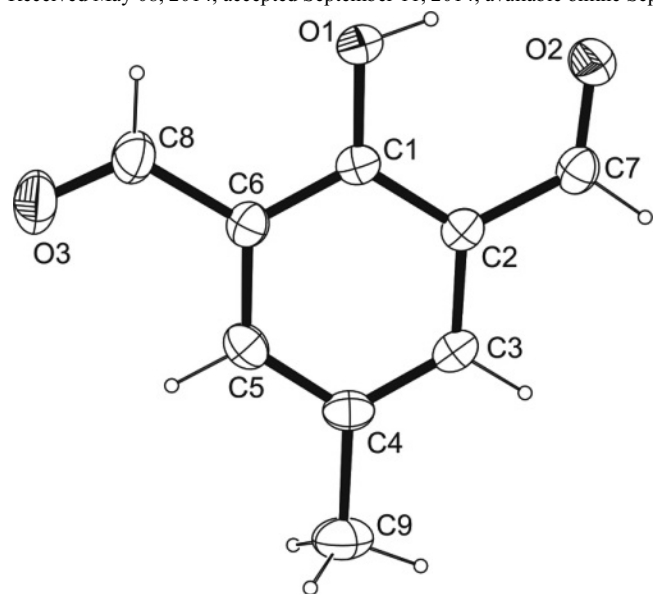


Redetermination of the crystal structure of 2,6-diformyl-4-methylphenol, at 200 K, $C_9H_8O_3$

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Abstract

$C_9H_8O_3$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 3.9020(2)$ Å, $b = 7.5260(3)$ Å, $c = 25.916(1)$ Å, $V = 761.1$ Å³, $Z = 4$, $R_{gt}(F) = 0.0343$, $wR_{ref}(F^2) = 0.1012$, $T = 200$ K.

Table 1. Data collection and handling.

Crystal:	green platelets, size 0.06×0.465×0.547 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ :	1.08 cm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7696, 1156
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1085
$N(param)_{refined}$:	111
Programs:	SHELX, WinGX, MERCURY, PLATON [4–7]

Source of material

The compound was obtained upon hydrolysis the two-fold Schiff-base derived from the title compound and 2-(piperidin-1-yl)ethanamine. The mixture was refluxed in aqueous methanol overnight. Crystals suitable for the diffraction studies were obtained upon evaporation from methanol at room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for both the aromatic as well as the formyl carbon atoms) and were included in the refinement in the riding model approxi-

mation, with $U_{iso}(H)$ set to $1.2U_{eq}(C)$. The H atoms of the methyl group were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [6]), with $U_{iso}(H)$ set to $1.5U_{eq}(C)$. The H atom of the hydroxyl group was allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [6]), with $U_{iso}(H)$ set to $1.5U_{eq}(O)$. Due to the absence of a strong anomalous scatterer, the Friedel opposites (731 pairs) have been merged.

Discussion

The synthesis of metal-organic framework (MOF) structures has been a topic of considerable research activity over the past years. Owing to the many envisioned applications of MOFs in catalytic processes, a rationalization of their synthesis procedures to allow for the tailored synthesis of various pore sizes seemed desirable. A modular approach based on individual secondary building blocks was suggested in this aspect that was specifically based on (multibasic) carboxylic acids [1]. Other polydentate ligands of the Schiff-base type have been less thoroughly researched in this aspect. As the latter seemed to be promising for the synthesis of polynuclear rhenium coordination compounds, a study focused on the synthesis and tailoring of such ligands was initiated. An important starting material for the intended condensation reactions was seen in the title compound whose molecular and crystal structure has been reported earlier [2, 3]. As the molecular structure and spatial requirements of intended target molecules are to be elucidated at low temperature, the crystal structure of the title compound was redetermined to allow for the comparison of metrical parameters. The molecule is essentially flat and shows one of the formyl group oxygen atoms deviating most from the least-squares plane by 0.0775(14) Å (r.m.s of all fitted non-hydrogen atoms = 0.0374 Å). The respective O–C–C–C dihedral angles of the two formyl groups are measured at $-2.3(3)^\circ$ and $-4.8(3)^\circ$, respectively. Both these values are smaller than the ones reported for the structure of the title compound at room temperature [3]. Surprisingly, the larger dihedral angle is formed involving the oxygen atom that acts as acceptor for the intramolecular hydrogen bond (*vide infra*). The latter O atom sticks out in yet another aspect as the two C=O bond lengths apparent in the molecule differ markedly from one another – with values of 1.209(2) Å and 1.225(2) Å – and the longer bond formed involving it. In comparison to the data available for the metrical parameters established at room temperature, both values found at lower temperature are greater in value [3]. In the crystal, a classical intramolecular O–H...O hydrogen bond can be observed between O1 and O2 (cf. fig.). The structure shows that the shortest intercentroid distance between two centers of gravity of adjacent six-membered rings was found to be 3.9020(11) Å.

