Z. Kristallogr. NCS **229** (2014) 433-434 / **DOI** 10.1515/ncrs-2014-9023

# Crystal structure of methyl 5-acetyl-2-hydroxybenzoate, at 200 K, $C_{10}H_{10}O_4$

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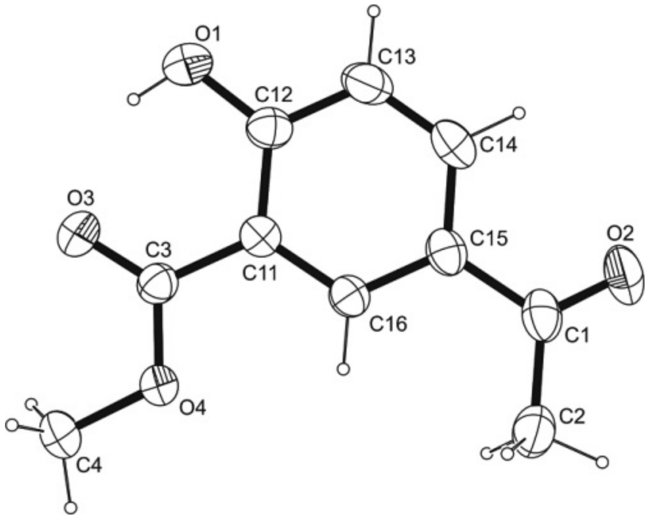
Received August 17, 2014, accepted October 31, 2014, available online November 10, 2014, CCDC no. 1267/4225



## Abstract

$C_{10}H_{10}O_4$, monoclinic, $P2_1/c$ (no. 14), $a = 8.7782(4)$ Å, $b = 7.4533(3)$ Å, $c = 14.7842(8)$ Å, $\beta = 103.364(2)°$, $V = 941.1$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.0410$, $wR_{ref}(F^2) = 0.1198$, $T = 200$ K.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colourless rods,<br>size 0.133×0.137×0.531 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 1.07 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II CCD, $\varphi$ and $\omega$ |
| $2\theta_{max}$: | 56.3° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 8620, 2279 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 1753 |
| $N(param)_{refined}$: | 130 |
| Programs: | SHELX, WinGX, MERCURY,<br>PLATON [9–12] |

## Source of material

The compound was obtained commercially (Aldrich). Crystals suitable for the diffraction study were obtained upon recrystallization of the powdery reagent from ethanol.

## Expermental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $U_{iso}$(H) set to $1.2U_{eq}$(C). The H atoms of the methyl groups were allowed to rotate with a fixed H–C–O/ H–C–C angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [9]), with $U_{iso}$(H) set to $1.5U_{eq}$(C). The H atom of the hydroxyl group was allowed to rotate with a fixed H–O–C angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [9]), with $U_{iso}$(H) set to $1.5U_{eq}$(O).

## Discussion

Acetyl salicylic acid – commonly known as Aspirin – is one of the most commonly used medications for pain relief. Its structure has been elucidated by means of X-ray diffraction many times (for a selection of structure determinations *cf.* [1–3]). Esters derived from simple aliphatic alcohols and salicylic acid have attracted considerable less attention from a structural point of view as, e.g., for the methyl ester only two coordination compounds involving zinc as the central atom are apparent in the literature with structural characterizations based on diffractometric data [4, 5]. At the onset of a study about coordination compounds applying aspirine and its esters as potential ligands we also sought to explore constitutional isomers of the latter two as potential starting materials such as the title compound. To allow for the comparison of metrical parameters in the free as well as the coordinated ligand, its crystal and molecular structure were determined. The title compound is a constitutional isomer of an esterified derivative of aspirine. The molecule is essentially planar (r.m.s of all fitted non-hydrogen atoms = 0.0600 Å) with the methyl group of the acetyl substituent deviating most from planarity by 0.1405(12) Å. The least-squares planes as defined by the non-hydrogen atoms of the ester substituent on the one hand and the carbon atoms of the aromatic system on the other hand enclose an angle of 3.87(8)° only, thus indicating a pronounced degree of resonance spanning the former substituent as well. Intracyclic C–C–C angles span a range of 118.28(12)–121.54(11)° with the smallest angle found on the carbon atom bearing the acetyl substituent and the largest angle present on the carbon atom in between the acetyl and the ester moiety. The two C=O bonds are nearly identical in length with values of 1.2148(17) Å and 1.2150(15) Å with the longer one realized for the ester substituent. In comparison to other acetylated benzene derivatives whose metrical parameters have been deposited with the Cambridge Structural Database [6], the values of the C=O bonds found in the present study are in good agreement with the most common ones observed. In the crystal, classical hydrogen bonds of the O–H···O type are observed next to C–H···O contacts whose range falls below the sum of van-der-Waals radii of the atoms participating in them. The classical hydrogen bond is bifurcated, forming an intramolecular as well as an intermolecular contact to the carbonyl-type oxygen atom of the ester group. The C–H···O contacts are apparent in between the methyl group of the ester substituent as donor and the oxygen atom of the hydroxyl group as acceptor. In addition, a second C–H···O interaction is supported by the methyl group and the oxygen atom of the acetyl substituent giving rise to dimeric units. In terms of

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graph-set analysis [7, 8], the descriptor for the classical hydrogen bonds is $S(6)R^2_2(12)$ on the unary level while the C–H···O contacts necessitate a $C^1_1(7)R^2_2(8)$ descriptor on the same level. Furthermore, a C–H···$\pi$ interaction is observed supported by another hydrogen atom on the methyl group of the acetyl substituent. In total, the molecules are connected to a three-dimensional network. The shortest intercentroid distance between two centers of gravity was measured at 4.3377(8) Å.

