

## The UV-Absorption of some 1 $\alpha$ , 5 $\alpha$ -Epidithio-steroids

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Recently Tweit and Dodson<sup>1</sup> isolated a disulfide from the reaction of 1,4-androstadiene-3,17-dione with hydrogen sulfide and sulfur in pyridine. For various reasons the disulfide linkage was proposed to be between carbon atoms one and five, and the disulfide bridge was placed on the  $\alpha$ -side of the molecule. The compound is thus 1 $\alpha$ , 5 $\alpha$ -epidithioandrostane-3,17-dione (I) which implies that the molecule contains the five-membered 1,2-dithiolane ring.

From a study of molecular models it appeared that the dihedral angle of the disulfide group in I, as in other dithiolane derivatives, cannot be very far from zero. In 1,2-dithiolane-4-carboxylic acid the dihedral angle has been found<sup>2</sup> to be 27°. Furthermore it can be concluded, that the sulfur-sulfur bond distance is certainly larger than the usual ( $2.08 \pm 0.03$  Å) since otherwise a large departure from the principle of maximum overlap for the carbon-sulfur bonds must be assumed. Since 1,2-dithiolane and many of its derivatives have an absorption band in the ultraviolet with maximum at about 330 m $\mu$  and since Bergson<sup>3</sup> has shown that an increase in the sulfur-sulfur bond distance might be expected to decrease the excitation energy, the thio steroid I might have

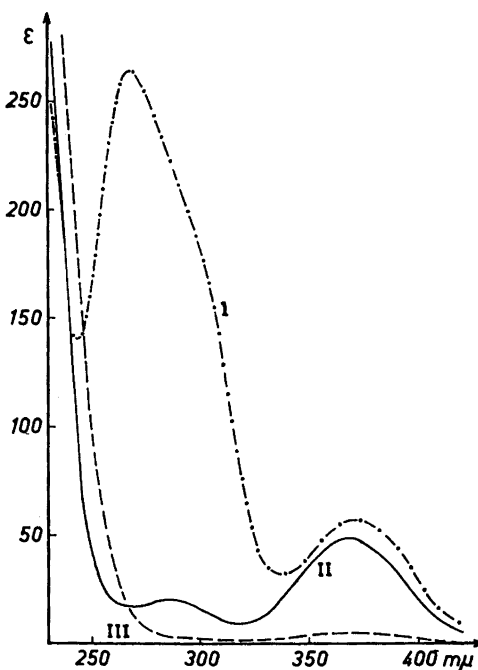
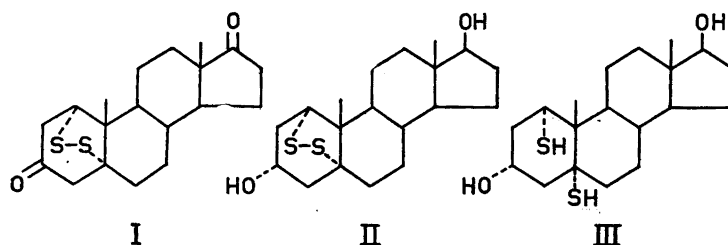


Fig. 1. Ultraviolet absorption in methanol of:

- I: 1 $\alpha$ ,5 $\alpha$ -epidithioandrostane-3,17-dione.
- II: 1 $\alpha$ ,5 $\alpha$ -epidithioandrostane-3 $\alpha$ ,17 $\beta$ -diol.
- III: 3 $\alpha$ ,17 $\beta$ -dihydroxyandrostane-1 $\alpha$ ,5 $\alpha$ -dithiol.

an absorption band at longer wavelengths than 330 m $\mu$ . The ultraviolet spectrum of 1 $\alpha$ ,5 $\alpha$ -epidithioandrostane-3,17-dione (I) and its reduction products 1 $\alpha$ ,5 $\alpha$ -epidithioandrostane-3 $\alpha$ ,17 $\beta$ -diol (II) and 3 $\alpha$ ,17 $\beta$ -dihydroxyandrostane-1 $\alpha$ ,5 $\alpha$ -dithiol (III) have therefore been reinvestigated in



detail. The results are given in Fig. 1. The disulfides I and II have a maximum at 371  $m\mu$  ( $\epsilon_{\max} = 58$ ) and 369  $m\mu$  ( $\epsilon_{\max} = 49$ ), respectively. We think that this band is due to a transition from the antibonding  $3p\pi$ -orbital to the antibonding  $\sigma$ -orbital of the disulfide group<sup>3,4</sup>. This is in harmony with its almost complete disappearance in the dithiol III; the very small remaining absorption is certainly due to the presence of a trace of II formed by the unavoidable oxidation of III. We cannot at present give a precise interpretation of the absorption at the shorter wave-lengths. Remarkable is the strong absorption maximum at 268  $m\mu$  for the keto-compound (I). This cannot be due solely to the keto-groups. It may possibly be due to a transannular interaction of the 3-keto-group and the disulfide bridge (*cf.* Leonard *et al.*<sup>5</sup>)

