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The molecular conformation of pentan-3-one studied in cholic acid pentan-3-one solvate

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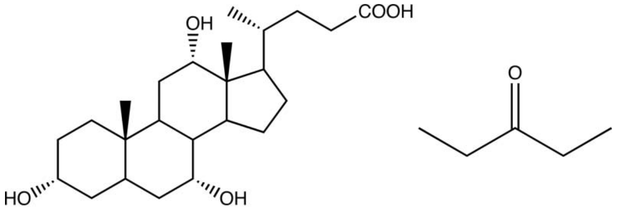
The crystal structure of cholic acid–pentan-3-one (1/1), $C_5H_{10}O{\cdot}C_{24}H_{40}O_5$, has been determined in order to deduce the molecular conformation of the small volatile ketone. Data were collected at 100 K to a resolution of $(\sin\theta)/\lambda = 0.91$ Å^{-1}. The structure contains a hydrogen-bonded cholic acid host network, forming only van der Waals interactions with the guest pentan-3-one molecules. The ketone molecules are disordered on general positions, with two clearly identifiable conformations. The majority conformer exhibits approximate C_2 symmetry and is similar to that recently observed by microwave spectroscopy in the gas phase.

Comment

Many solvates of cholic acid have been studied, often with the focus on crystal engineering: Version 5.31 of the Cambridge Structural Database (CSD; Allen, 2002) contains 247 error-free organic structures in which the steroid acts as a guest for small organic host molecules. We have recently identified cocrystallization with cholic acid as an effective strategy to obtain high-resolution data sets on low-melting compounds, provided the intensity data collections are performed at reasonably low temperatures. Crystals obtained with the odorants allyl acetate and isopropyl acetate have been of sufficient quality even for charge-density studies (Mouhib *et al.*, 2011). We intended to obtain information about possible conformations of the small volatile molecule pentan-3-one, also known as diethyl ketone, in the solid state. In view of its relatively low melting point of *ca* 233 K and our previous successful experiments, we decided to grow cocrystals with cholic acid and to study the crystal structure of the title cocrystal, (I), at low temperature.

The structure of (I) at room temperature has been reported previously (Caira *et al.*, 1994*a*). The compound crystallizes in the space group $P2_1$ with lattice parameters similar to those of related compounds (Caira *et al.*, 1994*b*). A displacement ellipsoid plot of the contents of the asymmetric unit is shown in Fig. 1. Our redetermination fully confirms the conclusions of the earlier authors with respect to the host structure, but the previously published data cannot provide details about the conformation of the guest molecule. In contrast, our intensity data collected at low temperature and up to high resolution allow us to compare the conformation of the ketone in the solid to that in the gas phase. Although single crystals of (I) were well diffracting up to a resolution $(\sin\theta)/\lambda = 0.91$ Å^{-1}, the resulting intensity data are not suitable for a charge-density study. After completion of the conventional refinement reported here, a difference Fourier synthesis shows local electron-density maxima centred on covalent bonds of the steroid host, in agreement with the expectation and in favour of a potential charge-density study. In the neighbourhood of the guest molecule, however, a less clear-cut and chemically not meaningful distribution is observed for the residual maxima, which precludes a more demanding interpretation of the electron density.



(I)

Classical O—H···O hydrogen bonds link the cholic acid molecules into layers parallel to the $(10\overline{1})$ planes (Fig. 2 and Table 2). Pairs of the host molecules reside in a comparatively large cavity with a volume of 366 Å^3 (Spek, 2009). One of the ethyl substituents in the pentan-3-one molecule is disordered over two conformations with a 0.545 (12):0.455 (12) ratio between the site occupancies. The majority conformation shown in Fig. 3(*a*) deviates only slightly from C_2 symmetry, in

