left eye looking at the left-hand figure and the right eye at the right-hand one. Better results can often be obtained if a sheet of paper is held upright between the two figures.

Table 2. *Anisotropic thermal vibration coefficients as used in the formula*
$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hk\,a^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*\,U_{23})]$

Estimated standard deviations in brackets.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·079 (2)	0·086 (4)	0·092 (3)	−0·015 (4)	−0·018 (3)	−0·009 (5)
C(2)	0·111 (4)	0·106 (4)	0·100 (4)	−0·023 (5)	0·011 (3)	−0·001 (6)
C(3)	0·110 (4)	0·095 (4)	0·097 (4)	0·014 (4)	0·025 (3)	0·014 (5)
C(4)	0·071 (2)	0·066 (3)	0·105 (4)	−0·002 (3)	0·015 (3)	−0·004 (4)
C(5)	0·069 (2)	0·049 (3)	0·086 (3)	0·002 (3)	0·011 (3)	−0·003 (4)
C(6)	0·059 (2)	0·101 (4)	0·108 (4)	−0·020 (4)	0·002 (3)	0·003 (5)
C(7)	0·048 (2)	0·118 (5)	0·106 (4)	0·006 (4)	−0·012 (3)	−0·015 (5)
C(8)	0·049 (2)	0·064 (3)	0·084 (3)	0·006 (3)	−0·004 (3)	−0·009 (4)
C(9)	0·051 (2)	0·059 (3)	0·083 (3)	−0·010 (3)	−0·006 (3)	−0·008 (4)
C(10)	0·061 (2)	0·057 (3)	0·085 (3)	−0·013 (3)	0·002 (3)	−0·003 (4)
C(11)	0·053 (2)	0·076 (4)	0·098 (4)	−0·001 (3)	−0·010 (3)	0·004 (4)
C(12)	0·053 (2)	0·079 (4)	0·091 (3)	−0·010 (4)	0·002 (3)	0·001 (4)
C(13)	0·074 (2)	0·046 (3)	0·085 (3)	0·004 (3)	−0·020 (3)	0·018 (4)
C(14)	0·055 (2)	0·053 (3)	0·079 (3)	0·010 (3)	−0·002 (3)	−0·000 (4)
C(15)	0·073 (2)	0·095 (4)	0·102 (4)	0·006 (4)	−0·011 (3)	0·000 (5)
C(16)	0·099 (4)	0·126 (5)	0·104 (4)	−0·003 (5)	−0·008 (3)	−0·031 (5)
C(17)	0·081 (2)	0·068 (4)	0·087 (3)	0·009 (4)	0·014 (3)	−0·006 (4)
C(18)	0·085 (2)	0·063 (4)	0·109 (4)	0·003 (4)	0·019 (3)	0·001 (4)
C(19)	0·114 (4)	0·052 (3)	0·104 (4)	−0·001 (4)	0·003 (3)	−0·013 (4)
C(20)	0·088 (4)	0·118 (5)	0·113 (4)	0·026 (4)	0·006 (3)	0·023 (5)
C(21)	0·099 (4)	0·179 (7)	0·108 (4)	0·023 (6)	0·036 (3)	0·035 (7)
C(22)	0·050 (2)	0·137 (5)	0·142 (4)	−0·002 (4)	0·005 (3)	0·027 (6)
O(23)	0·098 (2)	0·096 (3)	0·113 (2)	0·026 (3)	0·025 (3)	0·012 (3)
O(24)	0·131 (2)	0·192 (5)	0·233 (4)	0·066 (4)	0·061 (3)	0·066 (5)
O(25)	0·162 (2)	0·156 (4)	0·108 (3)	−0·042 (4)	0·017 (3)	0·036 (4)

Table 3. *Intermolecular* C–C *and* C–O *distances below* 4 Å

The following notation is used.

.../1	atom in molecule	$x'=x$	$y'=y$	$z'=z$
.../2	– – –	$x'=\frac{1}{2}-x$	$y'=-y$	$z'=\frac{1}{2}+z$
.../3	– – –	$x'=\frac{1}{2}+x$	$y'=\frac{1}{2}-y$	$z'=-z$
.../4	– – –	$x'=-x$	$y'=\frac{1}{2}+y$	$z'=\frac{1}{2}-z$
$\pm a$	– – –	$x'\pm 1$	y'	z'
$\pm b$	– – –	x'	$y'\pm 1$	z'
$\pm c$	– – –	x'	y'	$z'\pm 1$

