Crystal data

$C_{16}H_{16}O_3$
$M_r = 256.29$
Monoclinic
$C2/c$
$a = 19.515\ (3)$ Å
$b = 5.8352\ (9)$ Å
$c = 22.854\ (3)$ Å
$\beta = 90.669\ (9)°$
$V = 2602.3\ (7)$ Å^3
$Z = 8$
$D_x = 1.308$ Mg m^{-3}
$D_m = 1.30\ (1)$ Mg m^{-3}
D_m measured by flotation in cyclohexane/CCl_3Br
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 19 reflections
$\theta = 7.0$–$12.4°$
$\mu = 0.090$ mm^{-1}
$T = 295\ (2)$ K
Rhombus
0.60 × 0.20 × 0.10 mm
Colorless

Data collection

Siemens $P4$ diffractometer
$2\theta/\theta$ scans
Absorption correction: face-indexed numerical
$T_{min} = 0.972$, $T_{max} = 0.994$
3020 measured reflections
2276 independent reflections
1376 reflections with $F > 4\sigma(F)$
$R_{int} = 0.047$
$\theta_{max} = 25°$
$h = -1 \rightarrow 22$
$k = -1 \rightarrow 6$
$l = -27 \rightarrow 27$
3 standard reflections
every 97 reflections
intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.0555$
$wR(F^2) = 0.148$
$S = 0.904$
2276 reflections
178 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.353$ e Å^{-3}
$\Delta\rho_{min} = -0.193$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.0133 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) and hydrogen-bonding geometry (Å, °)*

O1—C6	1.207 (3)	C1—C6	1.522 (3)
O2—C7	1.229 (3)	C3—C7	1.474 (3)
O3—C7	1.263 (3)	C5—C6	1.483 (3)
C7—O3—H3*C*	122 (2)	C5—C6—C1	114.4 (2)
C2—C3—C7	123.0 (2)	O2—C7—O3	119.8 (2)
C7—C3—C4	113.7 (2)	O2—C7—C3	123.6 (2)
O1—C6—C5	122.9 (2)	O3—C7—C3	116.6 (2)
O1—C6—C1	122.7 (2)		
C1—C2—C3—C7	175.8 (2)	C2—C3—C7—O2	19.7 (4)
C7—C3—C4—C5	−155.5 (2)	C4—C3—C7—O2	−163.3 (3)
C4—C5—C6—O1	−118.9 (2)	C2—C3—C7—O3	−160.7 (3)
C2—C1—C6—O1	140.0 (3)	C4—C3—C7—O3	16.3 (4)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*C*···O2^i	0.98 (4)	1.66 (4)	2.622 (3)	169 (3)

Symmetry code: (i) $-x, 2-y, 1-z$.

All non-carboxyl H atoms, although found in electron-density difference maps, were replaced in calculated positions and allowed to refine as riding models. The displacement parameters of the methylene H atoms were refined as a group having a group U_{iso} of 0.063 (3). The aromatic H atoms refined to a group U_{iso} of 0.066 (4). The H atoms of the methyl group were treated as disordered with two different sets of three H atoms each [occupancy ratio 76 (3):24 (3)] and had a group U_{iso} of 0.058 (7). The carboxyl H3 atom was found in an electron-density difference map. Its positional parameters were refined but its isotropic temperature factor U_{iso} was held constant at 0.100.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1273). Services for accessing these data are described at the back of the journal.

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(+)-3-Oxoandrost-4-ene-17β-carboxylic Acid: Catemeric Hydrogen Bonding in a Steroidal Keto Acid

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Abstract

The title keto acid, $C_{20}H_{28}O_3$, forms translational carboxyl···ketone (O—H···O) hydrogen-bonding catemers [O···O 2.692 (3) Å], which follow no crystal-

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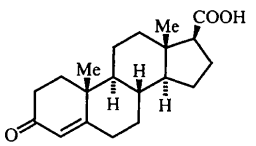
lographic axis. The cell contains two screw-related molecules having the same end-to-end orientation, each of which participates in a separate hydrogen-bonding chain.

Comment

While functionally unelaborated carboxylic acids almost always aggregate in the solid state as mutually hydrogen-bonded dimers, appending other functions makes additional hydrogen-bonding modes possible. For keto acids the commonest of the four known solid-state motifs is acid dimerization, in which the ketone is not involved. In order of diminishing prevalence, the others are carboxyl-to-ketone chains (catemers), intramolecular hydrogen bonds and carboxyl-to-ketone dimers (of which only one instance is known). We have previously referenced and discussed numerous examples (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).



