Table 2. *Selected geometric parameters (Å, °)*

N1—C71	1.361 (3)	C4—C5	1.385 (3)
N1—N2	1.362 (3)	C5—C6	1.431 (3)
N2—C3	1.322 (3)	C5—C8	1.492 (3)
C3—C31	1.422 (4)	C6—C7	1.365 (3)
C31—C4	1.404 (3)	C7—C71	1.397 (4)
C31—C71	1.405 (3)		
C71—N1—N2	111.6 (2)	C4—C5—C6	118.4 (2)
C3—N2—N1	106.2 (2)	C7—C6—C5	123.5 (2)
N2—C3—C31	111.3 (2)	C6—C7—C71	117.0 (2)
C4—C31—C71	120.3 (2)	N1—C71—C7	131.9 (2)
C4—C31—C3	135.4 (2)	N1—C71—C31	106.6 (2)
C71—C31—C3	104.3 (2)	C7—C71—C31	121.5 (2)
C5—C4—C31	119.2 (2)	C13—C8—C9	117.0 (2)
C4—C5—C8—C9	23.8 (4)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N2^{i}	0.89 (3)	2.05 (3)	2.920 (3)	164 (2)
C7—H7···N2^{ii}	1.03 (3)	2.78 (3)	3.670 (3)	145 (2)
C3—H3···Ring B^{iii}	0.98 (3)	2.68 (3)	3.460 (3)	136 (3)
C9—H9···Ring C^{iii}	0.99 (3)	2.89 (3)	3.770 (3)	149 (2)

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

The structure was determined by direct methods. The H atoms were located on a difference Fourier map and refined freely with isotropic displacement parameters in the last cycles of refinement. An empirical weighting scheme was found to give no trends in $<w\Delta^2F>$ *versus* $<|F_o|>$ and $<\sin\theta/\lambda>$ using *PESOS* (Martinez-Ripoll & Cano, 1975). Structural details were extracted with the aid of *PARST* (Nardelli, 1983).

Data collection: Seifert XRD3000-*S* software. Cell refinement: *LSUCRE* (Appleman, 1983). Data reduction: *Xtal*3.2 *DIFDAT SORTREF ADDREF* (Hall, Flack & Stewart, 1994). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Hydroxy-1,4-naphthoquinone

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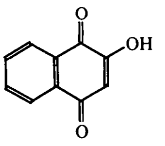
Abstract

The title compound, $C_{10}H_6O_3$, crystallizes with two molecules per asymmetric unit. In both molecules, the naphthoquinone ring system is approximately planar, with the hydroxyl H atoms located in the plane. The crystal packing shows the molecules assembled in infinite linear chains by means of O—H···O hydrogen bonds between alternating independent molecules.

Comment

The crystal structure of the title compound, (I), was determined in order to study its packing in relation to the various substituted derivatives of this compound reported in the literature. The observed C—O bond lengths confirm the presence of 2-hydroxy-1,4-naphthoquinone in the crystalline state as opposed to its tautomeric form (4-hydroxy-1,2-naphthoquinone).



(I)

A good agreement between corresponding bond lengths and angles of both unique molecules is observed. The two independent molecules are found to have an approximately planar naphthoquinone ring system (Fig. 1), with maximum deviations from the least-squares plane through the ring atoms of 0.024 (2) and 0.012 (2) Å, for molecules 1 and 2, respectively. The quinone and hydroxyl O atoms are located within the ring planes, with the maximum deviations found for the O102 [0.065 (1) Å] and O204 atoms [0.036 (1) Å].

