Cyclotene Hydrate, $C_6H_8O_2.H_2O$

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Abstract

The title compound exists as the 2-hydroxy-3-methyl-cyclopent-2-enone tautomer hydrogen bonded to a water molecule. All three H atoms bonded to O atoms are involved in a hydrogen-bonding network that assembles the molecules into chains along the *b* axis.

Comment

Cyclotene is a volatile compound commonly encountered in foods. It is found in coffee beans (Gianturco *et al.*, 1963), is extensively used as a flavouring component in the food industry and has been the subject of much study. For example, the mechanism of its formation from two molecules of acetol has recently been discussed (Nursten, 1997) and its formation from other precursors, such as ascorbic acid, has been reported. It plays a role in the Maillard reaction, particularly in the formation of certain volatile pyrazine derivatives, and it has been synthesized by a variety of methods (Strunz, 1983; Dos Santos & De Magalhaes, 1991). Cyclotene can, in principle, exist in many tautomeric forms (Nursten, 1997), but is usually represented in either the dicarbonyl form, (1*a*), or the enol form, (1*b*), since it displays reactions characteristic of both of these. In non-polar solutions, it exists as tautomer (1*b*). Cyclotene is often supplied as a crystalline hydrate, the nature of which has not been established. We now report an accurate low-temperature X-ray crystal structure of this compound.
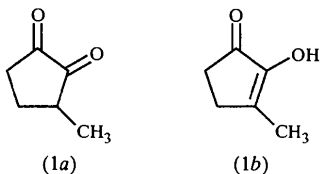
The successful location and refinement of the hydroxyl H atom, along with the bonding geometry (Table 1), unambiguously establish that in the solid state, cyclotene hydrate exists as the 2-hydroxycyclopent-2-enone tautomer, (1*b*) (Fig. 1). The cyclopentenone ring is essentially planar [maximum deviation from the mean plane is 0.003 (2) Å]. The geometry is similar to that in other crystallographically characterized cyclopentenones (Ley *et al.*, 1993; Tsuboi *et al.*, 1983).
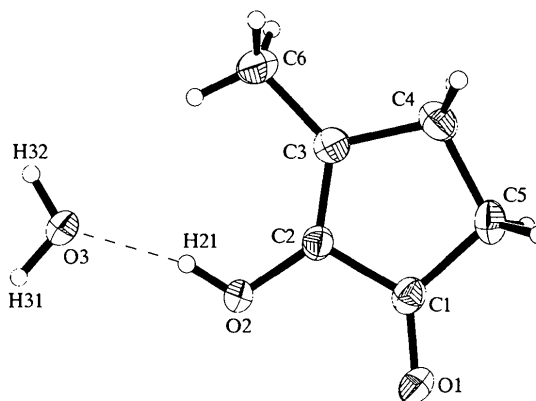

Fig. 1. Perspective view and atom labelling of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Each of the three oxygen-bonded H atoms is involved in an intermolecular hydrogen bond (Table 2). The cyclotene hydroxyl group is hydrogen bonded to the adjacent water O atom and each of the water H atoms is bonded to the carbonyl O atom of an adjacent molecule. This hydrogen-bonding network connects the molecules in chains along the *b* axis (Fig. 2).
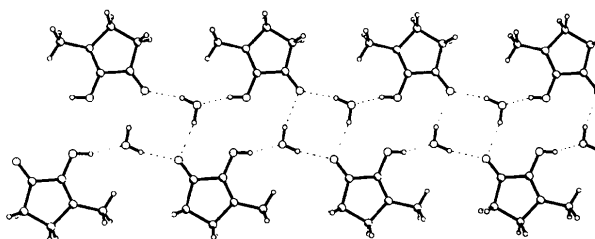

Fig. 2. Packing diagram, viewed down the *a* axis, showing the hydrogen-bonding network.

Experimental

The sample was freshly recrystallized from an aqueous solution of the title compound.

Crystal data

$C_6H_8O_2.H_2O$	Mo $K\alpha$ radiation
$M_r = 130.14$	$\lambda = 0.71073$ Å

Triclinic
$P\bar{1}$
$a = 6.8829\,(2)$ Å
$b = 6.9979\,(3)$ Å
$c = 7.8655\,(3)$ Å
$\alpha = 111.529\,(1)°$
$\beta = 95.615\,(2)°$
$\gamma = 106.786\,(2)°$
$V = 328.45\,(2)$ Å^3
$Z = 2$
$D_x = 1.316$ Mg m^{-3}
D_m not measured

Cell parameters from 3259
  reflections
$\theta = 2.86–26.44°$
$\mu = 0.105$ mm^{-1}
$T = 153\,(2)$ K
Block
$0.54 \times 0.46 \times 0.39$ mm
Colourless

Data collection

Siemens SMART CCD
  diffractometer
Exposures over 0.3° φ or ω
  rotation scans
Absorption correction: none
3259 measured reflections
1258 independent reflections
1152 reflections with
  $I > 2\sigma(I)$

$R_{int} = 0.050$
$\theta_{max} = 26.44°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -9 \rightarrow 9$
no standard reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.116$
$S = 1.135$
1258 reflections
92 parameters
H atoms treated by a
  mixture of independent
  and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.117P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.223$ e Å^{-3}
$\Delta\rho_{min} = -0.234$ e Å^{-3}
Extinction correction: none
Scattering factors from
  *International Tables for
  Crystallography* (Vol. C)

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

O1—C1	1.227 (2)	C3—C6	1.491 (2)
O2—C2	1.350 (2)	C3—C4	1.499 (2)
O2—H21	0.86 (2)	C4—C5	1.531 (2)
C1—C2	1.456 (2)	O3—H31	0.88 (3)
C1—C5	1.499 (2)	O3—H32	0.86 (3)
C2—C3	1.342 (2)		
O1—C1—C2	124.30 (14)	C2—C3—C6	127.21 (15)
O1—C1—C5	127.38 (14)	C2—C3—C4	110.99 (14)
C2—C1—C5	108.32 (13)	C6—C3—C4	121.80 (13)
C3—C2—O2	132.23 (14)	C3—C4—C5	105.34 (13)
C3—C2—C1	110.82 (14)	C1—C5—C4	104.53 (13)
O2—C2—C1	116.94 (13)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H21$\cdots$O3	0.86 (2)	1.78 (2)	2.618 (2)	165 (1)
O3—H31$\cdots$O1^i	0.88 (2)	2.02 (2)	2.888 (2)	166 (1)
O3—H32$\cdots$O1^{ii}	0.86 (2)	1.91 (2)	2.760 (2)	167 (1)

Symmetry codes: (i) $1 - x, 2 - y, 2 - z$; (ii) $x, y, z - 1$.

Crystal decay was monitored by measurement of duplicate reflections. The three oxygen-bonded H atoms were located by difference Fourier calculations and refined isotropically; other H atoms were placed geometrically and refined with a riding model (including free rotation of the methyl group).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Pro-

gram(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXL93*. Software used to prepare material for publication: *SHELXL93*.

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5,7-Dimethyl-3-phenyl-1,2,4-benzotriazine

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Abstract

The crystal structure of the title compound, C$_{15}$H$_{13}$N$_3$, has been determined by X-ray diffraction. The molecule is planar and the crystal packing is determined by van der Waals and graphitic interactions.

Comment

N-Substituted benzamidoximes show a complex behaviour in reactions with nitrile oxides depending on