Crystal structure of 3-iodo-4,6-dimethoxy-benzaldehyde, $C_9H_9IO_3$

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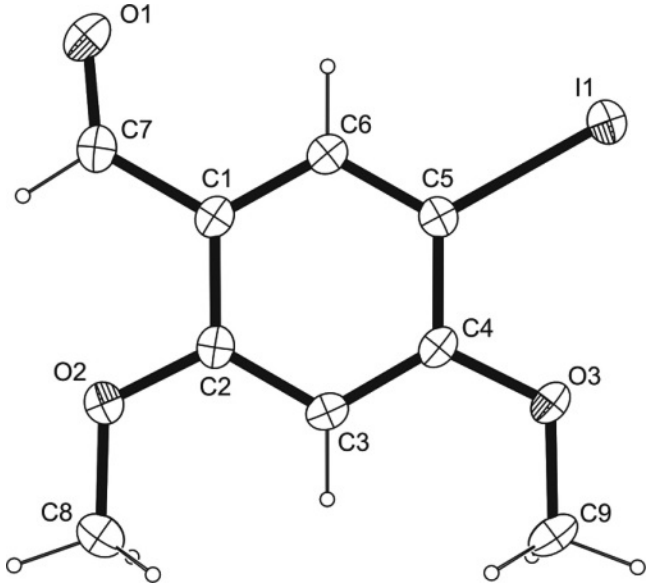

Abstract

$C_9H_9IO_3$, orthorhombic, *Pnma* (no. 62), a = 10.9655(5) Å, b = 6.5768(3) Å, c = 13.3770(6) Å, V = 964.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.0130, $wR_{ref}(F^2)$ = 0.0350, T = 200 K.

Table 1. Data collection and handling.

Crystal:	colourless platelets, size 0.228×0.230×0.483 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	32.91 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8906, 1299
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1248
$N(param)_{refined}$:	79
Programs:	SHELX, WinGX, MERCURY, PLATON [6–9]

Source of material

The compound was prepared upon iodination of 2,4-dimethoxybenzaldehyde in methanol [1]. Crystals suitable for the diffraction study were obtained upon free evaporation of the solvent at ambient conditions.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic and vinylic carbon atoms, C–H 0.98 Å for methyl groups) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C) (aromatic and vinylic carbon atoms) or 1.5U_{eq}(C) (methyl groups).

Discussion

Benzaldehyde and its core-substituted derivatives are versatile starting materials in organic synthesis. Especially the nucleophilicity of the formyl group as well as its potential use for Wittig- and McMurry-type reactions next to further functionalizations of the aromatic core foster this role. At the beginning of a multi-step synthesis of a complex target molecule, a threefold core-substituted derivative of benzaldehyde was synthesized and its molecular and crystal structure was secured by means of a single-crystal X-ray diffraction study. The crystal structures of 2,4-bis(prop-2-yn-1-yloxy)benzaldehyde [2], the monohydrate of 2,4,5-trimethoxybenzaldehyde [3] and 2,4,6-trimethoxybenzaldehyde [4] have been reported earlier. Due to resonance the title compound is planar. Intracyclic C–C–C angles cover a range of 118.71(16)–121.36(16)° with the smallest angle found on carbon atom bearing the formyl group and the largest angle present on the carbon atom in between the carbon atoms bearing the formyl group and the one bonded to the halogen atom. The C–I bond length was measured at 2.0922(17) Å which is in good agreement with the most common values reported for other iodinated phenyl derivatives whose metrical parameters have been deposited with the Cambridge Structural Database [5]. In the crystal structure, dispersive I···O contacts are obeserved. These are supported by the oxygen atom of the formyl group as acceptor. In total, the molecules are connected to undulated chains along the crystallographic a axis. π-Stacking is a prominent feature in the crystal structure of the title compound as the shortest intercentroid distance between two centers of gravity was measured at 3.6119(4) Å only.

