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## Crystal data (II) for some androstanes*.

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Norton, Lu & Campbell (1962) reported the single-crystal data for a series of androstanes. This paper reports the same data for a second set of androstanes (Table 1) using the same techniques described in the earlier paper. No further work on these compounds is contemplated.

### Reference

NORTON, D. A., LU, C. T. & CAMPBELL, A. E. (1962). *Acta Cryst.* **15**, 1189.

Table 1. *Crystal data* (II) *for some androstanes*

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Formula | $C_{19}H_{26}O_2$ | $C_{19}H_{26}O_2$ | $C_{19}H_{28}O_2$ | $C_{19}H_{28}O_2$ | $C_{19}H_{30}O_2$ | $C_{19}H_{30}O_2$ | $C_{19}H_{24}O_3$ | $C_{21}H_{30}O_3$ | $C_{26}H_{34}O_3$ |
| Mol. Wt. | 286·40 | 286·40 | 288·41 | 288·41 | 290·43 | 290·43 | 300·38 | 330·45 | 394·53 |
| $D_m$ (g.cm$^{-3}$) | 1·178 | 1·164 | 1·147 | 1·186 | 1·132 | 1·147 | 1·264 | 1·162 | 1·148 |
| $D_x$ (g.cm$^{-3}$) | 1·175 | 1·174 | 1·143 | 1·177 | 1·103 | 1·084 | 1·253 | 1·201 | 1·207 |
| Space group | $P2_12_12_1$ | $P2_12_12$ | $A2$ | $P2_1$ | $P2_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_1$ |
| $Z$ | 4 | 4 | 4 | 4 | 2 | 4 | 4 | 4 | 2 |
| $a$ (Å)* | 12·963 | 12·302 | 21·337 | 14·691 | 11·614 | 12·146 | 9·263 | 12·800 | 10·860 |
| $b$ (Å)* | 16·929 | 18·644 | 6·186 | 11·093 | 8·096 | 23·434 | 26·531 | 18·169 | 16·241 |
| $c$ (Å)* | 7·366 | 7·065 | 12·704 | 10·872 | 9·422 | 6·248 | 6·477 | 7·856 | 6·236 |
| $\beta$ (°) | — | — | 91·27 | 113·23 | 99·23 | — | — | — | 99·17 |
| $V$ (Å$^3$) | 1619 | 1620 | 1676 | 1628 | 874 | 1779 | 1592 | 1827 | 1086 |
| Solvent | Ethanol | Methanol | Unknown | Methanol | Ethanol | Ethanol | Methanol—acetone | Methanol | Ethanol |

* ± 0·009 Å

1. 4-Androsten-3,17-dione (androstenedione)
2. 1,4-Androstadien-17$\beta$-ol-3-one (1-dehydrotestosterone)
3. 5$\alpha$-Androstan-3,17-dione (androstanedione)
4. 4-Androsten-17$\beta$-ol-3-one (testosterone)
5. 5$\alpha$-Androstan-17$\beta$-ol-3-one (allodihydrotestosterone)
6. 5-Androsten-3$\beta$, 17$\beta$-diol (adrenostenediol)
7. 4-Androsten-3,11,17-trione (adrenosterone)
8. 4-Androsten-17$\beta$-ol-3-one 17-acetate (testosterone acetate)
9. 5$\alpha$-Androstan-17$\beta$-ol-3-one 17-benzoate (dihydrotestosterone benzoate)

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## An X-ray investigation of the stereochemistry of $Zn(NCS)_2(C_6H_5NH_2)_2$.

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(*Received* 22 *June* 1964)

The stereochemistry of the complex $Zn^{II}(NCS)_2(C_6H_5NH_2)_2$ is of interest in connection with studies in these laboratories on the factors governing the configuration of metal complexes. Nelson & Shepherd (unpublished work) have established, from magnetic and spectral data, that the corresponding Co(II) and Ni(II) complexes have octahedral (or tetragonal) structures with bridging NCS groups. X-ray powder patterns show that these and the corresponding Cd(II) complex are isomorphous, but that $Zn(NCS)_2(C_6H_5NH_2)_2$ has a different crystal structure. An attempt to determine this structure sufficiently to establish the coordination number of the zinc atom is described here.