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1) | 4*e* | 0.6544 | 0.0669 | 0.0833 | 0.069 |
| H(2A) | 4*e* | 1.2836 | 0.2618 | −0.0769 | 0.065 |
| H(2B) | 4*e* | 1.3846 | 0.4421 | −0.0562 | 0.065 |
| H(2C) | 4*e* | 1.1985 | 0.4529 | −0.0931 | 0.065 |
| H(4A) | 4*e* | 0.6457 | 0.1357 | −0.2819 | 0.072 |
| H(4B) | 4*e* | 0.5273 | 0.1673 | −0.2158 | 0.072 |
| H(4C) | 4*e* | 0.6005 | −0.0274 | −0.2228 | 0.072 |
| H(13) | 4*e* | 0.9677 | 0.2065 | 0.2406 | 0.051 |
| H(14) | 4*e* | 1.1885 | 0.3321 | 0.2062 | 0.048 |
| H(16) | 4*e* | 1.0052 | 0.2582 | −0.0687 | 0.035 |

**Table 3.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| O(1) | 4*e* | 0.7246(1) | 0.0887(2) | 0.13122(7) | 0.0441(6) | 0.0615(7) | 0.0355(5) | −0.0069(5) | 0.0160(4) | 0.0002(5) |
| O(2) | 4*e* | 1.3671(1) | 0.4459(2) | 0.10739(8) | 0.0389(6) | 0.0832(9) | 0.0508(7) | −0.0187(6) | −0.0096(5) | 0.0022(6) |
| O(3) | 4*e* | 0.6072(1) | 0.0605(2) | −0.04819(7) | 0.0349(5) | 0.0668(7) | 0.0402(5) | −0.0158(5) | 0.0120(4) | −0.0001(5) |
| O(4) | 4*e* | 0.7515(1) | 0.1463(1) | −0.14655(6) | 0.0308(5) | 0.0504(6) | 0.0279(4) | −0.0105(4) | 0.0049(4) | −0.0022(4) |
| C(1) | 4*e* | 1.2663(2) | 0.3839(2) | 0.0447(1) | 0.0291(7) | 0.0384(7) | 0.0435(7) | 0.0007(6) | −0.0026(5) | 0.0057(6) |
| C(2) | 4*e* | 1.2849(2) | 0.3853(2) | −0.0540(1) | 0.0333(7) | 0.0464(8) | 0.0495(8) | −0.0066(6) | 0.0079(6) | 0.0032(7) |
| C(3) | 4*e* | 0.7279(1) | 0.1220(2) | −0.06224(8) | 0.0293(6) | 0.0311(6) | 0.0312(6) | −0.0005(5) | 0.0089(5) | −0.0007(5) |
| C(4) | 4*e* | 0.6206(2) | 0.1019(2) | −0.2230(1) | 0.0397(8) | 0.067(1) | 0.0323(7) | −0.0155(7) | −0.0011(6) | −0.0017(7) |
| C(11) | 4*e* | 0.8611(1) | 0.1768(2) | 0.01318(8) | 0.0285(6) | 0.0267(6) | 0.0291(6) | 0.0032(5) | 0.0059(5) | −0.0009(5) |
| C(12) | 4*e* | 0.8505(2) | 0.1586(2) | 0.10637(9) | 0.0354(7) | 0.0348(7) | 0.0318(6) | 0.0037(5) | 0.0096(5) | 0.0011(5) |
| C(13) | 4*e* | 0.9746(2) | 0.2173(2) | 0.17768(9) | 0.0458(8) | 0.0531(9) | 0.0268(6) | 0.0044(7) | 0.0055(6) | 0.0015(6) |
| C(14) | 4*e* | 1.1061(2) | 0.2906(2) | 0.15717(9) | 0.0371(7) | 0.0457(8) | 0.0320(6) | 0.0037(6) | −0.0042(5) | −0.0012(6) |
| C(15) | 4*e* | 1.1210(2) | 0.3054(2) | 0.06469(9) | 0.0296(6) | 0.0297(6) | 0.0346(6) | 0.0035(5) | −0.0001(5) | 0.0023(5) |
| C(16) | 4*e* | 0.9971(1) | 0.2483(2) | −0.00592(8) | 0.0291(6) | 0.0283(6) | 0.0294(5) | 0.0022(5) | 0.0043(4) | 0.0011(5) |

*Acknowledgments.* The authors thank Mr Mike Aquilina for helpful discussions.

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