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Crystal structure of *ortho*-methoxy benzaldehyde, $C_8H_8O_2$ – a second polymorph and deposition of 3D coordinates

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.57 × 0.42 × 0.40 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.09 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	24,885, 3507, 0.015
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3225
$N(\text{param})_{\text{refined}}$:	183
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3], Mercury [4], PLATON [5]

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Abstract

$C_8H_8O_2$, tetragonal, $P4_32_12$ (no. 96), $a = 10.9521(5)$ Å, $c = 23.3014(17)$ Å, $V = 2795.0(3)$ Å³, $Z = 16$, $R_{\text{gt}}(F) = 0.0317$, $wR_{\text{ref}}(F^2) = 0.0883$, $T = 200$ K.

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The molecular structure is shown in Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Source of material

The compound was obtained commercially (Aldrich). Crystals suitable for the diffraction study were taken directly from the provided product.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic and vinylic carbon atoms) and were included in the refinement in the riding model approximation, with $U(H)$ set to 1.2 $U_{\text{eq}}(C)$.

The H atoms of the methyl groups 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 (Sheldrick, 2015)), with $U(H)$ set to 1.5 $U_{\text{eq}}(C)$.

Comment

Chelate ligands have found widespread use in coordination chemistry due to the increased stability of coordination compounds they can form in comparison to monodentate ligands [6]. Hydroxycarboxylic acids are particularly interesting in this aspect as they offer two hydroxyl groups of markedly different acidity as potential

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O11	−0.18858(13)	0.84809(15)	0.24935(6)	0.0591(4)
O12	0.07412(11)	0.60281(11)	0.26746(5)	0.0396(3)
C11	0.00298(13)	0.77413(13)	0.21721(6)	0.0303(3)
C12	0.09220(14)	0.68290(13)	0.22376(6)	0.0308(3)
C13	0.19099(15)	0.67855(15)	0.18622(7)	0.0371(3)
H13	0.250426	0.615794	0.189641	0.045 [*]
C14	0.20180(16)	0.76647(17)	0.14390(7)	0.0413(4)
H14	0.269438	0.763429	0.118416	0.050 [*]
C15	0.11619(16)	0.85904(17)	0.13776(6)	0.0404(4)
H15	0.125886	0.919855	0.109050	0.048 [*]
C16	0.01678(15)	0.86113(15)	0.17412(6)	0.0354(3)
H16	−0.043286	0.922991	0.169678	0.042 [*]
C17	−0.10425(16)	0.77789(17)	0.25512(7)	0.0402(4)
H17	−0.107502	0.721608	0.286101	0.048 [*]
C18	0.16567(18)	0.51204(16)	0.27772(9)	0.0474(4)
H18A	0.172700	0.458926	0.244038	0.071 [*]
H18B	0.142702	0.463066	0.311226	0.071 [*]
H18C	0.244242	0.552008	0.284929	0.071 [*]
O21	−0.09186(12)	0.04521(12)	0.06611(6)	0.0478(3)
O22	0.00587(12)	0.30392(11)	−0.04421(5)	0.0423(3)
C21	0.02898(13)	0.22007(13)	0.04779(6)	0.0304(3)
C22	0.06434(14)	0.30776(14)	0.00720(7)	0.0332(3)
C23	0.15482(17)	0.39240(16)	0.02112(8)	0.0428(4)
H23	0.181044	0.450882	−0.006357	0.051 [*]
C24	0.20578(18)	0.39016(17)	0.07527(9)	0.0496(4)
H24	0.266609	0.448542	0.084844	0.060 [*]
C25	0.17071(17)	0.30524(18)	0.11600(8)	0.0454(4)
H25	0.206862	0.305578	0.153063	0.055 [*]
C26	0.08281(15)	0.22018(15)	0.10225(7)	0.0367(3)
H26	0.058583	0.161238	0.129908	0.044 [*]
C27	−0.06362(15)	0.12742(15)	0.03419(7)	0.0356(3)
H27	−0.103721	0.132464	−0.001889	0.043 [*]
C28	0.0437(2)	0.38778(18)	−0.08790(8)	0.0487(4)
H28A	0.030053	0.471621	−0.074689	0.073 [*]
H28B	−0.003678	0.373165	−0.122897	0.073 [*]
H28C	0.130737	0.375916	−0.095993	0.073 [*]

bonding partners. Mandelic acids are especially versatile in this context as their aromatic moiety can be functionalized by means of various substituents at a sheer limitless scale. Mandelic acids are easily synthesized upon acidic hydrolysis of their pertaining cyanohydrines that – in turn – are accessible in good yield by the acid-catalyzed addition of hydrocyanic acid to the parent aldehyde [7]. To allow for a more detailed comparison of metrical parameters of the mandelic acid derived from *ortho*-methoxy benzaldehyde in envisioned coordination compounds, the crystal and molecular structure of the parent benzaldehyde was determined as a first step. The molecular and crystal structures of the title compound have been reported earlier (CSD Ref code: NARZUC) [8], however, a different space group was observed in this case, furthermore, no 3D

coordinates were deposited with the Cambridge Structural Database [9]. Structural information is also at hand for the title compound acting as a ligand towards boron [10, 11], aluminium [12, 13] and tin [14]. The structures of 4-methoxy-benzaldehyde [15] and 5-iodo-2,4-dimethoxy-benzaldehyde [16] have been reported earlier.

The title compound is the *ortho*-methoxy derivative of benzaldehyde. The structure solution shows the presence of two complete molecules in the asymmetric unit. Bond lengths and angles are in good agreement with the values previously reported for the other polymorph of the title compound, crystallized in space group *P*4₃, as well as other benzaldehyde derivatives whose metrical parameters have been deposited with the Cambridge Structural Database [9]. The intracyclic C–C–C angles cover ranges from 118.80(15)–121.60(15)° in the first molecule and from 119.21(16)–121.81(16)° in the second molecule. While the largest angle is invariably found on the carbon atom in *para* position to the formyl group, the smallest angle is found in *para* position to the methoxy group in the first molecule and in *ortho* position to the methoxy group in the second molecule present in the asymmetric unit. Both molecules are essential planar with the largest deviations found for an atom from the least-squares planes as defined by the respective non-hydrogen atoms at −0.056(2) and 0.056(1) Å. The least-squares planes as defined by the carbon atoms of the individual phenyl groups intersect at an angle of 78.13(8)°.

In the crystal, C–H⋯O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them are observed. These are established between the hydrogen atom of the C–H group in *ortho* position to the methoxy group on the one molecule as donor and the oxygen atom of the formyl group of the second molecule as acceptor. In total, the two molecules present in the asymmetric unit are connected to isolated dimers. In terms of graph-set analysis [17, 18], the descriptor for these contacts is *D* at the unary level. π -stacking is apparent in the crystal structure of the title compound with the shortest distance between two centers of gravity measured at 3.7826(9) Å only. These contacts are observed between the aromatic system of one of the two molecules and its symmetry-generated equivalents

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