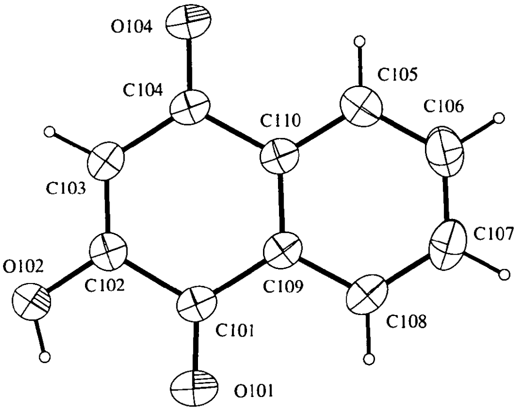
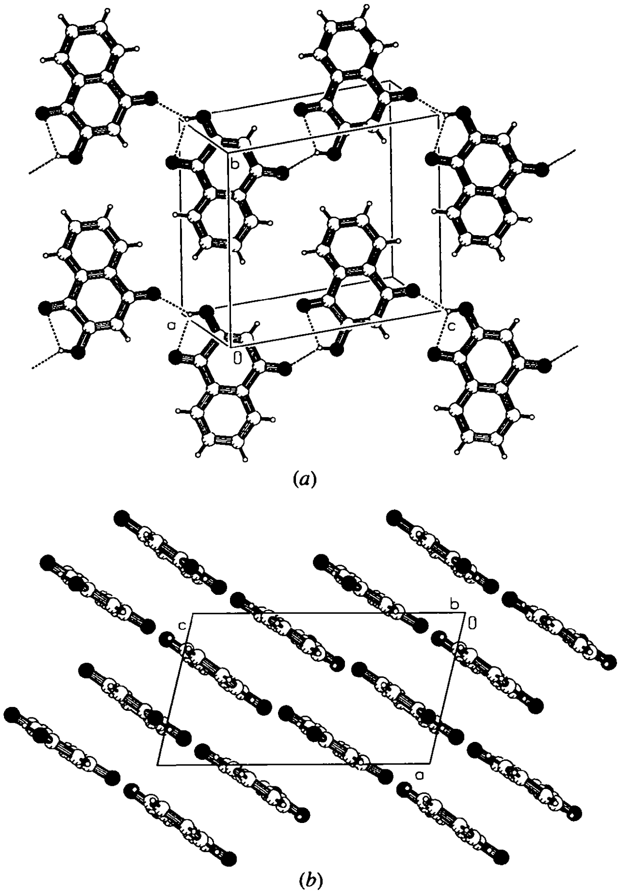


Fig. 1. A displacement ellipsoid plot of molecule 1 of 2-hydroxy-1,4-naphthoquinone at the 50% probability level. H atoms are shown as spheres of arbitrary radii. A similar plot of molecule 2 has been deposited.

The Q parameter, as introduced by Bertolasi, Ferretti, Gilli & de Benedetti (1993), which is zero for an ideal benzene ring and 0.138 for an ideal quinone ring, is found to be 0.112 (7) and 0.109 (7) for molecules 1 and 2, respectively. This is in accordance with the structural parameters found for other 2-hydroxy-1,4-naphthoquinones reported in the Cambridge Structural Database (Version 5.10 of October 1995; Allen & Kennard, 1993).

The unit-cell packing is displayed in Fig. 2. The naphthoquinones reported in the literature display three different types of crystal-packing motif. Although the coordinates of the hydroxyl H atoms of some of the structures were not reported, the presence of hydrogen bonds could be deduced from the positions of the donating and accepting O atoms.



(*a*)

(*b*)

Fig. 2. The crystal packing of 2-hydroxy-1,4-naphthoquinone showing (*a*) the infinite chains of hydrogen-bonded molecules in the [10$\bar{1}$] direction and (*b*) the packing of the molecules in layers parallel to the (202) planes.

The compounds 2,5-dihydroxy-3,8-dimethyl-1,4-naphthoquinone (Cowe, Cox, Cordell, Che, Fong & Howie, 1986) and 2,5-dihydroxy-3,8-dimethoxy-7-methyl-1,4-naphthoquinone (Cannon, Lojanapiwatna, Raston, Sinchai & White, 1980), and the monoclinic and triclinic forms of 2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone (Larsen, Andersen & Pedersen, 1992) form hydrogen-bonded dimers over an inversion center, involving the O2 atom as donor and the O1 atom as acceptor. Atom labels refer to the atom-numbering scheme adopted in the present article. The conformation of the hydroxyl group is further stabilized by an intramolecular hydrogen bond between the O1 and O2 atoms. In the case of the dihydroxydimethyl analog, the extra hydroxyl group links the dimers into one-dimensional chains through a hydrogen bond donated to the O4 atom.

The second type of crystal packing is found for 2-hydroxy-3-iodo-1,4-naphthoquinone (Courseille, Geoffre & Schvoerer, 1971) and 3-hydroxy-2-methyl-1,4-naphthoquinone (Gaultier & Hauw, 1965*b*). These crystals contain an infinite chain of molecules linked by hydrogen bonds donated from O2 to O1. The π systems are at an angle to the chain axis and are stacked on top of one another.

The last type of crystal packing found in the literature also displays infinite chains of molecules linked by hydrogen bonds. In this case, however, the hydrogen bond occurs between the O2 and O4 atoms. Judging from the position of the O atoms, O2 probably also forms an intramolecular hydrogen bond towards O1. The planes of the π systems are parallel to the chain axis and there is no π–π interaction between the naphthoquinone systems within the chain. This type of packing is observed for 2-chloro-3-hydroxy-1,4-naphthoquinone (Gaultier & Hauw, 1965*a*).