Single crystals obtained by recrystallization from ethanol were used. These were needle-shaped, approx 1·5 mm long, and 0·3 mm in cross section. The needle axis being taken as the $c$ axis, rotation photographs with Cu $K\alpha$ radiation about the [001] and [1$\bar{1}$0] axes and Laue photographs showed the unit cell to be orthorhombic with the cell dimensions:

$$a = 14{\cdot}56 \pm 0{\cdot}05 \text{ Å}$$
$$b = 9{\cdot}10 \pm 0{\cdot}05$$
$$c = 12{\cdot}7 \pm 0{\cdot}1$$

The values of $a$ and $b$ were derived from the observed spacings of 39 $h0l$ reflexions, and their uncertainties are an estimate based on the standard deviations of the observed and calculated values. $c$ was obtained from layer line measurements of a rotation photograph.

Reflexions present: *hkl*; $h+k+l$ even. *h0l*; $h=2n$.

Space group uniquely determined as *Ima*2 ($C_{2v}$). Density, calculated with 4 molecules per unit cell, 1·45 g.cm$^{-3}$. Observed density $\simeq 1{\cdot}4$ g.cm$^{-3}$. This was obtained by weighing well-formed crystals after measuring their dimensions under a microscope, and was believed to be accurate to about ±10%.

Indices and visual estimates of the relative intensities of the 67 reflexions observed on the [001] rotation photograph are given in Table 1. Calculated and observed values of 2 sin $\theta$ are listed when $l=0$ or 1. For indexing reflexions for which $l>1$, a Bernal chart was used.

Table 1. *Relative intensities of observed reflexions in* [001] *rotation photograph*

| *hkl* | 2 sin $\theta$ calculated | 2 sin $\theta$ observed | Intensity |
|---|---|---|---|
| 011 | 0·169 | 0·165 | *m* |
| 013 | | | *w* |
| 020 | 0·339 | 0·330 | *s* |
| 022 | | | *s* |
| 024 | | | *w* |
| 033 | 0·508 | 0·505 | *m* |
| 110 | 0·200 | 0·195 | *vs* |
| 112 | | | *vs* |
| 114 | | | *vs* |
| 121 | 0·355 | 0·350 | *m* |
| 123 | | | *vs* |
| 130 | 0·519 | 0·520 | *w* |
| 134 | | | *w* |
| 141 | 0·685 | 0·685 | *w* |
| 145 | | | *w* |
| 152 | 0·853 | 0·854 | *w* |
| 161 | 1·021 | 1·025 | *w* |
| 163 | | | *w* |
| 200 | 0·212 | 0·205 | *s* |
| 202 | | | *s* |
| 204 | | | *s* |
| 215 | 0·271 | 0·270 | *m* |
| 220 | 0·399 | 0·395 | *s* |
| 222 | | | *m* |
| 226 | | | *w* |
| 233 | 0·550 | 0·545 | *m* |
| 242 | 0·709 | 0·702 | *m* |
| 244 | | | *w* |
| 310 | 0·360 | 0·355 | *vs* |
| 312 | | | *s* |
| 321 | 0·464 | 0·465 | *s* |
| 323 | | | *m* |
| 330 | 0·599 | 0·595 | *s* |
| 334 | | | *m* |
| 345 | 0·748 | 0·750 | *m* |
| 400 | 0·423 | 0·420 | *vs* |
| 402 | | | *w* |
| 404 | | | *w* |
| 420 | 0·542 | 0·540 | *w* |
| 422 | | | *s* |
| 426 | | | *w* |
| 431 | 0·661 | 0·660 | *w* |
| 440 | 0·798 | 0·800 | *m* |
| 444 | | | *w* |
| 451 | 0·946 | 0·950 | *w* |
| 510 | 0·555 | 0·555 | *m* |
| 512 | | | *w* |
| 530 | 0·733 | 0·730 | *m* |
| 532 | | | *vw* |
| 534 | | | *m* |
| 541 | 0·859 | 0·860 | *m* |
| 600 | 0·635 | 0·630 | *s* |
| 604 | | | *w* |
| 613 | 0·657 | 0·650 | *m* |
| 633 | 0·813 | 0·810 | *w* |
| 712 | 0·760 | 0·760 | *vw* |
| 730 | 0·898 | 0·900 | *w* |
| 752 | 1·124 | 1·130 | *w* |
| 800 | 0·846 | 0·840 | *m* |
| 804 | | | *w* |
| 820 | 0·911 | 0·915 | *w* |
| 910 | 0·967 | 0·965 | *m* |
| 912 | | | *w* |
| 923 | 1·010 | 1·010 | *w* |
| 1000 | 1·058 | 1·050 | *m* |
| 1013 | 1·072 | 1·075 | *w* |
| 1022 | 1·111 | 1·110 | *w* |

