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# Two crystalline modifications of 2-hydroxycyclopent-2-enone

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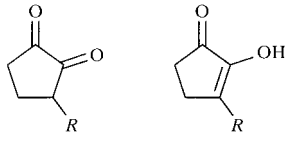
The orthorhombic form of 2-hydroxycyclopent-2-enone, $C_5H_6O_2$, consists of chains of hydrogen-bonded molecules aligned along a twofold screw axis. The monoclinic form contains two independent molecules, which have different orientations of the hydroxyl proton, and which assemble into ribbons along a twofold screw axis.

## Comment

As part of a study of the Maillard chemistry of dehydroascorbic acid and its decomposition products (Fayle *et al.*, 2000), we have reported the ability of the food additive cyclotene, (I), to act as a cross-linking reagent for model proteins (Fayle *et al.*, 1999). Recently, we reported the X-ray



(I*a*) $R$ = Me (I*b*) $R$ = Me
(II*a*) $R$ = H (II*b*) $R$ = H

crystal structure of the crystalline hydrate of cyclotene (Fayle *et al.*, 1998), which exists as the hydroxyenone tautomer, (I*b*). In a similar context, we are presently investigating the chemistry of the parent diketone, (II), which NMR solution studies clearly show exists as the enol tautomer, (II*b*). However, this compound displays chemistry that can be attributed to both the diketo tautomer, (II*a*), and the enol tautomer, (II*b*). During the course of this work, we managed to isolate two crystalline modifications of (II), which raised the intriguing possibility that these might be different stable tautomers of the same compound [a rare phenomenon sometimes called desmotropy (Guard & Steel, 1994; Desiraju, 1983)]. We now report the structures of these two crystalline forms.

The molecular structure in the orthorhombic form is shown in Fig. 1. The successful location and refinement of the potentially tautomeric hydroxyl-H atom, along with the bonding geometry (Table 1), unambiguously establish that, in this form, the title compound exists as the hydroxyenone tautomer, (II*b*). The cyclopentenone ring is essentially planar [maximum deviation from the mean plane = 0.022 (2) Å for C4]. The bonding geometry is very similar to that in cyclotene (I*b*) (Fayle *et al.*, 1998) and other crystallographically characterized cyclopentenones (Ley *et al.*, 1993; Tsuboi *et al.*, 1983). As shown in Fig. 2, the molecules connect into chains by means of intermolecular hydrogen bonds (Table 2).

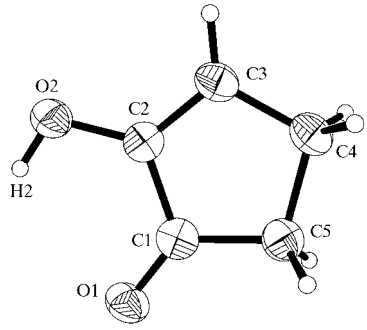



**Figure 1**
Perspective view and atom labelling of the orthorhombic form of (II*b*). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

The molecule in the monoclinic form exists as the same tautomer, (II*b*), and has two independent molecules in the asymmetric unit (Fig. 3), which differ in the orientation of the hydroxyl-H atom. One molecule has the OH group in an *s-cis* conformation, as in the orthorhombic form, while the other molecule has an *s-trans* conformation of the OH group, as was found for cyclotene (I*b*) (Fayle *et al.*, 1998). Apart from this difference, the two independent molecules have very similar geometries to one another (Table 3) and to the orthorhombic form. The two unique molecules are connected by a linear hydrogen bond (Table 4). These pairs of molecules further assemble into a puckered ribbon array (Fig. 4) by means of additional hydrogen bonds.

