

3-[(1*Z*)-1-Hydroxy-3-oxobut-1-en-1-yl]-7-methyl-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dioneN. Bouhaine,^a A. Gherrou^b‡ and A. van der Lee^{b*}^aFaculté des Sciences, Département de Chimie, Université Badji Mokhtar, 23000 Annaba, Algeria, and ^bInstitut Européen des Membranes, cc047, Université de Montpellier II, 34095 Montpellier Cedex 5, France

‡ Present address: Services ChemBrains, 240 Avenue Stirling, LaSalle, Quebec, Canada H8R 3P4.

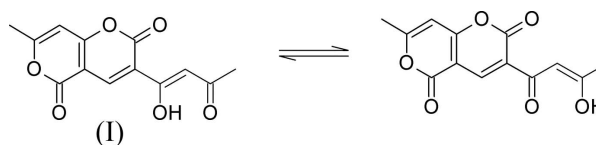
Correspondence e-mail: avderlee@univ-montp2.fr

The molecular structure of the title compound, C₁₃H₁₀O₆, contains a *cis*-enol ring disordered with respect to the position of the hydroxyl proton. The crystal structure contains sheets perpendicular to the *bc* plane.

Received 18 October 2006
Accepted 27 October 2006

Comment

The title compound, (I), was synthesized in the course of a study aiming to find new pyrone ring-containing compounds which are known to possess biological and pharmacological properties (Anderson *et al.*, 1976; Grivaky *et al.*, 1980; Kuo *et al.*, 1984; Cairns *et al.*, 1985).



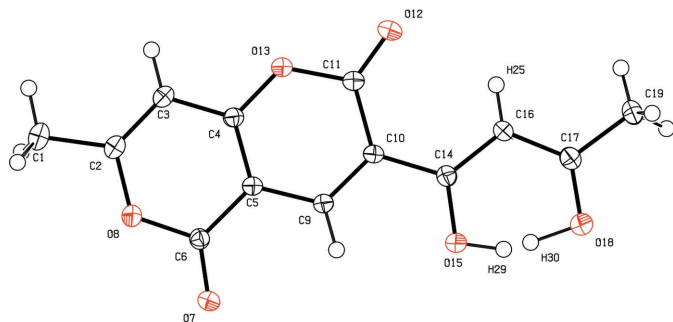
Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.039
 wR factor = 0.086
Data-to-parameter ratio = 25.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

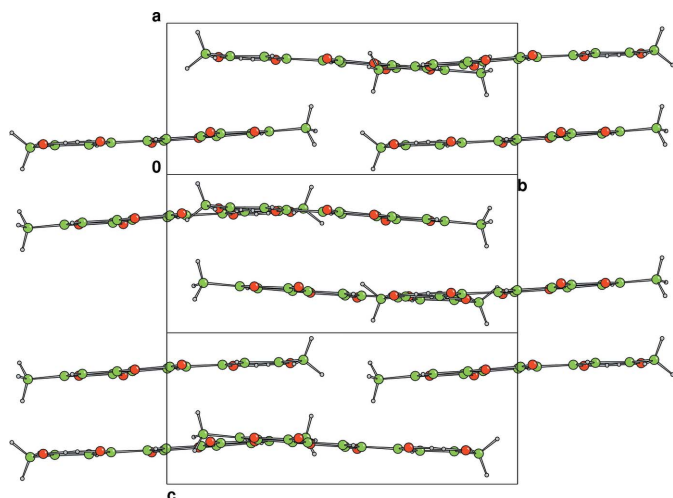
In the crystal structure of (I), the β angle in the alternative setting $P2_1/n$ is close to 90° at 120 K, *viz.* $90.938(2)^\circ$. At room temperature the β angle approaches 90° , *viz.* $90.05(1)^\circ$, without displaying even close to orthorhombic structural symmetry.

The molecular structure of (I) is shown in Fig. 1. In the title molecule the non-H atoms are almost coplanar, with a maximum deviation from the mean plane of $0.060(1)$ Å for atom C1 [mean planes calculated following the method of Rollett (1965)]. The glide-related molecules are inclined at an angle of 6.7° and form a sheet-like structure (Fig. 2) perpendicular to the *bc* plane. The in-plane arrangement of the molecules is shown in Fig. 3. The *cis*-enol rings of different molecules are arranged in lines parallel to the *a* axis. Very weak C—H...O interactions are found between the molecules in-plane. No significant π — π interactions are present between sheets. There is effectively one rather short intersheet distance, $3.109(2)$ Å, between the C11 atoms of molecules in adjacent sheets. The structure is rather close-packed; the volume occupied per non-H atom is 14.9 Å³, which is considerably lower than the usual 18 Å³ normally found for organic and organometallic structures, but not so uncommon for condensed aromatic systems.

The O...O distance in the *cis*-enol ring is $2.456(1)$ Å, which leads to very strong intramolecular hydrogen bonds between H30 and O15, and between H29 and O16. The C—O distances (Table 1) in the *cis*-enol ring lie in between the distances for a typical single (1.41 Å, Csp^3 —OH in alcohols) and a typical double bond (1.21 Å, Csp^2 —O, in ketones; Allen *et al.*, 1987). Similarly, the C14—C16 and C16—C17 distances lie in


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii. Atoms H29 and H30 have a site-occupancy factor of 0.50 each.