The crystal packing of 2-hydroxy-1,4-naphthoquinone is a new example of this last type [Fig. 2(*a*)]. The hydrogen bonds are found between alternating unique molecules: O102—H102···O204(x, y, $1-z$) [O···O 2.7130 (16) Å and O—H···O 144.0 (11)°] and O202—H202···O104($1+x$, $1+y$, $z-1$) [O···O 2.7299 (17) Å and O—H···O 143.3 (5)°], forming infinite linear chains in the [10$\bar{1}$] direction. These hydrogen bonds are bifurcated, as the H2 atom also has a short intramolecular contact to the O1 atom in both independent molecules [O102···O101 2.6702 (18) Å and O102—H102···O101 115.4 (7)°]. The sum of the angles involving the H atom of the bifurcated hydrogen bond amounts to 359.8 (14) and 359.4 (11)° for the H102 and H202 atoms, respectively. All molecules lie within the (202) planes, as illustrated in Fig. 2(*b*).

The crystallographically independent molecules are related by a rotation of 177.2° around an axis parallel to the *b* axis. The r.m.s. fit for the matching of the rotated image of molecule 1 to molecule 2($-x$, $-y$, $-z$) amounts to 0.14 Å. The rotation axis connecting these molecules does not coincide with one of the possible twofold rotation axes of the reciprocal lattice; the smallest angle is 13.9° with the (010) vector of the reciprocal lattice (an angle of 0° would be expected for a crystallographic rotation axis). The local rotation symmetry only holds for the described pair of molecules; at longer ranges significant differences in the packing of both molecules are observed. The combination of the local rotation symmetry with the crystallographic inversion symmetry gives rise to a pseudo-glide plane perpendicular to **b** with a shift of 6.22 Å in the [0.97,0,$\bar{1}$] direction.

Experimental

2-Hydroxy-1,4-naphthoquinone (Lawsone, Natural Orange 6, obtained from Aldrich) was recrystallized from acetonitrile solution.

Crystal data

$C_{10}H_6O_3$
$M_r = 174.16$
Triclinic
$P\bar{1}$
$a = 7.1195 (6)$ Å
$b = 9.5287 (8)$ Å
$c = 12.3059 (8)$ Å
$\alpha = 82.080 (7)°$
$\beta = 75.480 (6)°$
$\gamma = 76.480 (7)°$
$V = 782.98 (11)$ Å^3
$Z = 4$
$D_x = 1.477$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.63$–$19.06°$
$\mu = 0.11$ mm^{-1}
$T = 295$ K
Block
0.6 × 0.6 × 0.3 mm
Yellow

Data collection

Enraf–Nonius CAD-4*F* diffractometer
ω–2θ scans
Absorption correction: none
5703 measured reflections
3601 independent reflections
3601 observed reflections [$I \geq -1.5\sigma(I)$]

$R_{\rm int} = 0.033$
$\theta_{\rm max} = 27.47°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
2 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 4\sigma(F^2)] = 0.0424$
$wR(F^2) = 0.1258$
$S = 1.072$
3601 reflections
237 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 0.0492P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.204$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.242$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Molecule 1				
O101	0.3364 (2)	0.07895 (14)	0.42716 (10)	0.0660 (5)
O102	0.1977 (2)	−0.14519 (13)	0.54833 (10)	0.0629 (4)
O104	−0.0857 (2)	0.14799 (13)	0.84662 (9)	0.0514 (3)
C101	0.2401 (2)	0.1007 (2)	0.52129 (12)	0.0421 (4)
C102	0.1596 (2)	−0.0202 (2)	0.59480 (12)	0.0442 (4)
C103	0.0546 (3)	−0.0046 (2)	0.70066 (13)	0.0478 (5)
C104	0.0082 (2)	0.1332 (2)	0.74907 (11)	0.0391 (4)
C105	0.0298 (2)	0.3937 (2)	0.71969 (13)	0.0459 (5)
C106	0.0998 (3)	0.5091 (2)	0.65460 (15)	0.0517 (5)
C107	0.2194 (3)	0.4912 (2)	0.54856 (15)	0.0546 (6)
C108	0.2672 (3)	0.3572 (2)	0.50587 (13)	0.0495 (5)
C109	0.1950 (2)	0.2416 (2)	0.56907 (11)	0.0389 (4)
C110	0.0779 (2)	0.2588 (2)	0.67752 (11)	0.0364 (4)
Molecule 2				
O201	0.8277 (2)	0.82177 (13)	−0.07258 (9)	0.0612 (4)
O202	0.6919 (2)	1.05372 (11)	0.04619 (9)	0.0509 (4)
O204	0.3755 (2)	0.76462 (12)	0.34042 (9)	0.0507 (3)
C201	0.7260 (2)	0.8028 (2)	0.02073 (11)	0.0394 (4)
C202	0.6447 (2)	0.92806 (15)	0.09196 (11)	0.0379 (4)
C203	0.5291 (2)	0.9151 (2)	0.19557 (12)	0.0412 (4)
C204	0.4778 (2)	0.7777 (2)	0.24446 (11)	0.0379 (4)
C205	0.5084 (3)	0.5176 (2)	0.22076 (14)	0.0491 (5)

