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Structure of 9α,19-Dihydroxy-4-androstene-3,17-dione

By P. Dastidar, V. N. Shankar, K. M. Madyastha and T. N. Guru Row

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, *India*

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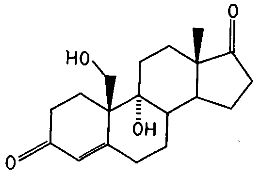
Abstract. $C_{19}H_{26}O_4$, $M_r = 318.41$, orthorhombic, $P2_12_12_1$, $a = 10.591$ (1), $b = 11.133$ (1), $c = 13.657$ (2) Å, $V = 1610.29$ Å^3, $Z = 4$, D_m (flotation in KI) = 1.301, $D_x = 1.313$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.85$ cm^{-1}, $F(000) = 688$, $T = 293$ K, $R = 0.057$ for 1253 significant reflections. The *A* ring is disordered with atoms C(2) and O(19) occupying two possible sites. The molecules are held together by a hydrogen bond [O(9)···O(17) = 2.89 Å].

Introduction. Many bacteria have been used to hydroxylate steroidal skeletons at different positions, oxidize an alcohol to a ketone, introduce a double bond, cleave a side chain *etc.* A soil microorganism belonging to the genus *Moraxella* was isolated and used to study the mode of metabolism of cholesterol and its analogues. In our study related to the cleavage of the C(17) side chain without degrading the *B* ring (Martin, 1977), a model system 5-cholestene-3β,19-diol 3-acetate was selected as the substrate. Such studies generated several metabolites, the major one being estrone. The crystal and molecular structure of one of the minor metabolites 9α,19-dihydroxy-4-androstene-3,17-dione (I) is reported in this article.



(I)

Experimental. Plate-like single crystals of the title compound were obtained from ethanol. Crystal size approximately 0.5 × 0.3 × 0.15 mm. Lattice parameters refined using 25 reflections in the θ range 10–15°. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. $\theta \leq 23.5°$, scan speed 1° min^{-1}, $\omega/2\theta$ mode. Three standard reflections (334, 253, 213) monitored every 100 reflections showed intensity variations of 4%. 1417 unique reflections collected ($0 \leq h \leq 11$, $0 \leq k \leq 12$, $0 \leq l \leq 15$), 1253 significant [$|F_o| \geq 3\sigma(|F_o|)$]. Data not corrected for absorption or extinction. Structure solved by direct methods (*SHELXS*86; Sheldrick, 1986). The best *E* map gave all non-hydrogen atoms. Full-matrix least-squares program *SHELX*76 (Sheldrick, 1976) used for refinement. In the isotropic stage of refinement, the thermal parameters of O(19) and C(2) were found to be large and two considerably high peaks were consistently seen in the electron density map in the vicinity of O(19) and C(2). By considering these two peaks as disordered atoms [O(19)′, C(2)′], the occupancy (*n*) of C(2), patched with O(19), with $(1-n)$ occupancies for C(2)′ and O(19)′, was refined. The thermal parameters for these four atoms were also refined with their current occupancies [C(2) = 0.80, C(2)′ = 0.20, O(19) = 0.80, O(19)′ = 0.20] fixed. Positional and anisotropic thermal parameters of all non-hydrogen atoms except C(2)′ and O(19)′ were refined. C(2)′ and O(19)′ were refined isotropically. 19 hydrogens were located by difference Fourier. H(19*A*), H(19*B*), H(16*A*) and H(16*B*) were fixed geometrically. The positional parameters of ten hydrogens [H(6*A*), H(6*B*), H(8), H(11*A*), H(11*B*), H(12*A*), H(12*B*), H(14), H(15*A*) and H(15*B*)] were refined while the contributions from others were considered for the structure-factor calculations. The isotropic thermal parameters for all the hydrogens were not refined. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, $w = 1.72/[\sigma(|F_o|)^2 + 0.000868|F_o|^2]$. At the end of the final cycle of refinement $R = 0.057$, $wR = 0.062$, $S = 1.63$, $\Delta/\sigma = 0.001$. The final difference map was featureless ($\Delta\rho \leq 0.1$ e Å^{-3}). Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are given in Table 1,* bond distances and angles are in Table 2, and an *ORTEP*II (Johnson, 1976) diagram for the title compound with numbering is given in Fig. 1. The atoms C(2) and O(19) occupy two possible

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54481 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0474]

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* ($\times 10^4$) *for non-hydrogen atoms*