(I)

We have investigated the hydrogen-bonding motif of the steroidal keto acid, (I), present as a single enantiomer. Fig. 1 shows the asymmetric unit with its steroid numbering. Among the few conformational options present, the carboxyl is turned so that the C16—C17 bond lies in the carboxyl plane, with C=O turned toward C16; the C16—C17—C20—O2 torsional angle is −10.3 (4)°. The H atoms of the two angular methyl groups are staggered relative to the substituents attached to C10 and C13.

Complete or partial averaging of the C—O bond lengths and C—C—O angles by disorder is frequent in carboxyl dimers (Leiserowitz, 1976). However, acids involved in catemeric hydrogen bonding have geometry that precludes any of the usual disordering mechanisms, and typically are highly ordered. In (I) no significant averaging is observed and the bond lengths are 1.195 (3) and 1.322 (4) Å, with angles 125.8 (3) and 111.4 (2)°. Our own survey of 28 catemeric keto acid structures gives average values of 1.197 and 1.320 Å and 124.5 and 112.8° for these lengths and angles. Values cited as typical for highly ordered dimeric carboxyls are 1.21 and 1.31 Å and 123 and 112° (Borthwick, 1980).

Fig. 2 illustrates the packing of (I) in the cell, which contains two diverging hydrogen-bonding chains. When hydrogen-bonding catemers occur, their components are most frequently screw-related, with the helices following a cell axis. In (I) neither of these is the

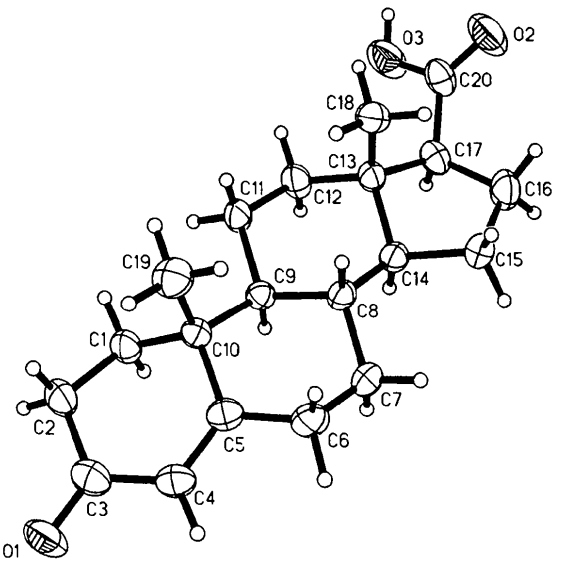


Fig. 1. Compound (I) with its steroidal numbering. Ellipsoids are set at the 40% probability level.

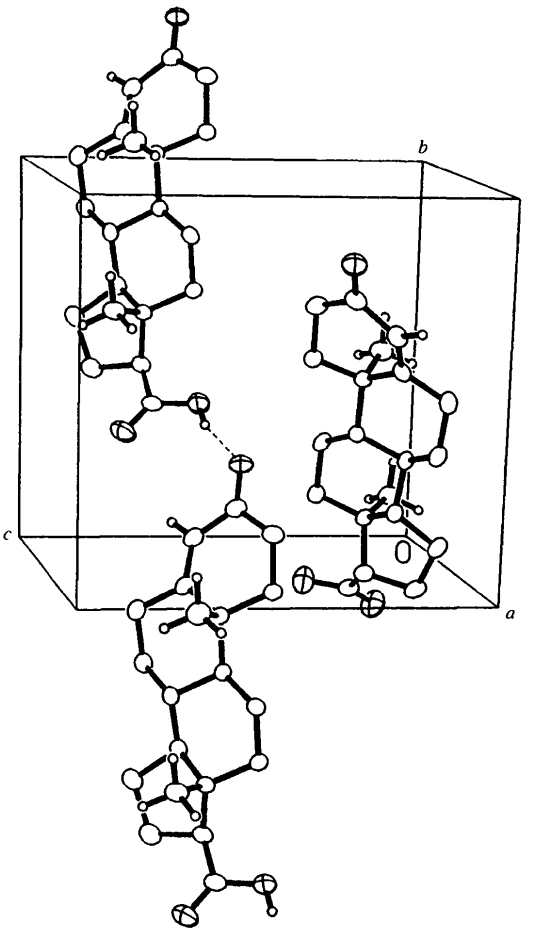


Fig. 2. A packing diagram. All methylene H atoms have been removed for clarity. Ellipsoids are set at the 30% probability level.

