IUCrData
ISSN 2414-3146

Methyl 2-hydroxy-4-iodobenzoate

Marten J. Kimble,[a]‡ Shea D. Myers[a]‡ and Jason B Benedict[b]*

[a]730 Natural Sciences Complex, Buffalo, NY 14260-3000, USA, and [b]771 Natural Sciences Complex, Buffalo, NY 14260, USA. *Correspondence e-mail: jbb6@buffalo.edu

Received 24 April 2024
Accepted 30 April 2024

Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

‡ Both authors contributed equally to this work.

Keywords: crystal structure; organic; co-former.

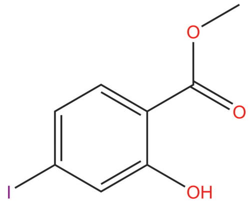
CCDC reference: 2352344

Structural data: full structural data are available from iucrdata.iucr.org

The structure of the title compound, $C_8H_7IO_3$, at 90 K has monoclinic ($P2_1/c$) symmetry. The extended structure is layered and displays intermolecular and intramolecular hydrogen bonding arising from the same OH group.

3D view

Chemical scheme



Structure description

2-Hydroxybenzoic acid methyl ester ($C_8H_8O_3$), commonly known as methyl salicylate, and its derivatives have been shown to display biological effects such as anti-inflammatory, anti-fungal, and process signaling (Yoon *et al.*, 2019; Li *et al.*, 2016; Park *et al.*, 2007). It can also be found in various foods (Duthie & Wood, 2011). The title compound, 2-hydroxy-4-iodobenzoic acid methyl ester (methyl 4-iodosalicylate, $C_8H_7IO_3$) allows for an effective way of incorporating the said methyl salicylates within larger organic molecules, using such methodologies as McClure protocols (Franchi *et al.*, 2010; McClure *et al.*, 2001), Stille (Yoon *et al.*, 2019; Stille, 1986) and Suzuki–Miyaura reactions (Fracaroli *et al.*, 2014; Miyaura *et al.*, 1979), which take advantage of the iodine atom at the 4-position of the aromatic ring for the formation of carbon–carbon bonds. The iodine atom is also capable of forming supramolecular synthons, which may be useful for crystal engineering (Desiraju, 1995; Cherukuvada *et al.*, 2016; Mitchell *et al.*, 2023).

At 90 K the title compound displays monoclinic ($P2_1/c$) symmetry with one molecule in the asymmetric unit (Fig. 1). Intermolecular hydrogen bonding interactions occur between the hydroxy groups of one molecule and the carbonyl oxygen atom of the methyl ester of an adjacent molecule to form a centrosymmetric dimeric pair (Table 1, Fig. 2) with H$\cdots$O = 2.53 (4) Å. An O3—H3$\cdots$O2 intramolecular hydrogen bond also exists with an H$\cdots$O distance of 2.05 (4) Å. The C5$\cdots$C8 [3.326 (3) Å] and O3$\cdots$H1*C* (2.51 Å) interactions provide the only short contacts between the stacks of offset ($\bar{1}02$) parallel sheets, which make up the crystal (Fig. 3). These sheets, in turn, contain the inversion-generated hydrogen-bonded dimers (Fig. 2). The non-hydrogen atoms of the molecule are essentially coplanar with no displacement from the mean molecular plane greater than 0.132 Å (Fig. 4).

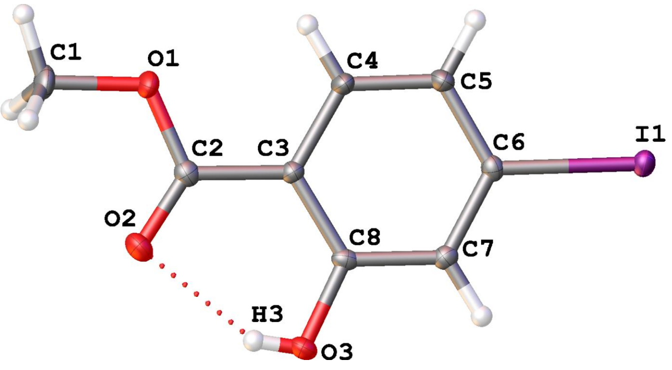


Figure 1
The molecular structure of the title compound showing 50% displacement ellipsoids. The intramolecular hydrogen bond is indicated by a red dashed line.