E.s.d.'s are given in parentheses. The temperature factor is of the form $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
C(1)	0.1252 (6)	0.8981 (5)	0.0631 (4)	547 (19)
C(2)	0.1005 (8)	0.7935 (5)	−0.0072 (5)	516 (23)
C(3)	0.0287 (5)	0.8385 (4)	−0.0944 (4)	478 (16)
O(3)	−0.0559 (4)	0.7795 (3)	−0.1336 (3)	581 (13)
C(4)	0.0759 (5)	0.9475 (4)	−0.1392 (3)	387 (15)
C(5)	0.1490 (5)	1.0263 (4)	−0.0905 (3)	375 (14)
C(6)	0.1969 (6)	1.1389 (5)	−0.1398 (4)	489 (18)
C(7)	0.1634 (5)	1.2526 (4)	−0.0819 (3)	394 (15)
C(8)	0.1993 (5)	1.2420 (4)	0.0260 (3)	324 (16)
C(9)	0.1405 (4)	1.1274 (4)	0.0713 (3)	344 (16)
O(9)	0.0074 (3)	1.1395 (3)	0.0534 (2)	392 (9)
C(10)	0.1867 (5)	1.0108 (4)	0.0161 (3)	364 (15)
C(19)	0.3333 (5)	0.9947 (5)	0.0171 (4)	533 (18)
O(19)	0.3889 (5)	0.9642 (5)	0.1072 (3)	618 (17)
C(11)	0.1648 (5)	1.1195 (4)	0.1826 (3)	382 (15)
C(12)	0.1314 (5)	1.2339 (4)	0.2389 (3)	398 (15)
C(13)	0.1980 (4)	1.3410 (4)	0.1925 (3)	343 (14)
C(14)	0.1574 (5)	1.3507 (4)	0.0851 (3)	340 (14)
C(15)	0.1983 (6)	1.4772 (4)	0.0541 (4)	463 (18)
C(16)	0.1653 (6)	1.5517 (4)	0.1451 (4)	519 (19)
C(17)	0.1636 (5)	1.4641 (4)	0.2304 (4)	421 (14)
C(18)	0.3426 (5)	1.3340 (5)	0.2080 (4)	467 (16)
O(17)	0.1391 (4)	1.4896 (3)	0.3146 (2)	553 (13)
C(2)′†	0.0279 (23)	0.8361 (22)	0.0166 (17)	306 (50)
O(19)′†	0.3658 (20)	0.8988 (17)	−0.0221 (14)	577 (49)

† Atoms were refined isotropically.

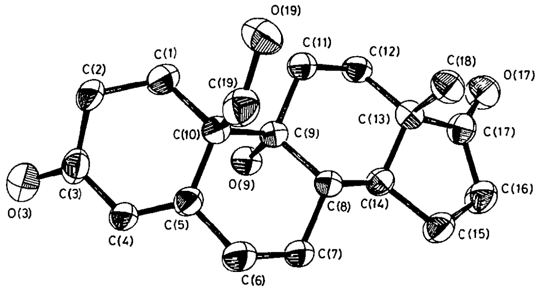

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I); non-hydrogen atoms are drawn as primary ellipses at the 50% probability level. C(2) and O(19) represent only the major component of the disordered atoms.

positions with refined occupancies C(2) = 0.80, C(2)′ = 0.20, O(19) = 0.80 and O(19)′ = 0.20. Similar disorder of the *A* ring has been reported previously (Eggleston & Lan-Hargest, 1990). The two disordered positions of C(2), labelled C(2) and C(2)′, define either a 2α- or 2β-sofa conformation in ring *A*. The deviations of the atoms C(2) and C(2)′ from the mean plane containing C(1), C(3), C(4), C(5) and C(10) are 0.575 (7) above and 0.382 (24) Å below the plane respectively. Atom O(19)′ of the 19-hydroxyl group is oriented over ring *A* with torsion angle C(1)—C(10)—C(19)—O(19)′ = 53.9 (11)°. Two structures have been reported previously (Weeks, Strong & Osawa, 1976; Duax & Osawa, 1980) which have a similar conformation. However, the 19-hydroxyl group is located between the *A* and *C* rings with the C(19)—O(19) bond approximately perpendicular to the C(9)—C(10) bond in two Δ^5 steroids (Duax, Weeks & Rohrer, 1976). O(19)′ is slightly closer to C(1) than to C(5) [C(1)—O(19)′ = 2.801, C(5)—O(19)′ = 2.856 Å] unlike the case reported earlier (Duax & Osawa, 1980). The hydroxyl group at C(9) was found to be *anti* with respect to C(19) with a C(19)—C(10)—C(9)—O(9) torsion angle of 172.3 (3)°. The molecules are stabilized in the crystal lattice by a hydrogen bond [O(9)···O(17) = 2.897, O(9)—H(9) = 0.96, H(9)···O(17) = 1.988 Å, O(9)—H(9)···O(17) = 156.8°].