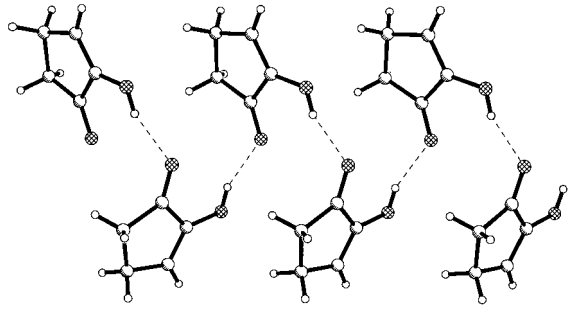


**Figure 2**
Packing diagram showing the hydrogen-bonded chains of molecules in the orthorhombic form.

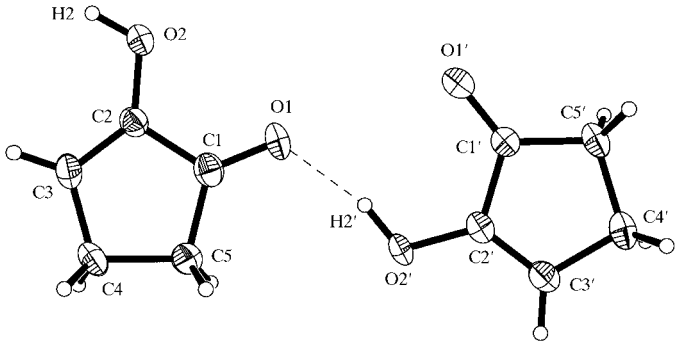



**Figure 3**
Perspective view and atom labelling of the two independent molecules in the monoclinic form of (II*b*). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

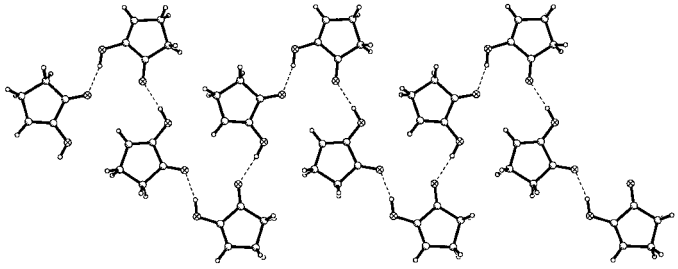


**Figure 4**
Packing diagram showing the hydrogen-bonded ribbons in the monoclinic form of (II*b*).

## Experimental

The title compound was prepared according to the literature procedure of Acheson (1956). Crystals of the orthorhombic form of (II) were obtained by low-temperature crystallization (195 K) from a mixture (5:1) of *n*-hexane and ethyl acetate. Vacuum distillation (351–359 K, 8 mmHg) of (II) furnished crystals of the monoclinic form.

### Orthorhombic (II)

*Crystal data*

$C_5H_6O_2$
$M_r$ = 98.10
Orthorhombic, $P2_12_12_1$
$a$ = 5.370 (5) Å
$b$ = 8.971 (8) Å
$c$ = 9.920 (9) Å
$V$ = 477.9 (8) Å$^3$
$Z$ = 4
$D_x$ = 1.363 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1694 reflections
$\theta$ = 3.1–25.0°
$\mu$ = 0.106 mm$^{-1}$
$T$ = 163 (2) K
Plate, colourless
0.68 × 0.18 × 0.01 mm

*Data collection*

Siemens SMART CCD diffractometer
Exposures over 0.5° $\varphi$ or $\omega$ rotation scans
Absorption correction: multi-scan (*SADABS*; Siemens, 1999)
$T_{min}$ = 0.806, $T_{max}$ = 0.968
5395 measured reflections
835 independent reflections
674 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.033
$\theta_{max}$ = 24.97°
$h = -6 \rightarrow 3$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.070
$S$ = 0.977
835 reflections
67 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.12 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.16 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| O1—C1 | 1.236 (2) | O2—H2 | 0.87 (2) |
| C1—C2 | 1.467 (3) | C2—C3 | 1.344 (3) |
| C1—C5 | 1.498 (3) | C3—C4 | 1.497 (3) |
| O2—C2 | 1.361 (2) | C4—C5 | 1.548 (3) |
| | | | |
| O1—C1—C2 | 124.1 (2) | C3—C2—C1 | 110.9 (2) |
| O1—C1—C5 | 128.1 (2) | O2—C2—C1 | 122.3 (2) |
| C2—C1—C5 | 107.8 (2) | C2—C3—C4 | 111.5 (2) |
| C2—O2—H2 | 109.6 (13) | C3—C4—C5 | 104.6 (2) |
| C3—C2—O2 | 126.8 (2) | C1—C5—C4 | 105.1 (2) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2···O1$^{i}$ | 0.87 (2) | 1.92 (2) | 2.745 (2) | 159.5 (18) |

Symmetry code: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$.