Crystallization

Methyl 4-iodosalicylate (32.8 mg, 0.118 mmol) was added to a 20 ml scintillation vial to which benzene (~2 ml) was added, and the vial shaken until the compound dissolved. The resulting solution was then left undisturbed, lightly capped, and in the dark for one week to allow for crystal formation while the solvent slowly evaporated.

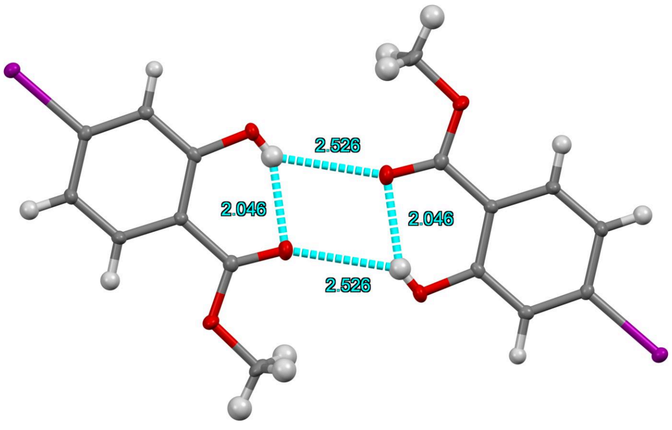


Figure 2
The dimer of title compound showing intra- and intermolecular hydrogen bonds depicted with blue dashed lines with corresponding O···H distances for each O—H···O interaction.

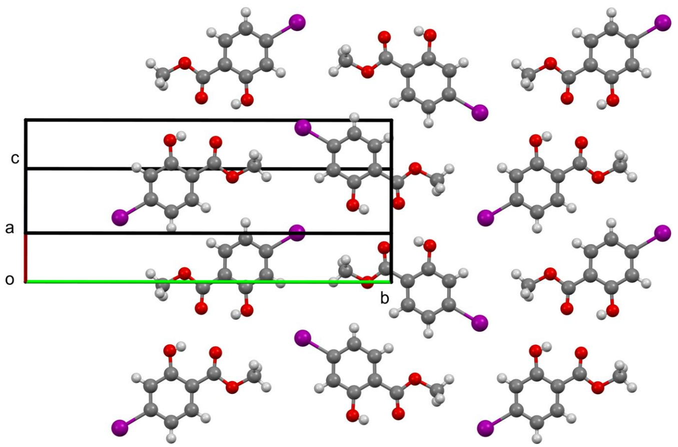


Figure 3
Packing diagram viewed perpendicular to ($\overline{1}02$).

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.70 (4)	2.05 (4)	2.670 (3)	149 (4)
O3—H3···O2^{i}	0.70 (4)	2.53 (4)	3.087 (2)	139 (4)

Symmetry code: (i) $-x+2, -y+1, -z+2$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_7IO_3$
M_r	278.04
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	90
a, *b*, *c* (Å)	4.3286 (8), 21.334 (4), 9.2941 (16)
β (°)	93.744 (4)
V (Å^3)	856.4 (3)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	3.70
Crystal size (mm)	0.80 × 0.20 × 0.02
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.564, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23320, 3651, 3315
R_{int}	0.049
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.809
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.057, 1.11
No. of reflections	3651
No. of parameters	114
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.27, −1.92

Computer programs: *APEX2* and *SAINT* V8.40B (Bruker, 2016), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2.

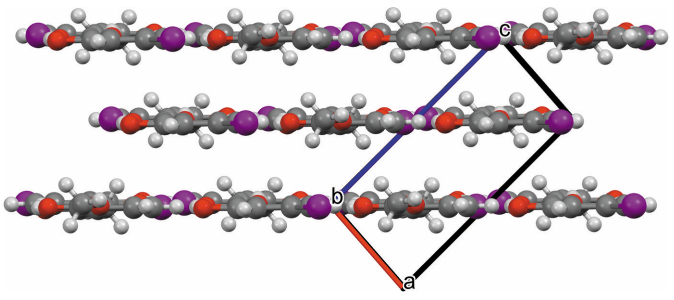


Figure 4
Packing diagram viewed along *b*-axis and parallel to ($\overline{1}02$).

Funding information

Funding for this research was provided by: National Science Foundation (award No. DMR-2003932).

References

Bruker (2016). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cherukuvada, S., Kaur, R. & Guru Row, T. N. (2016). *CrystEngComm*, **18**, 8528–8555.

Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Duthie, G. G. & Wood, A. D. (2011). *Food Funct.* **2**, 515–520.