		Distance			Distance
C(1)	C(12)/4	3·97	C(19)	C(4)/1 − *b*	3·64
C(2)	O(24)/4 − *b*	3·42	C(19)	C(5)/1 − *b*	3·85
C(3)	C(15)/2 − *c*	3·94	C(20)	C(21)/4 + *c*	3·96
C(4)	C(15)/2 − *c*	3·53	C(21)	C(16)/4 − *b* + *c*	3·69
C(4)	C(19)/1 + *b*	3·64	C(21)	C(20)/4 − *b* + *c*	3·96
C(5)	C(15)/2 − *c*	3·89	C(21)	O(23)/4 − *b* + *c*	3·93
C(5)	C(19)/1 + *b*	3·85	C(21)	O(25)/4 − *b*	3·66
C(6)	O(25)/2 + *b*	3·96	C(22)	C(16)/2 − *c*	3·70
C(7)	O(25)/2 + *b*	3·38	C(22)	O(24)/3 + *c*	3·99
C(12)	C(1)/4 − *b*	3·97	C(22)	O(25)/2	3·48
C(15)	C(3)/2	3·94	O(23)	C(21)/4 + *c*	3·93
C(15)	C(4)/2	3·53	O(24)	C(2)/4	3·42
C(15)	C(5)/2	3·89	O(24)	C(22)/3 − *a* + *c*	3·99
C(16)	C(21)/4 + *c*	3·69	O(25)	C(6)/2 + *b* − *c*	3·96
C(16)	C(22)/2	3·70	O(25)	C(7)/2 + *b* − *c*	3·38
C(17)	C(18)/1 + *b*	3·90	O(25)	C(21)/4	3·66
C(18)	C(17)/1 − *b*	3·90	O(25)	C(22)/2 − *c*	3·48

Table 4. C–H *mean bond lengths and related angles with their calculated errors*

The figures in column 2 could be interpreted as standard deviations only if the figures in column 1 were to represent correct values for each of the individual quantities.

	$\bar{p}=\sum p/n$	$\sqrt{\sum(p-\bar{p})^2/n}$	E.s.d. as calculated from least-squares refinement
C–H bond lengths	1·09 Å	0·11 Å	0·04 Å
C–C–H bond angles	109°	6·8°	2·3°
H–C–H bond angles	112°	9·7°	3·2°

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The Crystal Structure of a Samarium–Zinc Compound with Approximate Composition $SmZn_{11}$*

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The crystal structure of the high temperature form of the most zinc-rich compound in the Sm–Zn system has been found to be hexagonal with lattice constants $a=8{\cdot}974$, $c=8{\cdot}918$ Å and space group $P6/mmm$. The structure is disordered and was found to have a stoichiometry of approximately $SmZn_{11}$. This is a new structure type in the family of structures related to the $CaZn_5$ ($D2_d$) type. The relations of this new structure to the AB_5 structure and the low temperature tetragonal form of $SmZn_{12}$ are discussed. A simple mechanism for the transformation from the hexagonal to the tetragonal form is proposed.

Introduction

A number of investigations of the binary phase diagrams of the rare earths with Group IIB elements have revealed the presence of a large number of intermetallic compounds (Gschneidner, 1961). Common features of these systems are: (*a*) the occurrence of no less than three to four compounds with more than 50 atomic per cent of the Group B element, (*b*) the existence of most of the compounds as line compounds or with a very limited composition range, (*c*) the uncertainties of the stoichiometric description of some of the compounds and the lack of agreement between various workers (Kuz'ma, Kripyakevich & Ugrin, 1966; Chiotti & Mason, 1967; Veleckis, Schablaske, Johnson & Feder, 1967) as to the number of compounds present. The last remarks apply particularly to the area of the phase diagrams with high Group IIB element content. These are also the areas which are of most practical importance in the field of reprocessing of fuel elements (Chiotti & Klepfer, 1965).

The most zinc-rich compound in the samarium–zinc system has been reported by both Kuz'ma, Kripyakevich & Ugrin (1966) and Iandelli & Palenzona (1967). Both investigators used powder diffraction methods only and concluded that the compound in question was $SmZn_{12}$ of the crystal type $ThMn_{12}$ (space group $I4/mmm$). The lattice constants reported by Iandelli & Palenzona were: $a=8{\cdot}927\pm0{\cdot}003$, $c=5{\cdot}215\pm0{\cdot}002$ Å. Veleckis, Schablaske & Tani (1966) also did powder work and found two modifications of $SmZn_{12}$. The low temperature form prepared at 475 °C was of the $ThMn_{12}$ type. The high temperature form of the compound prepared at 600 °C was hexagonal with lattice parameters of $a=8{\cdot}972$ and $c=8{\cdot}912$ Å.

Chiotti & Mason (1967) investigated the samarium–zinc system but did not positively identify the stoichiometry of the most zinc-rich compound. The present work was undertaken to determine the crystal structure and thus the stoichiometry of the high-temperature form of this compound.

Experimental procedure

The materials and general techniques used for preparing samarium–zinc alloys have been outlined by Chiotti & Mason (1967). Owing to the difficulty in obtaining homogeneous bulk samples, meaningful

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