### Monoclinic (II)

*Crystal data*

$C_5H_6O_2$
$M_r$ = 98.10
Monoclinic, $P2_1/n$
$a$ = 9.100 (7) Å
$b$ = 10.761 (8) Å
$c$ = 10.124 (7) Å
$\beta$ = 106.491 (11)°
$V$ = 950.6 (12) Å$^3$
$Z$ = 8
$D_x$ = 1.371 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1577 reflections
$\theta$ = 2.7–25.0°
$\mu$ = 0.106 mm$^{-1}$
$T$ = 163 (2) K
Plate, colourless
0.45 × 0.18 × 0.03 mm

**Table 3**
Selected geometric parameters (Å, °) for monoclinic (II).

| | | | |
|---|---|---|---|
| O1—C1 | 1.231 (3) | O1′—C1′ | 1.232 (3) |
| C1—C2 | 1.461 (3) | C1′—C2′ | 1.460 (3) |
| C1—C5 | 1.505 (3) | C1′—C5′ | 1.502 (3) |
| O2—C2 | 1.360 (3) | O2′—C2′ | 1.353 (3) |
| O2—H2 | 0.89 (2) | O2′—H2′ | 0.94 (3) |
| C2—C3 | 1.341 (3) | C2′—C3′ | 1.333 (3) |
| C3—C4 | 1.499 (3) | C3′—C4′ | 1.502 (3) |
| C4—C5 | 1.538 (3) | C4′—C5′ | 1.543 (3) |
| | | | |
| O1—C1—C2 | 125.1 (2) | O1′—C1′—C2′ | 124.6 (2) |
| O1—C1—C5 | 126.4 (2) | O1′—C1′—C5′ | 128.1 (2) |
| C2—C1—C5 | 108.5 (2) | C2′—C1′—C5′ | 107.3 (2) |
| C2—O2—H2 | 113.9 (15) | C2′—O2′—H2′ | 113.5 (15) |
| C3—C2—O2 | 131.4 (2) | C3′—C2′—O2′ | 126.8 (2) |
| C3—C2—C1 | 110.5 (2) | C3′—C2′—C1′ | 111.3 (2) |
| O2—C2—C1 | 118.1 (2) | O2′—C2′—C1′ | 121.9 (2) |
| C2—C3—C4 | 111.5 (2) | C2′—C3′—C4′ | 111.9 (2) |
| C3—C4—C5 | 105.3 (2) | C3′—C4′—C5′ | 103.9 (2) |
| C1—C5—C4 | 104.2 (2) | C1′—C5′—C4′ | 105.5 (2) |

*Data collection*

Siemens SMART CCD diffractometer
Exposures over 0.5° $\varphi$ or $\omega$ rotation scans
Absorption correction: multi-scan (*SADABS*; Siemens, 1999)
$T_{min}$ = 0.838, $T_{max}$ = 0.968
10377 measured reflections
1669 independent reflections
973 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.059
$\theta_{max}$ = 25°
$h = -10 \rightarrow 10$
$k = -8 \rightarrow 12$
$l = -12 \rightarrow 12$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.115
$S$ = 0.914
1669 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.23 e Å$^{-3}$

**Table 4**
Hydrogen-bonding geometry (Å, °) for monoclinic (II).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2′—H2′···O1 | 0.94 (3) | 1.77 (3) | 2.694 (3) | 165 (2) |
| O2—H2···O1′$^{i}$ | 0.89 (2) | 1.82 (2) | 2.709 (3) | 175 (2) |

Symmetry code: (i) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The tautomeric hydroxyl-H atoms were located by difference Fourier calculations and their positions refined. The H(—C) atoms were placed in calculated positions (0.95–0.99 Å for both modifications). The absolute configuration of the orthorhombic form could not be determined, as judged by the Flack parameter [−0.4 (18); Flack, 1983].

For both compounds, data collection: *SMART* (Siemens, 1999); cell refinement: *SAINT* (Siemens, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1148). Services for accessing these data are described at the back of the journal.

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