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	4a	−0.2166	0.8536	0.0200	0.045
H(3)	4a	−0.1291	1.2778	0.1372	0.030
H(5)	4a	0.3633	0.8505	0.1938	0.031
H(7)	4a	−0.4016	1.2709	0.0532	0.031

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
O(1)	4a	−0.1147(4)	0.7893(2)	0.04163(4)	0.0413(8)	0.0246(6)	0.0251(5)	0.0044(6)	−0.0046(6)	−0.0055(4)
O(2)	4a	−0.4037(4)	1.0809(2)	0.00673(4)	0.0395(8)	0.0304(6)	0.0278(6)	0.0020(6)	−0.0052(6)	0.0013(5)
O(3)	4a	0.4610(5)	0.5498(2)	0.14894(6)	0.055(1)	0.0295(7)	0.0542(8)	0.0088(7)	−0.0127(8)	0.0067(6)
C(1)	4a	−0.0330(4)	0.8871(2)	0.08343(6)	0.0227(7)	0.0213(7)	0.0213(7)	−0.0028(7)	0.0031(6)	−0.0009(5)
C(2)	4a	−0.1358(4)	1.0649(2)	0.08865(6)	0.0215(7)	0.0216(7)	0.0230(7)	−0.0016(7)	0.0045(6)	0.0011(5)
C(3)	4a	−0.0555(5)	1.1581(2)	0.13378(6)	0.0261(8)	0.0212(7)	0.0275(7)	−0.0006(7)	0.0052(7)	−0.0033(6)
C(4)	4a	0.1286(5)	1.0804(2)	0.17367(6)	0.0258(8)	0.0310(9)	0.0235(7)	−0.0048(8)	0.0038(7)	−0.0043(6)
C(5)	4a	0.2343(5)	0.9055(2)	0.16715(6)	0.0235(8)	0.0302(8)	0.0235(7)	−0.0027(7)	0.0001(6)	0.0040(6)
C(6)	4a	0.1581(5)	0.8078(2)	0.12294(6)	0.0243(8)	0.0218(7)	0.0264(7)	−0.0014(7)	0.0021(7)	0.0020(6)
C(7)	4a	−0.3290(5)	1.1519(2)	0.04777(6)	0.0279(8)	0.0220(7)	0.0281(7)	0.0008(7)	0.0043(7)	0.0033(6)
C(8)	4a	0.2777(5)	0.6226(2)	0.11782(7)	0.036(1)	0.0225(8)	0.0372(9)	0.0014(8)	−0.0023(8)	0.0029(7)
C(9)	4a	0.2146(6)	1.1822(3)	0.22216(7)	0.041(1)	0.048(1)	0.0318(8)	−0.002(1)	−0.0023(9)	−0.0140(8)

Table 2. continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(8)	4a	0.2065	0.5568	0.0884	0.038
H(9A)	4a	0.1034	1.1255	0.2518	0.060
H(9B)	4a	0.1327	1.3048	0.2189	0.060
H(9C)	4a	0.4634	1.1824	0.2273	0.060

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References

- Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M.: Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks. *Acc. Chem. Res.* **34** (2001) 319–330.
- Sarkar, P. B.; Gupta, S. P. S.: *Indian J. Phys.* **A55** (1981) 206.
- Ray, T.; Gupta, S. P. S.: *Cryst. Struct. Commun.* **11** (1982) 59.
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
- Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
- Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A.: Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* **41** (2008) 466–470.
- Spek, A. L.: Structure validation in chemical crystallography. *Acta Crystallogr.* **D65** (2009) 148–155.