

A redetermination of 4'-hydroxyacetophenone

A. Jerry Kresge, Alan J. Lough*
and Yu ZhuDepartment of Chemistry, University of Toronto,
Toronto, Ontario, Canada M5S 3H6Correspondence e-mail:
alough@chem.utoronto.ca

The structure of 4'-hydroxyacetophenone, $C_8H_8O_2$, (1), has been redetermined at 150 K. There are two molecules in the asymmetric unit and the equivalent bond lengths and angles in each molecule are the same. Pairs of independent $O-H\cdots O$ hydrogen-bonded molecules ($H\cdots O$ 1.87 Å) are linked, in turn, by different $O-H\cdots O$ hydrogen bonds ($H\cdots O$ 1.90 Å), through 2_1 screw axes, to form chains in the c direction.

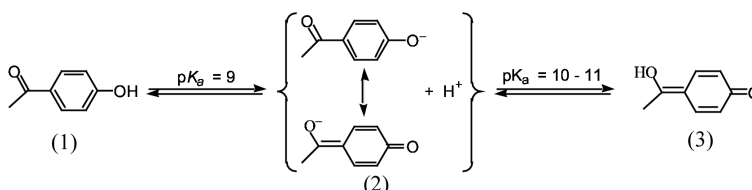
Received 23 August 2002
Accepted 29 August 2002
Online 13 September 2002

Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(C-C) = 0.003$ Å
 R factor = 0.034
 wR factor = 0.087
Data-to-parameter ratio = 7.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Comment

Ionization of 4'-hydroxyacetophenone, (1), as an oxygen acid gives an anion, (2), whose negative charge can be delocalized into its acetyl group (see *Scheme*). This gives the anion an additional basic site, whose protonation provides the enolic species (3).



Enols are weakly acidic substances with $pK_a = 10-11$ (Keeffe & Kresge, 1990), and $pK_a = 9$ may be estimated for the hydroxyl group of (1) using a $\sigma-\rho$ relationship that correlates acidity constants of phenols (Perrin *et al.*, 1981). Combination of these two values then gives $pK = 9 - (10-11) = -(1-2)$ for the equilibrium constant relating (1) and (3). This suggests that (3), and not (1), is the structure of 4'-hydroxyacetophenone.

In order to determine whether or not this is so, we carried out the present X-ray diffraction analysis. The results show unequivocally that the correct structure is the phenolic one shown as (1), and not the enolic one shown as (3).

This conclusion is unexpected on the basis of the argument involving pK_a 's made above. That argument, however, failed to take into account the fact that ionization of (3) converts a cyclohexadiene ring into a ring having some benzenoid character. The ionization therefore benefits from a gain in benzenoid resonance energy, and that makes (3) a substantially stronger acid than the estimate made above.

The crystal structure of (1) was originally determined by Vainshtein *et al.* (1974), using visually estimated intensities, which were recorded on photographic film. We have redetermined the structure of (1) at low temperature with more accurate data collected using a CCD area detector. In (1), as in the earlier structure, the space group is $P2_12_12_1$ and there are two independent molecules in the asymmetric unit, but there is an expected contraction in the volume of the unit cell of

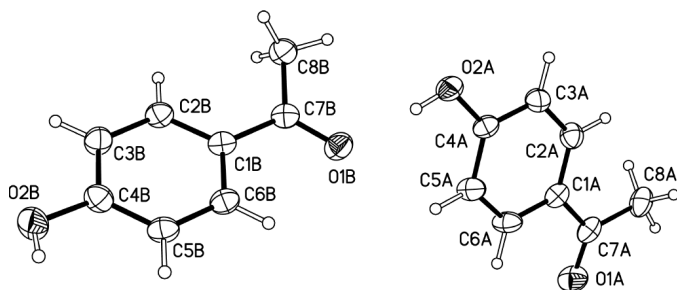


Figure 1
View of both independent molecules in (1), with displacement ellipsoids drawn at the 50% probability level.

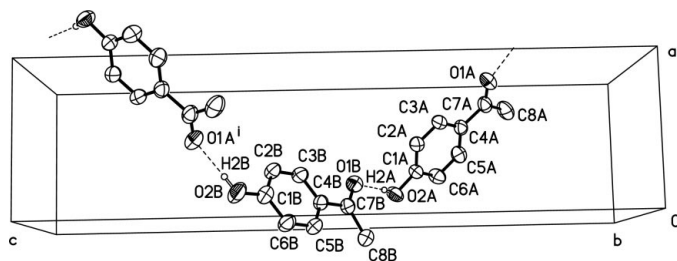


Figure 2
View of the hydrogen bonding in (1) [symmetry code: (i) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$].

about 1%. In our low-temperature structure the equivalent bond lengths and angles in each independent molecule (*A* and *B*) are the same within experimental error. The only minor difference between molecules *A* and *B* is the extent of the rotation of the acetyl group about the C1–C7 bond, with respect to the phenyl ring. This is reflected in the torsion angles of $4.8(3)^\circ$ for C2A–C1A–C7A–C8A and $9.6(3)^\circ$ for C2B–C1B–C7B–C8B.

