Lubabalo Ndimba, Eric C. Hosten and Richard Betz*

Crystal structure of 2-hydroxy-4-methoxy benzaldehyde, $C_8H_8O_3$

Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	0.30 × 0.24 × 0.13 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.11 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13,163, 3573, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2615
$N(\text{param})_{\text{refined}}$:	203
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3], Mercury [4], PLATON [5]

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Abstract

$C_8H_8O_3$, monoclinic, $P2_1/c$ (no. 14), $a = 6.3037(3)$ Å, $b = 33.102(2)$ Å, $c = 7.0471(4)$ Å, $\beta = 102.105(3)^\circ$, $V = 1437.79(14)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0433$, $wR_{\text{ref}}(F^2) = 0.1087$, $T = 200$ K.

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

Source of material

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

*Corresponding author: Richard Betz, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa, e-mail: Richard.Betz@mandela.ac.za. <https://orcid.org/0000-0002-5730-2152>

Lubabalo Ndimba and Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa. <https://orcid.org/0000-0003-4173-2550> (E.C. Hosten)

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 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 [2], with $U(H)$ set to 1.5 $U_{\text{eq}}(C)$.

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 [2], with $U(H)$ set to 1.5 $U_{\text{eq}}(O)$.

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 bonding partners. Upon varying the substitution pattern on the hydrocarbon backbone, the acidity of the respective hydroxyl groups can be finetuned over a wide range and they may, thus, serve as probes for establishing the rules in which pK_a range coordination to various central atoms can be observed. Mandelic acids are especially versatile in this

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}
O12	0.77169 (16)	0.28241 (3)	0.08257 (17)	0.0398 (3)
H12	0.7283	0.3065	0.0734	0.060*
O14	0.48916 (17)	0.14855 (3)	0.00827 (17)	0.0434 (3)
O17	0.48032 (19)	0.34135 (3)	0.00634 (19)	0.0490 (3)
C11	0.3874 (2)	0.27195 (4)	−0.0196 (2)	0.0298 (3)
C12	0.6001 (2)	0.25733 (4)	0.0377 (2)	0.0286 (3)
C13	0.6403 (2)	0.21605 (4)	0.0493 (2)	0.0312 (3)
H13	0.7844	0.2062	0.0890	0.037*
C14	0.4679 (2)	0.18941 (4)	0.0021 (2)	0.0309 (3)
C15	0.2550 (2)	0.20339 (5)	−0.0570 (2)	0.0348 (3)
H15	0.1381	0.1848	−0.0901	0.042*
C16	0.2174 (2)	0.24405 (4)	−0.0666 (2)	0.0333 (3)
H16	0.0727	0.2536	−0.1059	0.040*
C17	0.3431 (2)	0.31454 (5)	−0.0302 (2)	0.0394 (4)
H17	0.1957	0.3226	−0.0686	0.047*
C18	0.7010 (3)	0.13191 (5)	0.0691 (3)	0.0584 (5)
H18A	0.7932	0.1411	−0.0184	0.088*
H18B	0.6920	0.1024	0.0659	0.088*
H18C	0.7634	0.1409	0.2016	0.088*
O22	0.67480 (16)	0.06923 (3)	0.60077 (18)	0.0448 (3)
H22	0.7137	0.0933	0.5904	0.067*
O24	0.98216 (16)	−0.05922 (3)	0.79910 (16)	0.0390 (3)
O27	0.95097 (19)	0.12924 (3)	0.61272 (19)	0.0509 (3)
C21	1.0611 (2)	0.06257 (4)	0.70486 (19)	0.0291 (3)
C22	0.8508 (2)	0.04615 (4)	0.6675 (2)	0.0296 (3)
C23	0.8181 (2)	0.00532 (4)	0.6970 (2)	0.0305 (3)
H23	0.6756	−0.0056	0.6706	0.037*
C24	0.9950 (2)	−0.01916 (4)	0.76523 (19)	0.0290 (3)
C25	1.2062 (2)	−0.00340 (4)	0.8040 (2)	0.0331 (3)
H25	1.3269	−0.0204	0.8513	0.040*
C26	1.2365 (2)	0.03665 (4)	0.7729 (2)	0.0321 (3)
H26	1.3798	0.0472	0.7979	0.039*
C27	1.0962 (2)	0.10476 (5)	0.6722 (2)	0.0374 (3)
H27	1.2416	0.1143	0.6985	0.045*
C28	0.7724 (3)	−0.07775 (5)	0.7640 (2)	0.0413 (4)
H28A	0.6841	−0.0651	0.8467	0.062*
H28B	0.7881	−0.1067	0.7938	0.062*
H28C	0.7014	−0.0742	0.6274	0.062*

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 2-hydroxy-4-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 4-methoxy-benzaldehyde and 2-hydroxy-benzaldehyde have been reported earlier [8].

The title compound is a two-fold-substituted derivative of benzaldehyde featuring a hydroxy-group in *ortho*-position and a methoxy-group in *para*-position as substituents on the aromatic system. The asymmetric unit comprises two complete molecules which differ only in a slightly more tilted-out-of-plane methoxy group. All bond lengths are in good agreement with values reported for comparable structures whose values have been deposited with the Cambridge Structural Database [9]. The respective non-hydrogen atoms of each molecule are almost co-planar with the largest deviation from the least-squares planes as defined by them found at 0.018(2) Å for the first molecule and only – 0.006(1) Å for the second molecule present in the asymmetric unit. This finding can be rationalized by assuming resonance involving all substituents on the aromatic system. The least-squares planes as defined by the carbon atoms of the individual phenyl rings intersect at an angle of 11.46(4)°.

In the crystal, classical hydrogen bonds of the O–H···O type are observed next to C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the participating atoms. Each hydroxyl group supports a bifurcated classical hydrogen bond with one bond being intramolecular towards the oxygen atom of the formyl group as acceptor and the other bond being intermolecular towards the keto-type oxygen atom of the formyl group, thus denoting the latter atom as two-fold acceptor. The result is the formation of almost centrosymmetric dimers that resemble classical carboxylic acids; however, the tilted-out-of-plane geometry of one methoxy groups described earlier precludes the presence of a pertaining center of inversion. Furthermore, one hydrogen atom on each methyl group gives rise to C–H···O contacts. However, only oxygen atoms on the molecule whose methoxy group deviates more from co-planarity within itself act as acceptors, i.e. the oxygen atom of the hydroxyl group as well as the methoxy group. In terms of graph-set analysis [10, 11], the descriptor for the classical hydrogen bonds is *SSDD* on the unary level and *R*₂²(12) on the binary level. The corresponding descriptor for the C–H···O contacts is *DR*₂²(14) at the unary level. In total, the contacts connect the molecules to undulated sheets along [1 0 1]. π -stacking is observed in the crystal structure of the title compound with the shortest distance in between two centers of gravity measured at only 3.5534(8) Å. This distance is observed between the aromatic systems of the molecule whose methoxy group deviates more from co-planarity with the other non-hydrogen atoms present in the same molecule.

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