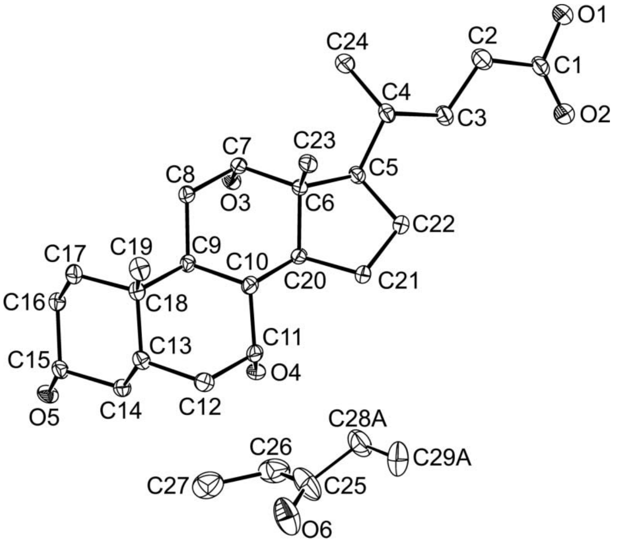


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. Atoms belonging to the minor conformer of pentan-3-one and all H atoms have been omitted for clarity.

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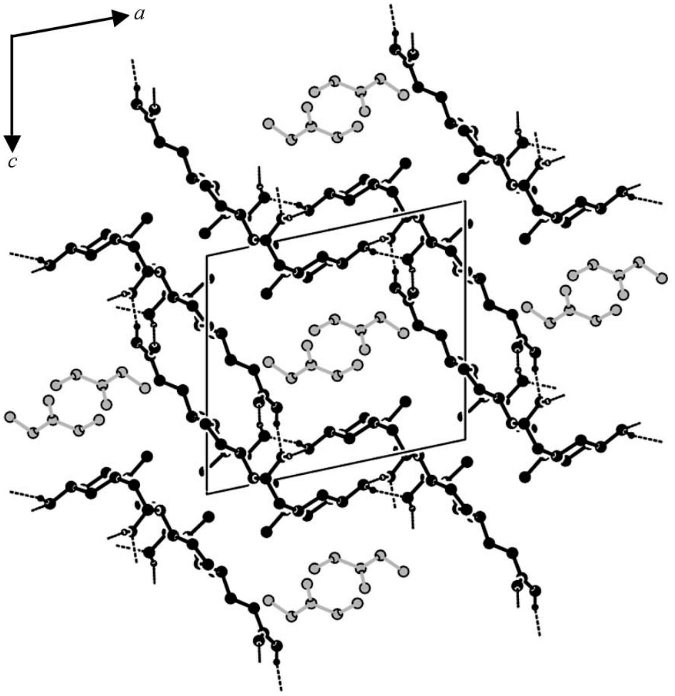

Figure 2
Packing diagram of (I), viewed along [010], showing the hydrogen-bonded layers of cholic acid host molecules in black and the pentan-3-one guest molecules in grey.

good agreement with the experimental results for the gas-phase conformation obtained from Fourier transform microwave spectroscopy, and also with the expectation from theory (Nguyen & Stahl, 2011). The minority conformer (Fig. 3*b*) is less symmetrical and belongs to point group C_1. The only previous low-temperature crystal structure containing pentan-3-one (Goldup *et al.*, 2008) shows an unexpected C—C—C bond angle of 141° in one of the ethyl substituents and therefore does not allow one to deduce the conformation of this molecule reliably.

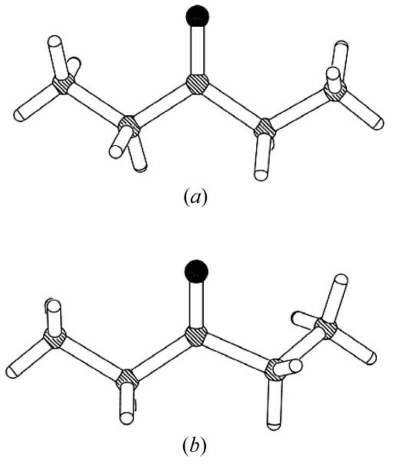

Figure 3
The molecular conformations of pentan-3-one in (I), showing (*a*) the major conformer, similar to the gas-phase structure, and (*b*) the minor conformer.