Table 2. *Bond distances* (Å) *and bond angles* (°) *involving non-hydrogen atoms*

C(1)—C(2)	1.531 (8)	C(9)—O(9)	1.437 (5)
C(1)—C(10)	1.552 (7)	C(9)—C(10)	1.578 (6)
C(1)—C(2)′	1.393 (24)	C(9)—C(11)	1.544 (5)
C(2)—C(3)	1.499 (8)	C(10)—C(19)	1.563 (7)
C(3)—O(3)	1.233 (6)	C(19)—O(19)	1.405 (7)
C(3)—C(4)	1.448 (6)	C(19)—O(19)′	1.243 (19)
C(3)—C(2)′	1.516 (23)	C(11)—C(12)	1.529 (6)
C(4)—C(5)	1.345 (6)	C(12)—C(13)	1.523 (6)
C(5)—C(6)	1.510 (7)	C(13)—C(14)	1.532 (5)
C(5)—C(10)	1.519 (5)	C(13)—C(17)	1.509 (6)
C(6)—C(7)	1.534 (7)	C(13)—C(18)	1.548 (6)
C(7)—C(8)	1.526 (5)	C(14)—C(15)	1.533 (6)
C(8)—C(9)	1.548 (6)	C(15)—C(16)	1.534 (7)
C(8)—C(14)	1.520 (6)	C(16)—C(17)	1.519 (7)

C(10)—C(1)—C(2)′	121.4 (10)	C(5)—C(10)—C(9)	106.4 (3)
C(2)—C(1)—C(10)	115.2 (4)	C(1)—C(10)—C(9)	109.7 (3)
C(1)—C(2)—C(3)	109.2 (4)	C(1)—C(10)—C(5)	112.1 (4)
C(1)—C(2)′—C(3)	116.2 (16)	C(9)—C(10)—C(19)	113.4 (3)
C(2)—C(3)—C(4)	116.1 (4)	C(5)—C(10)—C(19)	106.4 (3)
C(2)—C(3)—O(3)	122.3 (4)	C(1)—C(10)—C(19)	108.6 (4)
C(4)—C(3)—C(2)′	116.0 (9)	C(10)—C(19)—O(19)′	111.7 (10)
O(3)—C(3)—C(2)′	114.8 (9)	C(10)—C(19)—O(19)	116.8 (4)
O(3)—C(3)—C(4)	120.9 (4)	C(9)—C(11)—C(12)	114.1 (3)
C(3)—C(4)—C(5)	122.4 (4)	C(11)—C(12)—C(13)	109.6 (3)
C(4)—C(5)—C(10)	123.4 (4)	C(12)—C(13)—C(18)	111.2 (3)
C(4)—C(5)—C(6)	120.9 (4)	C(12)—C(13)—C(17)	117.1 (3)
C(6)—C(5)—C(10)	115.6 (4)	C(12)—C(13)—C(14)	108.8 (3)
C(5)—C(6)—C(7)	112.1 (4)	C(17)—C(13)—C(18)	103.7 (3)
C(6)—C(7)—C(8)	112.1 (3)	C(14)—C(13)—C(18)	114.3 (3)
C(7)—C(8)—C(14)	112.2 (3)	C(14)—C(13)—C(17)	101.3 (3)
C(7)—C(8)—C(9)	110.4 (3)	C(8)—C(14)—C(13)	111.7 (3)
C(9)—C(8)—C(14)	109.0 (3)	C(13)—C(14)—C(15)	104.4 (3)
C(8)—C(9)—C(11)	111.9 (3)	C(8)—C(14)—C(15)	120.1 (3)
C(8)—C(9)—C(10)	111.2 (3)	C(14)—C(15)—C(16)	102.0 (3)
C(8)—C(9)—O(9)	104.4 (3)	C(15)—C(16)—C(17)	106.0 (3)
C(10)—C(9)—C(11)	111.8 (3)	C(13)—C(17)—C(16)	108.4 (3)
O(9)—C(9)—C(11)	109.6 (3)	C(16)—C(17)—O(17)	125.4 (4)
O(9)—C(9)—C(10)	107.4 (3)	C(13)—C(17)—O(17)	126.1 (4)

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References

Duax, W. L. & Osawa, Y. (1980). *J. Steroid Biochem.* **13**, 383–386.

Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by N. L. Allinger & E. L. Eliel, pp. 271–383. New York: John Wiley.
Eggleston, D. S. & Lan-Hargest, H. Y. (1990). *Acta Cryst.* C**46**, 1686–1691.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Martin, C. K. A. (1977). *Adv. Appl. Microbiol.* **22**, 29–58.
Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
Weeks, C. M., Strong, P. & Osawa, Y. (1976). *Cryst. Struct. Commun.* **5**, 915–918.

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Structure of Bis(butylenedithio)tetrathiafulvalene: an Organic π-Donor Molecule

By Kalyan Das and U. C. Sinha

Department of Physics, Indian Institute of Technology, Bombay-400 076, *India*

S. Kalyan Kumar and Harkesh B. Singh

Department of Chemistry, Indian Institute of Technology, Bombay-400 076, *India*

and A. Mishnev

Institute of Organic Synthesis, Latvian SSR Academy of Sciences, 226 006 *Riga, Latvia*

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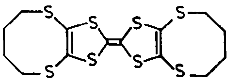
Abstract. 2,2′-Bi(5,6,7,8-tetrahydro-1,3-dithiolo-[4,5-*b*][1,4]dithiocinylidene) (BBDT-TTF), $C_{14}H_{16}S_8$, $M_r = 440.75$, m.p. = 424 K, monoclinic, $P2_1/c$, $a = 5.233\,(1)$, $b = 14.274\,(4)$, $c = 13.430\,(3)$ Å, $\beta = 109.44\,(2)°$, $V = 944.10$ Å^3, $Z = 2$, $D_x = 1.551$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ(Mo $K\alpha$) = 0.857 mm^{-1}, $F(000) = 456$, $T = 288$ K, final $R = 0.0403$, $wR = 0.0400$ for 132 parameters and 2167 observed reflections. The C_6S_8 backbone of the BBDT-TTF molecule is planar and stacked along the *a* axis. Three intermolecular S···S distances [$S2\cdots S2^{i} = 3.686\,(1)$, $S1\cdots S4^{ii} = 3.668\,(1)$ and $S3\cdots S4^{iii} = 3.705\,(1)$ Å; (i) $2-x, 1-y, -z$; (ii) $-1+x, y, z$; (iii) $-1+x, \frac{3}{2}-y, -\frac{1}{2}+z$] are close to the sum of the van der Waals radii of sulfur. In the crystal, the molecules are arranged in pairs.

Introduction. Ambient-pressure superconductivity has been observed in several cation-radical salts derived from the neutral organic electron donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (Parkin, Engler, Schumaker, Lagir, Lee, Scott & Greene, 1983). For the crystal packing, in particular, two-dimensional S···S intermolecular interactions seem to play an important role in allowing the superconducting state at low temperatures (Williams & Kuroda, 1990). Investigations are being undertaken to understand the phenomena and also to increase the transition temperature (T_c) for organic supercoductors. These considerations have prompted the synthesis of the title compound (Kumar, Singh, Das, Sinha & Mishnev, 1991). The present work comprises the crystal structure analysis of BBDT-TTF and a comparative study of its structural parameters with those of related sulfur-containing π-donor molecules.



BBDT-TTF

Experimental. Reaction of 4,5-dimercapto-1,3-dithiole-2-thione disodium salt with 1,4-dibromobutane afforded 4,5-(butylenedithio)-1,3-dithiole-2-thione. The thione was coupled in the presence of triethylphosphite to yield the title compound (Kumar, Singh, Das, Sinha & Mishnev, 1991). The compound was purified by column chromatography (silica gel, CH_2Cl_2) and was recrystallized as dark-orange needles from dichloromethane solution.

A crystal, 0.25 × 0.30 × 0.40 mm, was used for intensity data collection on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation. The lattice parameters were refined from 25 reflections in the range $8 \le \theta \le 12°$. A total of 2759 unique reflections were scanned, $\omega/2\theta$ mode, in the range $2 \le 2\theta \le 60°$; $0 \le h \le 7$, $0 \le k \le 20$ and $-17 \le l \le 17$. Intensity control reflections (219 and $2,\bar{1},\overline{16}$), checked in 3600 s intervals,

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