C206	0.5885 (3)	0.3966 (2)	0.1595 (2)	0.0569 (6)
C207	0.7119 (3)	0.4085 (2)	0.0543 (2)	0.0558 (6)
C208	0.7550 (2)	0.5408 (2)	0.00888 (14)	0.0478 (5)
C209	0.6771 (2)	0.66199 (15)	0.06936 (11)	0.0373 (4)
C210	0.5540 (2)	0.6504 (2)	0.17654 (11)	0.0375 (4)

Table 2. *Selected geometric parameters (Å, °)*

Molecule 1		Molecule 2	
O101—C101	1.2068 (19)	O201—C201	1.2094 (18)
O102—C102	1.333 (2)	O202—C202	1.3309 (18)
O104—C104	1.2280 (18)	O204—C204	1.2293 (18)
O101—C101—C102	119.15 (16)	O201—C201—C202	118.86 (15)
O101—C101—C109	123.64 (15)	O201—C201—C209	123.65 (15)
O102—C102—C101	115.93 (13)	O202—C202—C201	116.23 (12)
O102—C102—C103	121.67 (16)	O202—C202—C203	121.77 (14)
O104—C104—C103	121.66 (15)	O204—C204—C203	121.49 (15)
O104—C104—C110	119.92 (16)	O204—C204—C210	119.88 (15)

The unit-cell parameters were checked for the presence of higher lattice symmetry (Spek, 1988). Data were collected during 78 h of X-ray exposure time. Reflections were measured with Zr-filtered Mo $K\alpha$ radiation, a scan angle $\Delta\omega$ of $(0.67 + 0.35\tan\theta)^\circ$, and horizontal and vertical apertures of 3.00 and 5.00 mm, respectively. The structure was solved by direct methods in space group $P1$, since no interpretable Fourier maps could be derived in space group $P\bar{1}$. After detection of an inversion center, the coordinates were transformed to comply with space group $P\bar{1}$. The aromatic H atoms were included in the refinement at calculated positions, riding on their carrier atoms. The hydroxyl H atom was included in the refinement in a rigid-group position, allowing for rotation along the C—O bond while retaining a C—O—H angle of 109.5°. The starting position was derived from the maximum electron density found in a circular $\Delta\rho$ map around the hydroxyl O atom. The H atoms were refined with a fixed isotropic displacement parameter related to the equivalent isotropic displacement parameter of the carrier atom by a factor of 1.2 for the aromatic H atoms and 1.5 for the hydroxyl H atoms. All non-H atoms were refined with anisotropic displacement parameters.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON* (Spek, 1994). Software used to prepare material for publication: *PLATON* (Spek, 1990).

The X-ray data were kindly collected by A. M. M. Schreurs.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a displacement ellipsoid plot of molecule 2, have been deposited with the IUCr (Reference: AB1365). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Three Testosterone Derivatives

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Abstract

The crystal structures of three testosterone derivatives are discussed and compared. Both *anti*- and *syn*-3-benzyloxyiminoandrost-4-en-17β-yl acetate, $C_{28}H_{37}NO_3$, and their parent compound, 3-oxoandrost-4-en-17β-yl acetate, $C_{21}H_{30}O_3$, are important for the correlation between the *syn–anti* geometry of unsaturated oximes and their circular dichroism for the longest wavelength CD bands.

Comment

To the best of our knowledge, no crystal structures of 3-oximino steroid derivatives have been determined so far. In this study, we present the structures of *anti*- and *syn*-3-benzyloxyiminoandrost-4-en-17β-yl acetate [compounds (2) and (3), respectively] together with that of their parent compound, 3-oxoandrost-4-en-17β-yl acetate, (1).