Experimental

Single crystals of (I) were obtained by dissolving cholic acid (30 mg, 0.07 mmol) in pentan-3-one (10 ml) at 313 K. Slow evaporation over a period of *ca* 7 d at room temperature afforded colourless plates. The crystal fragment chosen for the diffraction experiment was cut to an appropriate size while covered with mother liquor and transferred directly to the stream of cold N_2 (100 K) on the diffractometer.

Crystal data

$C_5H_{10}O{\cdot}C_{24}H_{40}O_5$
$M_r = 494.69$
Monoclinic, $P2_1$
$a = 12.5606$ (7) Å
$b = 8.0425$ (5) Å
$c = 13.9139$ (8) Å
$\beta = 102.002$ (3)°
$V = 1374.84$ (14) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 100$ K
0.16 × 0.13 × 0.11 mm

Data collection

Bruker SMART APEX CCD diffractometer
33615 measured reflections
13745 independent reflections
9042 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.081$
$wR(F^2) = 0.200$
$S = 1.06$
13745 reflections
357 parameters
26 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.69$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.321 (2)	O6—C25	1.216 (4)
O2—C1	1.213 (2)	C25—C26	1.493 (5)
O3—C7	1.446 (2)	C25—C28*A*	1.507 (5)
O4—C11	1.435 (2)	C25—C28*B*	1.566 (7)
O5—C15	1.438 (2)	C26—C27	1.519 (5)
C1—C2	1.512 (3)	C28*A*—C29*A*	1.512 (10)
C2—C3	1.519 (3)	C28*B*—C29*B*	1.531 (12)
C3—C4	1.540 (3)		
O6—C25—C26	123.0 (3)	C26—C25—C28*B*	122.8 (5)
O6—C25—C28*A*	124.6 (3)	C25—C26—C27	115.1 (2)
C26—C25—C28*A*	111.2 (3)	C25—C28*A*—C29*A*	113.1 (7)
O6—C25—C28*B*	111.1 (5)	C29*B*—C28*B*—C25	107.4 (8)
O6—C25—C26—C27	16.7 (5)	O6—C25—C28*B*—C29*B*	−66.6 (12)
O6—C25—C28*A*—C29*A*	17.7 (9)		

A total of 22 similarity restraints (C—C distances, C—C—C angles and displacement parameters for split positions) were used to model the disordered ethyl group of the solvent molecule. Coordinates and isotropic displacement parameters were refined for H atoms attached to O atoms, with O—H distances restrained to 0.85 (2) Å. H atoms attached to C atoms were treated as riding, with C—H = 0.98 Å for CH_3, C—H = 0.99 Å for CH_2 and C—H = 1.00 Å for CH groups, and with $U_{\rm iso}$(H) = 1.2 or 1.5$U_{\rm eq}$(C). Methyl groups were allowed to rotate about their local threefold axes. In the absence of significant anomalous scattering effects, the Flack (1983) parameter is indeterminate. The absolute structure is assigned on the basis of the known configuration of the chiral cholic acid molecule. Friedel pairs were not merged.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O4^{i}	0.87 (3)	1.84 (3)	2.672 (2)	160 (4)
O3—H3⋯O2^{i}	0.83 (2)	2.08 (2)	2.879 (2)	160 (2)
O4—H4⋯O5^{ii}	0.86 (2)	1.81 (2)	2.6499 (19)	165 (2)
O5—H5⋯O3^{ii}	0.82 (2)	2.10 (3)	2.869 (2)	157 (2)

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

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3016). Services for accessing these data are described at the back of the journal.

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