case: the catemers are translational and not aligned with any crystallographic axis. The hydrogen-bonding links advance in stepwise fashion, so that each involves translationally related molecules one cell apart in both the *a* and *b* directions. The O···O separation in the hydrogen bond is 2.692 (3) Å and the O—H···O angle is 161 (3)°. The dihedral angle between the plane of the ketone (C2—C3—C4—O1) and that of the carboxyl group (C17—C20—O2—O3) in any hydrogen bond is 27.6 (2)°. Each cell contains a screw-related pair of molecules (Z = 2), both oriented lengthwise in the *b* direction. Each cell thus holds members of two separate translational hydrogen-bonding catemers, which are screw-related to each other and oriented similarly along *b*, but which diverge in the *a* direction, so that the chains lie parallel to the 110 and the $\bar{1}10$ planes.

The KBr IR spectrum of (I) displays absorptions at 1722 (carboxyl) and 1640 cm^{-1} (ketone), with an additional peak at 1631 cm^{-1}. These C=O positions conform to the known shifts due to removal of hydrogen bonding from carboxylic C=O and addition of hydrogen bonding to a conjugated ketone, and are comparable with the KBr values (1723, 1637 cm^{-1}) found for the catemeric species 10-carboxy-Δ^1-octal-1-one (Lalancette, Thompson & Vanderhoff, 1991). In $CHCl_3$ solution, where dimers predominate, the peaks for (I) appear, normally, at 1709 and 1662 cm^{-1}, with a small peak for C=C at 1615 cm^{-1}.

Experimental

Compound (I) was purchased as the (+)-enantiomer from Steraloids Inc., Wilton, NH, USA, and used as purchased. The crystals, m.p. 527 K, were obtained from methanol.

Crystal data

$C_{20}H_{28}O_3$
M_r = 316.44
Monoclinic
$P2_1$
a = 6.988 (1) Å
b = 11.254 (1) Å
c = 11.480 (2) Å
β = 102.06 (1)°
V = 882.9 (2) Å^3
Z = 2
D_x = 1.190 Mg m^{-3}
D_m = 1.191 (1) Mg m^{-3}
D_m measured by flotation in cyclohexane/CCl_4
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 21 reflections
θ = 5.4–18.2°
μ = 0.078 mm^{-1}
T = 293 (2) K
Triangular prism
0.38 × 0.30 × 0.24 mm
Colorless

Data collection

Siemens P4 diffractometer
$2\theta/\theta$ scans
Absorption correction: face-indexed numerical
T_{min} = 0.964, T_{max} = 0.983
4621 measured reflections
3886 independent reflections
2727 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 27.5°
$h = -9 \rightarrow 10$
$k = -15 \rightarrow 17$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections
intensity decay: 0.35%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.130
S = 1.02
3870 reflections
228 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.0823P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ <0.001
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXTL/PC* (Sheldrick, 1994)
Extinction coefficient: 0.000 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 1.4 (17)

Table 1. *Selected geometric parameters (Å, °)*

O1—C3	1.223 (3)	O3—C20	1.322 (4)
O2—C20	1.195 (3)	O3—H3	0.87 (4)
O1—C3—C4	122.0 (3)	O2—C20—O3	122.9 (3)
O1—C3—C2	120.7 (3)	O2—C20—C17	125.8 (3)
C17—C16—C15	106.2 (2)	O3—C20—C17	111.4 (2)
C16—C17—C13	104.5 (2)		
C16—C17—C20—O2	−10.3 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^i	0.87 (4)	1.86 (4)	2.692 (3)	161 (3)

Symmetry code: (i) $1 + x, y - 1, z$.

All non-carboxyl H atoms were found in electron-density difference maps but replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms. The carboxyl H atom was found in an electron-density difference map and was allowed to refine with its temperature factor also free to refine.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS* (Siemens, 1991). Data reduction: *XSCANS* (Siemens, 1991). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1258). Services for accessing these data are described at the back of the journal.