In (1), pairs of independent molecules (*A* and *B*) are linked through one type of $\text{O} \cdots \text{H} \cdots \text{O}=\text{C}$ hydrogen bond ($\text{H} \cdots \text{O}$ 1.87 Å) and each hydrogen-bonded pair is linked, in turn, through 2_1 screw axes to form chains in the *c* direction via another type of $\text{O} \cdots \text{H} \cdots \text{O}=\text{C}$ hydrogen bond ($\text{H} \cdots \text{O}$ 1.90 Å) (see Fig. 2 and Table 2). Since there are two distinct $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds, the primary graph set (N_1) is *DD* and the secondary graph set (N_2) is $C_2^2(16)$ (Bernstein *et al.*, 1995).

Experimental

Crystals of 4'-hydroxyacetophenone (Sigma–Aldrich) suitable for X-ray analysis were obtained by allowing solvent from an ethanol solution of this substance at room temperature to evaporate slowly over the course of several days.

Crystal data

$\text{C}_8\text{H}_8\text{O}_2$	Mo $K\alpha$ radiation
$M_r = 136.14$	Cell parameters from 1020 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 2.6\text{--}25.0^\circ$
$a = 6.1886(4)$ Å	$\mu = 0.09\text{ mm}^{-1}$
$b = 9.0710(6)$ Å	$T = 150(1)$ K
$c = 24.5261(15)$ Å	Needle, colourless
$V = 1376.82(15)$ Å ³	$0.40 \times 0.30 \times 0.25$ mm
$Z = 8$	
$D_x = 1.314\text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.032$
φ scans and ω scans with κ offsets	$\theta_{\text{max}} = 25.0^\circ$
3693 measured reflections	$h = -7 \rightarrow 7$
1405 independent reflections	$k = -10 \rightarrow 10$
1284 reflections with $I > 2\sigma(I)$	$l = -29 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.1416P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.087$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.09\text{ e \AA}^{-3}$
1405 reflections	$\Delta\rho_{\text{min}} = -0.11\text{ e \AA}^{-3}$
186 parameters	Extinction correction: <i>SHELXTL/PC</i>
H-atom parameters constrained	Extinction coefficient: 0.037 (11)

Table 1

Selected geometric parameters (Å, °).

O1A–C7A	1.224 (3)	O1B–C7B	1.234 (3)
O2A–C4A	1.354 (2)	O2B–C4B	1.359 (3)
C1A–C7A	1.479 (3)	C1B–C7B	1.478 (3)
C7A–C8A	1.499 (3)	C7B–C8B	1.497 (3)
O1A–C7A–C1A	121.5 (2)	O1B–C7B–C1B	120.64 (19)
O1A–C7A–C8A	120.4 (2)	O1B–C7B–C8B	120.15 (19)
C1A–C7A–C8A	118.1 (2)	C1B–C7B–C8B	119.2 (2)
C2A–C1A–C7A–O1A	−174.0 (2)	C2B–C1B–C7B–O1B	−171.5 (2)
C2A–C1A–C7A–C8A	4.8 (3)	C2B–C1B–C7B–C8B	9.6 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
O2A–H2A \cdots O1B	0.84	1.87	2.707 (2)	171
O2B–H2B \cdots O1A ⁱ	0.84	1.90	2.732 (2)	172

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

All H atoms were included in calculated positions, with distances of 0.95 and 0.98 Å for C–H and of 0.84 Å for O–H. In the refinement, H atoms were included in a riding-motion approximation, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ ($1.5U_{\text{eq}}$ for methyl H atoms) of the carrier atom. Owing to a lack of significant anomalous scatterers, the absolute stereochemistry could not be determined and Friedel pairs were merged before refinement cycles. Successive attempts to crystallize the sample gave crystals that were brittle needles and were difficult to cut. The best crystal possible that was finally selected for data collection gave diffuse diffraction spots, indicating the crystal had a large mosaic spread. As a result of this, a few of the diffraction spots were overlapping and the integration of these spots could not be carried out properly by the processing software. A small portion of the reflections collected were therefore rejected on the basis that they were measured incorrectly. Despite this, the title structure was refined using 97.6% of the possible data, which is adequate to give a precise structure.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL*.

The authors acknowledge NSERC Canada and the University of Toronto for financial support.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Keeffe, J. R. & Kresge, A. J. (1990). *The Chemistry of Enols*, edited by Z. Rappoport, pp. 399–480. New York: Wiley.
- Perrin, D. D., Dempsey, B. & Serjeant, E. P. (1981). *pK_a Predictions for Organic Acids and Bases*, p. 130. New York: Chapman and Hall.
- Nonius (1997–2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (2001). *SHELXTL/PC*. Version 6.12 for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Vainshtein, B. K., Lobanova, G. M. & Gurskaya, G. V. (1974). *Kristallografiya*, **19**, 531–538.