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	4*c*		0.2809	¼	0.3903	0.026
H(6)	4*c*		0.5850	¼	0.6361	0.024
H(7)	4*c*		0.7050	¼	0.3868	0.030
H(8A)	4*c*		0.4525	¼	0.1735	0.054
H(8B)	8*d*	0.5	0.3615	0.3717	0.2454	0.054
H(8C)	8*d*	0.5	0.3615	0.1283	0.2454	0.054
H(9A)	4*c*		0.0199	¼	0.5335	0.051
H(9B)	8*d*	0.5	0.1068	0.1283	0.4583	0.051
H(9C)	8*d*	0.5	0.1068	0.3717	0.4583	0.051

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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}
I(1)	4*c*	0.35261(1)	¼	0.765415(9)	0.02318(8)	0.03488(8)	0.01913(8)	0	0.00245(4)	0
O(1)	4*c*	0.7720(1)	¼	0.5138(1)	0.0174(6)	0.0416(8)	0.0359(8)	0	0.0002(6)	0
O(2)	4*c*	0.5031(1)	¼	0.3161(1)	0.0220(6)	0.0419(8)	0.0188(6)	0	0.0015(5)	0
O(3)	4*c*	0.1942(1)	¼	0.5738(1)	0.0139(6)	0.0458(8)	0.0256(7)	0	0.0013(5)	0
C(1)	4*c*	0.5574(2)	¼	0.4855(1)	0.0173(7)	0.0194(7)	0.0226(8)	0	0.0012(6)	0
C(2)	4*c*	0.4654(2)	¼	0.4123(1)	0.0192(8)	0.0212(7)	0.0207(8)	0	0.0027(6)	0
C(3)	4*c*	0.3427(2)	¼	0.4400(1)	0.0165(8)	0.0260(9)	0.0224(9)	0	–0.0027(6)	0
C(4)	4*c*	0.3113(2)	¼	0.5405(1)	0.0146(7)	0.0234(8)	0.0243(9)	0	0.0010(6)	0
C(5)	4*c*	0.4024(2)	¼	0.6144(1)	0.0206(8)	0.0227(8)	0.0184(7)	0	0.0007(6)	0
C(6)	4*c*	0.5235(2)	¼	0.5861(1)	0.0176(7)	0.0214(7)	0.0220(8)	0	–0.0004(6)	0
C(7)	4*c*	0.6869(2)	¼	0.4563(1)	0.0220(8)	0.0292(9)	0.0240(9)	0	0.0042(7)	0
C(8)	4*c*	0.4125(2)	¼	0.2391(1)	0.030(1)	0.058(2)	0.0196(9)	0	–0.0021(7)	0
C(9)	4*c*	0.0995(2)	¼	0.5002(2)	0.0139(8)	0.052(1)	0.036(1)	0	–0.0036(8)	0

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References

1. Becker, H. G. O.; Beckert, R.; Domschke, G.; Fanghänel, E.; Habicher, W. D.; Metz, P.; Pavel, D.; Schwetlick, K.: Organikum. (2001) 21st ed. Weinheim Wiley-VCH.
2. Esakkiammal, M.; Selvarani, V.; Neelakantan, M. A.; Silambarasan, V.; Velumurugan, D.: 2,4-Bis[(prop-2-ynyl)oxy]benzaldehyde. Acta Crystallogr. **E68** (2012) o2465.
3. Asiri, A. M.; Khan, S. A.; Tahir, M. N.: 2,4,5-Trimethoxybenzaldehyde monohydrate. Acta Crystallogr. **E66** (2010) o3270.
4. Pan, Z.; Xu, M.; Cheung, E. Y.; Platts, J. A.; Harris, K. D. M.; Constable, E. C.; Housecroft, C. E.: Solid-state structural properties of 2,4,6-trimethoxybenzene derivatives, determined directly from powerd X-ray diffraction data in conjunction with other techniques. J. Solid State Chem. **179** (2006) 3214–3223.
5. Allen, F. H.: The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. **B58** (2002) 380–388.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
7. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
8. 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.
9. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.