

- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kuma (1989). *KM-4 User's Guide*. Version 3.1. Kuma Diffraction, Wroclaw, Poland.
- Molecular Simulations (1998). *Cerius²*, Version 3.5. Molecular Simulations, 9685 Scranton Road, San Diego, CA 92121-3752, USA, and 240/250 The Quorum, Barnwell Road, Cambridge CB5 8RE, England.
- Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.
- Nangia, A. & Anthony, A. (1996). *Synth. Commun.* **26**, 225–236.
- Nangia, A. & Anthony, A. (1997). *Indian J. Chem.* **36B**, 1113–1118.
- Numazawa, M., Mutsumi, A., Asano, N. & Ito, Y. (1993). *Steroids*, **58**, 40–46.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Steiner, T. (1996). *Cryst. Rev.* **6**, 1–57.
- Steiner, T. (1997). *Chem. Commun.* pp. 727–729.
- Wahl, M. C. & Sundaralingam, M. (1997). *Trends Biochem. Sci.* **22**, 97–102.

Acta Cryst. (1998). **C54**, 1898–1900

5 β -Androstan-3,17-dione

ADDLAGATTA ANTHONY,^a MARIUSZ JASKOLSKI,^b ASHWINI NANGIA^a AND GAUTAM R. DESIRAJU^a

^a*School of Chemistry, University of Hyderabad, Hyderabad 500 046, India, and* ^b*Institute of Bioorganic Chemistry, Polish Academy of Sciences, and Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, Poznan, Poland. E-mail: ansc@uohyd.ernet.in*

(Received 6 April 1998; accepted 8 June 1998)

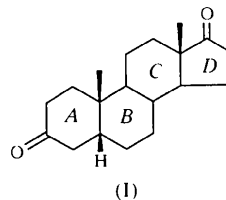
Abstract

The title compound, C₁₉H₂₈O₂, has the 5 β configuration and a bowing angle of 71.76 (5)° at the A/B ring junction. The crystal structure is stabilized by weak intermolecular C—H $\cdots$ O and van der Waals interactions.

Comment

The configuration at C5 is known to play an important role in the hormonal responses of steroids (Lawrence *et al.*, 1986). The activity of steroid analogues and their ability to bind to the receptor varies depending on whether the configuration at C5 is α or β , because of differences in the overall shape of the two epimers. The 5 α steroids are flat, whereas the 5 β epimers are bent at the A/B ring junction. 5 α - and 5 β -androstan-3,17-dione are important compounds in steroid metabolism and their biological activity has been studied extensively. In the Cambridge Structural Database (CSD; Allen & Kennard, 1993), two crystal structures of 5 α -androstan-

3,17-dione [CSD refcodes: ANDION10 (Coiro *et al.*, 1973) and ANDRDO (Peck *et al.*, 1974)] and the cell parameters for the 5 β -epimer [CSD refcode: ZZZPDK (Norton *et al.*, 1962)] are reported. Here we report the crystal structure of 5 β -androstan-3,17-dione, (I).



Ring A is in a half-chair conformation, rings B and C are in a chair conformation and ring D adopts the commonly found 14 α -envelope conformation (Duax & Norton, 1975; Paixão *et al.*, 1998). The bowing angle in (I) [71.76 (5)°] is comparable to the corresponding angles found in other 5 β -steroids reported recently [81.53 (9) and 81.97 (9) (Andrade *et al.*, 1997) and 58.91 (6)° (Ramos Silva *et al.*, 1996)]. There are three conformers of 5 α -androstan-3,17-dione available for comparison with the 5 β -epimer (I): ANDION10 and two symmetry-independent molecules of ANDRDO. The overlay plot of (I) with the three 5 α -androstandione conformers shows that the B, C and D rings overlap with very low r.m.s. deviations (0.082, 0.059 and 0.066 Å), while the conformational flexibility in ring A is considerable.