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4. Bergson, G. *Arkiv Kemi* **12** (1958) 233.
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Received December 16, 1959.

## Studies on the Zirconium-Aluminium and Hafnium-Aluminium Systems

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The following phases have been observed in the zirconium-aluminium system:  $Zr_3Al$ ,  $Zr_2Al$ ,  $Zr_4Al_3$ ,  $Zr_3Al_2$ ,  $Zr_4Al_3$ ,  $ZrAl$ ,  $Zr_2Al_3$ ,  $ZrAl_2$  and  $ZrAl_3$ <sup>1</sup>. The crystal structures have been reported for  $Zr_3Al$ <sup>2</sup>,  $Zr_4Al_3$ <sup>3</sup>,  $ZrAl_2$ <sup>4</sup> and  $ZrAl_3$ <sup>5</sup>.

In the present investigation, metals of high purity were used, *viz.* aluminium (99.99 %) and zirconium (iodide zirconium 99.9 %, oxygen 260 ppm, Foote Mineral Company). The alloys were prepared by melting in an electric arc furnace under an argon atmosphere and heat-treated in

sealed evacuated silica tubes. Tantalum foils protected the alloys from reacting with the silica.

The phase analyses were performed by means of X-ray powder patterns taken in a Guinier camera, potassium chloride being added to the specimens as an internal standard<sup>6</sup>. Single crystal data were obtained in a Weissenberg camera with  $CuK$  radiation.

While the crystal structures of  $Zr_4Al_3$  and  $ZrAl_2$  were being studied at this Institute, Wilson *et al.*<sup>3,4</sup> published the structures of these compounds. Thus,  $Zr_4Al_3$  was reported to have the  $D8_g$  type of structure while  $ZrAl_2$  was found to be of the  $C14$  type. The data given for  $ZrAl_2$  are in perfect agreement with our results but this is, however, not the case with  $Zr_4Al_3$ .

Single crystals of  $Zr_4Al_3$  could be obtained from a melt of the approximate composition  $ZrAl_{0.50}$ . The single crystal and powder data showed the structure to be tetragonal with the following unit cell axes:

$$a = 11.049 \text{ \AA}, \quad c = 5.396 \text{ \AA}.$$

The Patterson projections along  $[001]$  and  $[100]$  were calculated and the following structure was derived:

Unit cell content: 4  $Zr_4Al_3$ .

Space-group:  $I4/mcm$  (No. 140)

	$x$	$y$	$z$
16 Zr in 16 ( $k$ )	0.077	0.218	0
4 Zr in 4 ( $b$ )	0	$\frac{1}{2}$	$\frac{1}{4}$
8 Al in 8 ( $h$ )	0.16	0.66	0
4 Al in 4 ( $a$ )	0	0	$\frac{1}{4}$

This structure of the  $D8_m$  type is represented by  $W_5Si_3$  (Aronsson<sup>7</sup>). It may be that the occurrence of the  $D8_g$  and the  $D8_m$  structures depends on the heat-treatment of the sample. It has, however, been suggested that the  $Me_5X_3$  phases with the  $D8_g$  type of structure are stabilized by the presence of impurities such as boron, carbon, nitrogen and oxygen<sup>8-10</sup>. This interesting hypothesis seems to be supported by the observation that a mixture of zirconium, aluminium and aluminium oxide with a composition close to the formula  $Zr_{10}Al_6O$  upon melting gave a product with a pure  $D8_g$  structure. The powder pattern was found to give the following parameters for the hexagonal unit cell:

$$a = 8.177 \text{ \AA}, \quad c = 5.674 \text{ \AA}.$$

The axes reported by Wilson *et al.*<sup>3</sup> for the  $D8_g$  phase are 8.184 and 5.702  $\text{\AA}$ , respectively.