Table 2 gives similar information derived from the [1$\bar{1}$0] rotation photograph. Intensity scales are comparable, as shown by the reflexions common to the Tables. As there are 4 Zn atoms in the unit cell, they must lie at one of the special positions (*a*) or (*b*). As the position of the origin on the diad axis is arbitrary, *z* may be put equal to zero, and the coordinates are:

Table 2. *Relative intensities of observed reflexions in* [1$\bar{1}$0] *rotation photograph*

| *hkl* | 2 sin $\theta$ calculated | 2 sin $\theta$ observed | Intensity |
|---|---|---|---|
| 110 | 0·200 | 0·200 | *s* |
| 002 | 0·242 | 0·243 | *vs* |
| 112 | | | *vs* |
| 220 | 0·399 | 0·397 | *s* |
| 222 | | | *m* |
| 330 | 0·599 | 0·600 | *m* |
| 334 | | | *w* |
| 226 | | | *w* |

Position (*a*), Zn at 000; $\frac{1}{2}$00; 0$\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.
The shortest distance between Zn atoms is $a/2=7{\cdot}28$ Å, and the molecules must have a diad axis parallel to the *c* axis.

Position (*b*), Zn at $\frac{1}{4}, y, 0$; $\frac{3}{4}, y, 0$; $\frac{3}{4}, \frac{1}{2}+y, \frac{1}{2}$; $\frac{1}{4}, \frac{1}{2}-y, \frac{1}{2}$.
The shortest distance between Zn atoms is $c/2=6{\cdot}35$ Å, when $y=b/4$. The molecule must have a mirror plane of symmetry parallel to (100).

We may note that if the Zn atoms are in position (*a*) they make no contribution to the reflexions with *h* odd. The scattering by Zn being greater than that from any other single atom, we should expect reflexions with *h* odd to be weaker than those with *h* even. The reverse is the case, but the difference is not marked, and position (*a*) was considered as a possible site for Zn atoms.

The possible configurations of $Zn(NCS)_2(C_6H_5NH_2)_2$ can be classified under two main headings:

I. Discrete molecules exist, with no linkage between Zn atoms.

II. Zn atoms are linked through –N–C–S– bridges.

These may be subdivided as follows, on the basis of the Zn coordination.

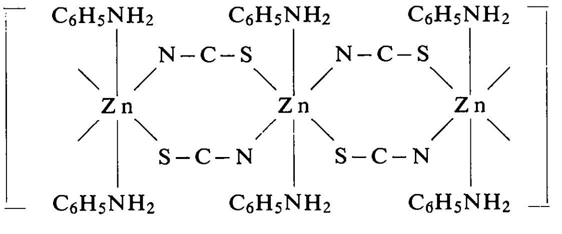
I. (i) Zn coordination tetrahedral.
  (*A*) The molecule possesses a diad axis and two perpendicular planes of symmetry through this axis.

(*B*) The molecule, derived from the above by rotation of an aniline group about the N–C bond, possesses one plane of symmetry.

(ii) Zn coordination square planar.
(*A*) A *cis* arrangement.
(*B*) A *trans* arrangement.

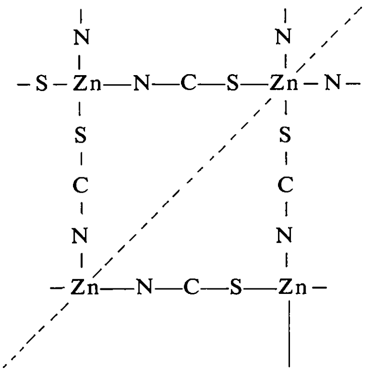
II. Zn coordination octahedral, each Zn atom being bonded to two S atoms as well as to two N atoms and two aniline groups.