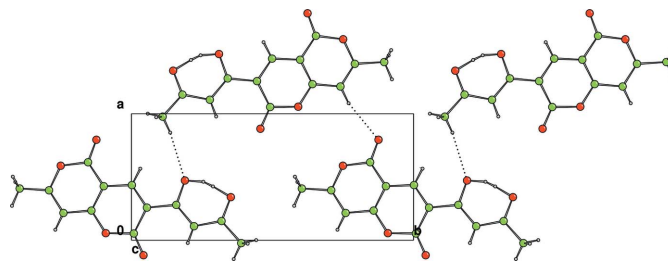

Figure 2

View perpendicular to the *bc* plane, showing the molecular stacking.

between the distances for a typical $Csp^2=Csp^2$ double bond (1.34 Å) and a typical Csp^2-Csp^2 single bond (1.46 Å; Allen *et al.*, 1987). Herbstein *et al.* (1999) have given a classification of *cis*-enol rings in terms of order, disorder and charge (de)localization based on a few structural parameters, such as $q_1 = d_1 - d_4$ [here $d_1 - d_4 = d(C14-O15) - d(C17-O18)$] and $q_2 = d_2 - d_3$ [here $d_2 - d_3 = d(C14-C16) - d(C16-C17)$]. The observed q_1 [0.010 (1) Å] and q_2 [-0.003 (1) Å] values are indicative either of a delocalized *cis*-enol ring, or of a disordered (statically or dynamically) superposition of two valence tautomers. The fact that a double-well potential is found atoms H29/H30 (see *Experimental* section) leads to the conclusion that the present structure has a disordered *cis*-enol ring.

Experimental

A solution of 4-hydroxy-6-methyl-2-pyrone (20 mmol) in ethyl orthoformate (10 ml) and ethanol (25 ml) was maintained under reflux for 3 h. After cooling, a yellow-red powder-like product was obtained by filtration and recrystallization from ethanol. Needle-shaped orange crystals were isolated from the powder.


Figure 3

In-plane arrangement of the molecules of (I), with the very weak C-H...O interactions indicated as dotted lines.

Crystal data

$C_{13}H_{10}O_6$
 $M_r = 262.22$
 Monoclinic, $P2_1/c$
 $a = 8.8290$ (4) Å
 $b = 14.1820$ (5) Å
 $c = 12.5238$ (5) Å
 $\beta = 133.882$ (2)°
 $V = 1130.27$ (9) Å³

$Z = 4$
 $D_x = 1.541$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 120$ K
 Needle, orange
 0.30 × 0.05 × 0.05 mm

Data collection

Bruker APEX 2 diffractometer
 ω scans
 Absorption correction: none
 26469 measured reflections

4322 independent reflections
 2755 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.037$
 $\theta_{max} = 33.2^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.086$
 $S = 1.02$
 4313 reflections
 172 parameters
 H-atom parameters not refined

$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2 / [10.2T_0(x) + 13.2T_1(x) + 3.67T_2(x)]$ where T_i are Chebyshev polynomials and $x = F_o/F_{max}$ (Watkin, 1994; Prince, 1982)
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.46$ e Å⁻³
 $\Delta\rho_{min} = -0.31$ e Å⁻³

Table 1

Selected bond lengths (Å).

O7—C6	1.2111 (14)	O15—C14	1.3016 (14)
O8—C2	1.3670 (15)	O18—C17	1.2913 (15)
O8—C6	1.3855 (14)	C10—C14	1.4824 (16)
O12—C11	1.2001 (14)	C14—C16	1.3983 (16)
O13—C4	1.3478 (14)	C16—C17	1.4062 (17)
O13—C11	1.4147 (15)	C17—C19	1.4915 (17)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O15—H29...O18	0.93	1.58	2.456 (2)	154
O18—H30...O15	1.05	1.44	2.456 (2)	161
C3—H23...O7 ⁱ	0.93	2.38	3.2928 (19)	166
C19—H26...O15 ⁱⁱ	0.90	2.52	3.405 (2)	165

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

Nine reflections that were in the vicinity of the beam-stop, *i.e.* those for which $(\sin\theta/\lambda)^2 < 0.01$, were not used in the least-squares refinement. All H atoms were visible in difference maps. There was H-atom disorder at the O15 and O18 sites of the *cis*-enol ring, and the disorder was modelled by fixing the occupancy parameters for atoms

H29 and H30 at 0.5. No attempts were made to refine the occupancy factors of these two H atoms. H atoms were not refined (O–H = 0.93–1.05 Å and C–H = 0.90–0.97 Å), with $U_{\text{iso}}(\text{H})$ values set at 1–1.5 times the U_{eq} of the parent atoms for C-bound H atoms.

Data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *APEX2*; data reduction: *SAINT-Plus* (Bruker–Nonius, 2004); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Anderson, G. L., Shim, J. L. & Brown, A. D. (1976). *J. Org. Chem.* **41**, 1095–1099.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Bruker–Nonius (2004). *APEX2* and *SAINT-Plus*. Bruker–Nonius BV, Delft, The Netherlands.
- Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.
- Cairns, H., Cox, D., Gould, K. J., Ingall, A. H. & Suschitzky, J. L. (1985). *J. Med. Chem.* **28**, 1832–1842.
- Grivaky, E. M., Lee, S., Siyal, C. W., Duch, D. S. & Nichol, C. A. (1980). *J. Med. Chem.* **23**, 327–329.
- Herbstein, F. H., Iversen, B. B., Kapon, M., Larsen, F. K., Madsen, G. K. H. & Reisner, G. M. (1999). *Acta Cryst.* **B55**, 767–787.
- Kuo, S. G., Huang, L. J. & Nakamura, H. (1984). *J. Med. Chem.* **27**, 539–544.
- Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
- Rollett, J. S. (1965). Editor. *Computing Methods in Crystallography*, pp. 67–68. Oxford: Pergamon Press.
- Watkin, D. (1994). *Acta Cryst.* **A50**, 411–437.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.