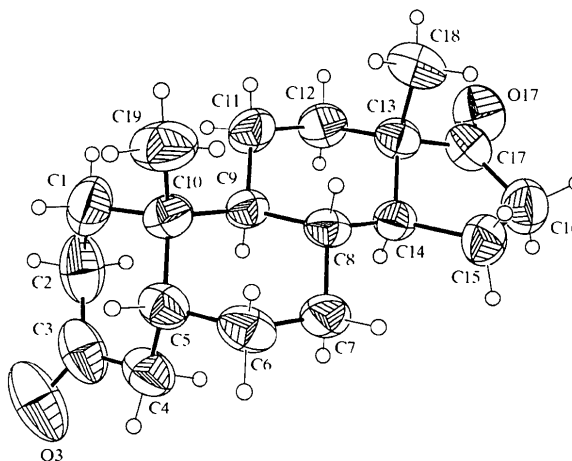


Fig. 1. *ORTEP* (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

The crystal structure of (I) (Fig. 2) is stabilized by weak C—H $\cdots$ O hydrogen bonds (Desiraju, 1996). A hydrogen-bonded chain runs along [010], involving C7 β —H and O3 atoms (H $\cdots$ O 2.68 Å, C—H $\cdots$ O 130°) of translation-related molecules. Additionally, the C5 β —H and C19—H donors are hydrogen bonded along [001] to O3 of a screw-related molecule (2.73 Å, 152°; 2.69 Å, 147°). The C3 carbonyl-O atom thus

behaves as a trifurcated acceptor, making two hydrogen bonds with a 2_1 -related molecule and one bond with a translated molecule. $C4\alpha-H$ and $C9\alpha-H$ of the androstane are hydrogen bonded to O17 of a screw-related molecule ($2.69\text{ \AA}$, 146° ; $2.63\text{ \AA}$, 165°) leading to a bifurcated $C-H\cdots O$ motif along $[001]$. Even though the $C-H\cdots O$ bonds in (I) are at the limit of the van der Waals radii ($H\cdots O\ 2.7\text{ \AA}$), they should be considered in the crystal structure analysis because it has recently been shown that most $C-H\cdots O$ contacts exhibit the characteristics of hydrogen bonds and could play a structure-determining role even at long distances (Steiner *et al.*, 1998; Steiner & Desiraju, 1998).

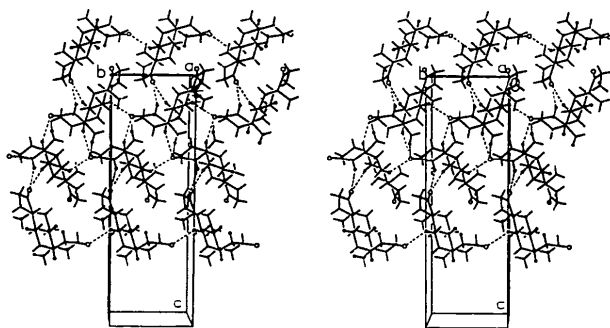


Fig. 2. Stereoview down $[100]$, showing the bifurcated and trifurcated $C-H\cdots O$ hydrogen-bonding motifs at O17 and O3, respectively. Notice that the hydrogen bonds (shown as dashed lines) occur on the α -face with O17 and on the β -face with O3. The H and O atoms involved in hydrogen bonding are shown as empty circles.

Since none of the atoms in the molecule is a strong enough anomalous scatterer at the Cu $K\alpha$ wavelength, the absolute configuration was not determined from X-ray data; the chirality assigned is as derived from the chemical synthesis.

Experimental

The title compound was obtained by hydrogenation of androst-4-ene-3,17-dione with 5% Pd/C catalyst in ethyl acetate at ambient temperature and pressure. The structure of (I) was confirmed by IR and 1H NMR. Crystals for X-ray diffraction were obtained by slow evaporation of the steroid from a mixture of ethyl acetate and hexane.