(i) Two -N-C-S- bridges occur between a pair of Zn atoms, forming a 'chain' arrangement:



This configuration has been found in cadmium and platinum complexes, (Owston & Rowe, 1960; Cavalaca, Nardelli & Fava, 1960). A similar configuration with the direction of one of the -N-C-S links reversed was also considered.

(ii) Only one -N-C-S- bridge occurs between each pair of linked Zn atoms, forming a 'plate' arrangement:



The Zn–N bonds to the aniline group are perpendicular to the plane of the paper. If Zn, N, C and S are coplanar, this structure has a diad axis along the dotted diagonal and mirror planes in and perpendicular to the plane of the paper. A variant of the 'plate' structure has the nitrogen atoms coordinated to a zinc atom *trans* to one another. Each of the bridged configurations (II) requires a framework of Zn atoms of specified size and shape. The possibility of providing this with Zn atoms in special positions (*a*) and (*b*) was investigated, and all models of the bridged type were rejected except the 'chain' configuration II(i) with Zn in position (*b*).

The configurations in class I are not subject to this condition, and they were examined, with the help of rough models, for steric overlap of the molecules. Assuming NCS to be bound through nitrogen the tetrahedral models (i)*A* and (i)*B* and the square planar model (ii)*B*, with Zn in position (*b*) in all cases, could be placed so that symmetry and steric requirements were satisfied.

The relative intensities of the X-ray reflexions calculated from the four models not already rejected were next examined for some of the planes of large spacing. Those most helpful in discriminating between the different models were found to be the 200 and 002. Only in the case of the tetrahedral model I(i)*B* was the observed inequality $I(002) > I(200)$ satisfied.

Class I models with NCS coordinating through the S atom were similarly examined and symmetry and steric requirements were satisfied by I(i)*A*, I(i)*B* and I(ii)*B*. Of these, only I(i)*A* could be rejected on grounds of reflexion intensities.

The X-ray data thus show the zinc atom to be 4-coordinate with one of three structures, I(i)*B* (N-bonded NCS), I(i)*B* or I(ii)*B* (S-bonded NCS). The fundamental stretching modes of the NCS group are often diagnostic of M–N–C–S and M–S–C–N bonds. (Lewis, Nyholm & Smith, 1961). We were unable to identify a bond corresponding to $\nu_{C-S}$ in the infrared spectrum and the value of $\nu_{C-N} = 2210 \pm 4$ cm$^{-1}$ did not allow a definite assignment of the coordinating atom.

Although sulphur coordination cannot be ruled out, we consider it unlikely in view of (1) the fact that in $Zn(NCS)_2L_2$ where L = pyridine, $\beta$-picoline and $\gamma$-picoline the NCS is N-bound ($\nu_S = 845 \pm 5$ cm$^{-1}$), the complexes being tetrahedral (Nelson & Shepherd, unpublished work) and (2) the predominantly class (*a*) character of zinc (Ahrland, Chatt & Davies, 1958).

On these grounds, we suggest the following structure for $Zn(NCS)_2(C_6H_5NH_2)_2$. The zinc atom is tetrahedrally coordinated, in such a way that the -N-C-S groups coordinated through the nitrogen are nearly parallel to the plane of one aniline group, and the aniline groups are at about 115° to each other (Fig. 1). A plane of symmetry bisects the molecule, and is parallel to (100). The Zn atom lies in the special position (*b*), with $y \simeq 0$, and the plane of one aniline group, and of the -N-C-S groups, make an angle of about 17° with (001). The accuracy of the work is not sufficient to show any small deviations from regularity in the tetrahedron about the Zn atom.