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4-Amino-2-chloro-6,7-dimethoxyquinazoline Methanol Solvate

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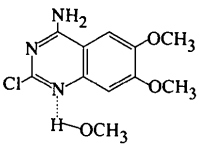
Abstract

Molecules of 4-amino-2-chloro-6,7-dimethoxyquinazoline, $C_{10}H_{10}ClN_3O_2.CH_4O$, form base-paired N—H···N hydrogen-bonded dimers in the solid state with N···N = 3.088 (2) Å. The quinazoline moieties are each flanked by a methanol molecule *via* N···H—O hydrogen bonding [N···O = 2.887 (2) Å].

Comment

4-Amino-2-chloro-6,7-dimethoxyquinazoline, (I), has been widely used in medicinal chemistry, particularly in the synthesis of cardiovascular agents such as telazosin (Winn, Kyncl, Dunnigan & Jones, 1977) and doxazosin (Campbell, Davey, Hardstone, Lewis & Palmer, 1987), which are members of a new class of antihypertensive agents.



(I).CH_4O

Single-crystal X-ray structure analysis shows that the unit cell contains molecules of (I) and the solvent methanol. Fig. 1 is an *ORTEP*II (Johnson, 1976) representation of (I).CH_4O. The molecules form base-paired N—H···N hydrogen-bonded dimers in the solid state. Furthermore, the quinazoline moieties are each flanked by a methanol molecule *via* N···H—O hydrogen bonding [N···O2.887(2) Å] as shown in Fig. 2.

The self-base-paired dimer is very similar to that of 6-amino-4-methoxy-2-methylthiopyrimidine, (II) (Low *et al.*, 1996). The bond length of the intermolecular

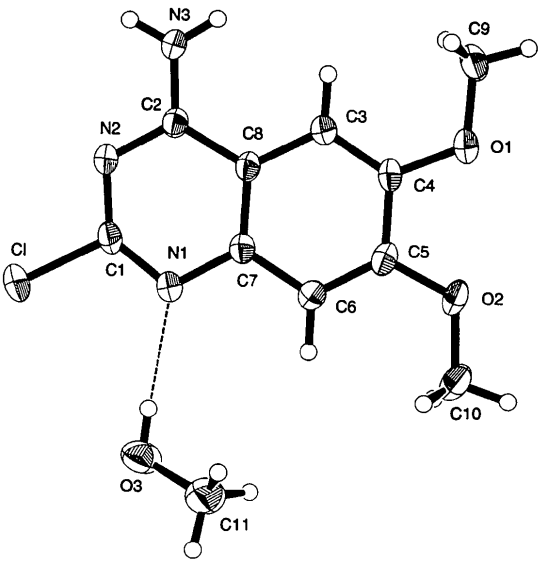


Fig. 1. *ORTEP*II (Johnson, 1976) representation of compound (I); displacement ellipsoids are drawn at the 50% probability level.

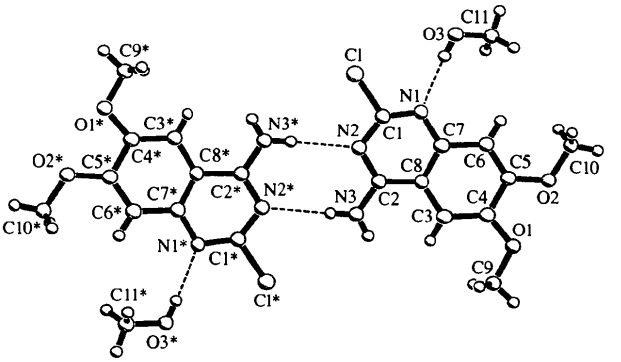


Fig. 2. A view of the hydrogen bonding in the unit cell with the atom-numbering scheme.

N···N hydrogen bond is 3.088 (2) Å in the present structure (symmetry operator: $1-x$, $1-y$, $1-z$) and 3.060 (3) Å in (II). In addition, there is only a single N—H···N hydrogen bond; the other amino H atom does not participate in hydrogen bonding because of steric hindrance in (I) and (II). Therefore, this structural feature indicates that self-base-pairing to a dimer occurs readily not only in the crystal structure of nucleobase compounds but also in that of nucleobase-like compounds, provided that an amine group of a ring C atom is adjacent to an unsubstituted ring N atom where neither group is sterically hindered.

The ten-membered bicyclic ring is essentially planar with a mean deviation of 0.028 (2) Å and a maximum deviation of 0.053 (2) Å. The methoxy groups are almost coplanar with the quinazoline ring [torsion angles C5—C4—O1—C9 179.6 (2) and C4—C5—O2—C10 −178.0 (2)°]. All the other bond distances and bond angles are in the normal range.

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