Crystal data

$C_{19}H_{28}O_2$
 $M_r = 288.41$
 Orthorhombic
 $P2_12_12_1$
 $a = 7.9475(5)\text{ \AA}$
 $b = 8.3767(7)\text{ \AA}$
 $c = 25.019(2)\text{ \AA}$
 $V = 1665.6(2)\text{ \AA}^3$
 $Z = 4$
 $D_x = 1.150\text{ Mg m}^{-3}$
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54178\text{ \AA}$
 Cell parameters from 50 reflections
 $\theta = 15-76^\circ$
 $\mu = 0.561\text{ mm}^{-1}$
 $T = 293(2)\text{ K}$
 Prism
 $0.4 \times 0.4 \times 0.4\text{ mm}$
 Colourless

Data collection

Kuma KM-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 1835 measured reflections
 1835 independent reflections
 1608 reflections with
 $I > 2\sigma(I)$

$\theta_{\max} = 70.09^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 30$
 2 standard reflections
 every 100 reflections
 intensity decay: $<2.5\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.093$
 $S = 1.049$
 1833 reflections
 191 parameters
 H atoms fixed
 $w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.2105P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.109\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.106\text{ e \AA}^{-3}$
 Extinction correction:
 SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.0025(4)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 1. Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C4-H41\cdots O17^i$	0.97	2.69	3.535(3)	146
$C5-H51\cdots O3^{ii}$	0.98	2.73	3.624(3)	152
$C7-H72\cdots O3^{iii}$	0.97	2.68	3.392(3)	130
$C9-H91\cdots O17^i$	0.98	2.63	3.585(2)	165
$C15-H151\cdots O17^{iv}$	0.97	2.91	3.594(3)	129
$C19-H192\cdots O3^{ii}$	0.96	2.69	3.536(4)	147

Symmetry codes: (i) $x - \frac{1}{2}, -\frac{3}{2} - y, -z$; (ii) $-2 - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (iii) $x, 1 + y, z$; (iv) $x - \frac{1}{2}, -\frac{1}{2} - y, -z$.

Data collection: *Kuma KM-4 User's Guide* (Kuma, 1989). Cell refinement: *Kuma KM-4 User's Guide*. Data reduction: *Kuma KM-4 User's Guide*. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976) and PLUTO (Motherwell & Clegg, 1978). Software used to prepare material for publication: SHELXL93.

AA thanks the CSIR for fellowship support. AN and GRD acknowledge financial support from the DST (SP/S1/G-25/91). This work was made possible in part by the Indo-Polish Cooperation Programme (INT/POL/POC/P-22/96). MJ thanks Professor U. Wrzeczio and Dr A. Gzella at the K. Marcinkowski University of Medical Sciences, Poznan, for making their X-ray laboratory available. The research of MJ was supported by the HHMI.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1287). Services for accessing these data are described at the back of the journal.

References

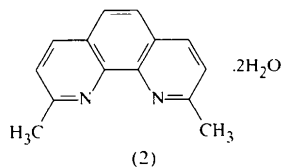
- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31-37.
- Andrade, L. C. R., Paixão, J. A., de Almeida, M. J., Tavares da Silva, E. J., Sá e Melo, M. L. & Campos Neves, A. S. (1997). *Acta Cryst. C53*, 938-940.

- Coiro, V. M., Giglio, E., Lucano, A. & Puliti, R. (1973). *Acta Cryst.* **B29**, 1404–1409.
- Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
- Duax, W. L. & Norton, D. A. (1975). In *Atlas of Steroid Structure*, Vol. 1. New York: Plenum.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kuma (1989). *KM-4 User's Guide*. Version 3.1. Kuma Diffraction, Wroclaw, Poland.
- Lawrence, W. D., Osawa, Y. M., Davis, P. J. & Blas, S. D. (1986). *Endocrinology*, **119**, 2803–2808.
- Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.
- Norton, D. A., Lu, C. T. & Campbell, A. E. (1962). *Acta Cryst.* **15**, 1189.
- Paixão, J. A., Andrade, L. C. R., de Almeida, M. J., Costa, M. M. R. R., Tavares da Silva, E. J., Sá e Melo, M. L. & Campos Neves, A. S. (1998). *Acta Cryst.* **C54**, 89–91.
- Peck, D. N., Langs, D. A., Eger, C. & Duax, W. L. (1974). *Cryst. Struct. Commun.* **3**, 573–578.
- Ramos Silva, M., Paixão, J. A., de Almeida, M.-J. M., Tavares da Silva, E. J., Sá e Melo, M. L. & Campos Neves, A. S. (1996). *Acta Cryst.* **C52**, 2892–2894.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Steiner, T. & Desiraju, G. R. (1988). *Chem. Commun.* pp. 891–892.
- Steiner, T., Lutz, B., van der Maas, J., Schreurs, A. M. M., Kroon, J. & Tamm, M. (1998). *Chem. Commun.* pp. 171–172.