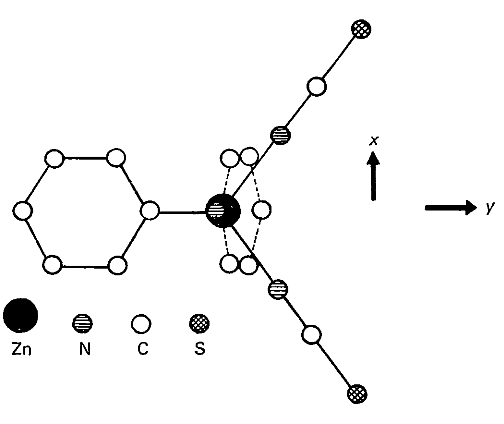


Fig. 1. Proposed configuration of the molecule viewed along the *z* axis.

No further crystallographic work on this complex is contemplated.

The authors thank Dr S. M. Nelson, who suggested the problem, for helpful discussions.

One of us (T. M. S.) thanks the Ministry of Education of Northern Ireland for a Research Studentship and Queen's University, Belfast for a Foundation Studentship.

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## Twinning in *p*-aminobenzoic acid.

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(*Received* 17 *December* 1964)

*p*-Aminobenzoic acid is a growth factor for several microorganisms. Its presence enables the organisms to synthesize the more complex molecule of vitamin Bc.

Groth (1908) has quoted that crystals of *p*-aminobenzoic acid belong to the monoclinic prismatic class with axial ratios 1·4403 : 1 : 0·7312, $\beta = 100^\circ\,10'$ and density 1·393 g.cm$^{-3}$ at 20 °C. This observation was verified by Prasad, Kapadia & Thakar (1937) who published unit-cell dimensions $a = 12{\cdot}26$, $b = 8{\cdot}61$, $c = 6{\cdot}30$ Å, $\beta = 100^\circ\,10'$, which gave axial ratios 1·424 : 1 : 0·732 and calculated density 1·38 g.cm$^{-3}$. Prasad *et al.* mention crystallization difficulties and indicate that the crystals were rhombic plates obtained by repeated slow crystallization from aqueous alcohol. The present authors have attempted to repeat this work with the purpose of verifying that *p*-aminobenzoic acid molecules associate as dimers. Recrystallization of commercially available *p*-aminobenzoic acid from the solvents listed in Table 1 gave three distinct crystallographic forms. Despite repeated recrystallization the rhombic plate modification has not been obtained.

From the approximate nature of the *mmm* symmetry, the *C*-face centring that is indicated, and the fact that the systematic absences do not conform to any space group, it is deduced that all three modifications are twins. In addition many of the photographs of the upper levels of form I showed streaks attributed to disorder, although the streaks never appeared on photographs of the *hk*0 reflexions. Careful examination indicated that physical separation of the twins appeared unlikely and that the crystals are probably polysynthetic twins. Under these circumstances one is forced to work with the twinned material, and indeed, a trial structure was obtained for the (001) projection of form I before general data were collected and it was realized that the crystal was twinned.

The (001) projection of form I, which has *mm* symmetry and apparent axes of 12·75 Å and 13·58 Å has pseudo *pgg* plane space group, there being a few relatively weak axial reflexions having $h = 2n + 1$ and one exceptionally weak $k = 2n + 1$ which cannot be explained as Renninger reflexions. The trial structure was obtained by computing an $(E^2 - 1)$ Patterson function for the (001) projection with the data collected by the multiple-film Weissenberg technique. The presence of a benzene ring was immediately obvious and

Table 1. *Crystallographic modifications of p-aminobenzoic acid*

| Solvent | Morphological habit | Crystallographic modification | Symmetry class of reciprocal space | Axial lengths (Å) *a* | *b* | *c* | Comments |
|---|---|---|---|---|---|---|---|
| Anhydrous ethanol<br>Aqueous ethanol<br>Methanol<br>Water<br>Acetone<br>Ether and petroleum spirit | Acicular and fibrous | I | Approximately *mmm* | 25·50 | 27·16 | 3·85 | White crystals which become straw coloured on exposure to the atmosphere. |
| Acetone and water | Blades and fibrous | | | | | | |
| Acetone acid | Spherolitic | | | | | | |
| Dioxan | (*a*) Prismatic | II | Approximately *mmm* | 43·88 | 12·00 | 20·68 | Straw coloured rapidly decomposing to white powder unless sealed in glass tube. II and III have different systematic absences. |
| | (*b*) Bladed | III | Approximately *mmm* | 43·88 | 12·00 | 20·68 | |

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