of slight deviations from the crystallographic mirror symmetry.

Comment

2,9-Dimethyl-1,10-phenanthroline (neocuproine) is a versatile ligand frequently used in the synthesis of metal–organic complexes (Baggio *et al.*, 1996, 1997). A hemihydrate form of the free molecule, (1), has already been described (Britton *et al.*, 1991) as crystallizing in tetragonal *I*₄/a. We report here the crystal and molecular structure of a second monoclinic dihydrated crystal form, (2), of free neocuproine.



The molecule is planar, with expected values for interatomic distances and angles, and molecular geometry in agreement, within experimental error, with that of (1).

The most substantial difference is in the packing. Molecule (1) can be considered to be formed by pairs of neocuproine molecules bridged by single water molecules, which lie on twofold axes. These units, in turn, interact weakly through long C—H...OH₂ contacts (H...O 2.56 Å) to form two sets of orthogonal linear chains parallel to the *a* and *b* axes. In (2), water

Acta Cryst. (1998). **C54**, 1900–1902

2,9-Dimethyl-1,10-phenanthroline Dihydrate

SERGIO BAGGIO,^a RICARDO BAGGIO^b AND ALVARO W. MOMBRÚ^c

^aUniversidad Nacional de la Patagonia, Sede Puerto Madryn, and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, ^bDepartamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, and ^cLaboratorio de Cristalografía y Química del Estado Sólido, Facultad de Química, Universidad de la República, Montevideo, Uruguay. E-mail: baggio@cnea.edu.ar

(Received 18 May 1998; accepted 17 July 1998)

Abstract

A novel dihydrated form of 2,9-dimethyl-1,10-phenanthroline (neocuproine), C₁₄H₁₂N₂·2H₂O, is described. The molecule is very similar to that already reported in the literature, the main differences being in the packing. The positioning of the H atoms had a great influence in the convergence of the refinement process. This was performed in *C*2/*m*, though there were some suggestions

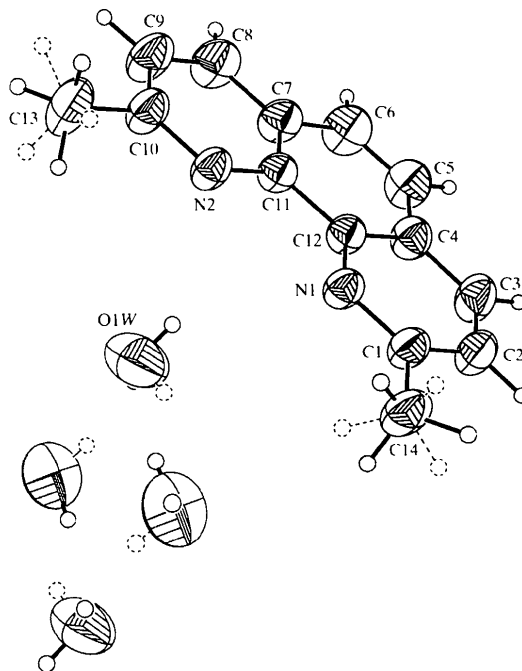


Fig. 1. The molecular diagram of (2) showing the numbering of atoms. Note the cluster of four hydration water molecules with disordered H atoms which build up around the twofold symmetry axis. Displacement ellipsoids are drawn at the 40% probability level.