Fracaroli, A. M., Furukawa, H., Suzuki, M., Dodd, M., Okajima, S., Gándara, F., Reimer, J. A. & Yaghi, O. M. (2014). *J. Am. Chem. Soc.* **136**, 8863–8866.

Franchi, L., Rinaldi, M., Vignaroli, G., Innitzer, A., Radi, M. & Botta, M. (2010). *Synthesis*, pp. 3927–3933.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Li, J., Yin, Y., Wang, L., Liang, P., Li, M., Liu, X., Wu, L. & Yang, H. (2016). *Molecules*, **21**, 1544.

McClure, M. S., Glover, B., McSorley, E., Millar, A., Osterhout, M. H. & Roschangar, F. (2001). *Org. Lett.* **3**, 1677–1680.

Mitchell, T. B., Zhang, X., Jerozal, R. T., Chen, Y.-S., Wang, S. & Benedict, J. B. (2023). *IUCrJ*, **10**, 694–699.

Miyaura, N., Yamada, K. & Suzuki, A. (1979). *Tetrahedron Lett.* **20**, 3437–3440.

Park, S.-W., Kaimoyo, E., Kumar, D., Mosher, S. & Klessig, D. F. (2007). *Science*, **318**, 113–116.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Stille, J. K. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 508–524.

Yoon, M., Kim, M., Kim, M. H., Kang, J.-G., Sohn, Y. & Kim, I. T. (2019). *Inorg. Chim. Acta*, **495**, 119008.

IUCrData (2024). **9**, x240394 Kimble *et al.* • $C_8H_7IO_3$ **3 of 3**

full crystallographic data

IUCrData (2024). **9**, x240394 [https://doi.org/10.1107/S2414314624003948]

Methyl 2-hydroxy-4-iodobenzoate

Marten J. Kimble, Shea D. Myers and Jason B Benedict

Methyl 2-hydroxy-4-iodobenzoate

Crystal data

$C_8H_7IO_3$
$M_r = 278.04$
Monoclinic, $P2_1/c$
$a = 4.3286$ (8) Å
$b = 21.334$ (4) Å
$c = 9.2941$ (16) Å
$\beta = 93.744$ (4)°
$V = 856.4$ (3) Å^3
$Z = 4$
$F(000) = 528$
$D_x = 2.156$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6811 reflections
$\theta = 2.9$–34.1°
$\mu = 3.70$ mm^{-1}
$T = 90$ K
Plate, pale yellow
0.80 × 0.20 × 0.02 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{\min} = 0.564$, $T_{\max} = 0.747$
23320 measured reflections
3651 independent reflections
3315 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.049$
$\theta_{\max} = 35.1°$, $\theta_{\min} = 2.4°$
$h = -6\rightarrow6$
$k = -33\rightarrow34$
$l = -14\rightarrow15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.057$
$S = 1.11$
3651 reflections
114 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 1.660P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.27$ e Å^{-3}
$\Delta\rho_{\min} = -1.92$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The O-bound H atom was located in a difference map and its position was freely refined. The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
I1	0.05964 (3)	0.25795 (2)	0.54095 (2)	0.01430 (4)
O3	0.7859 (4)	0.39459 (9)	0.91310 (18)	0.0170 (3)
O1	0.4603 (4)	0.56516 (8)	0.72915 (18)	0.0180 (3)
O2	0.7790 (4)	0.51960 (9)	0.89865 (19)	0.0212 (4)
C6	0.2313 (5)	0.34266 (10)	0.6295 (2)	0.0127 (4)
C7	0.4516 (5)	0.34172 (10)	0.7453 (2)	0.0128 (4)
H7	0.522507	0.302965	0.785568	0.015*
C8	0.5675 (5)	0.39821 (10)	0.8018 (2)	0.0121 (3)
C1	0.5827 (6)	0.62513 (11)	0.7783 (3)	0.0203 (5)
H1A	0.499780	0.658300	0.713823	0.030*
H1B	0.809060	0.624553	0.777897	0.030*
H1C	0.522278	0.633151	0.876394	0.030*
C5	0.1189 (5)	0.39860 (11)	0.5688 (2)	0.0161 (4)
H5	−0.033554	0.398522	0.490504	0.019*
C3	0.4577 (5)	0.45534 (10)	0.7425 (2)	0.0123 (4)
C2	0.5823 (5)	0.51534 (11)	0.7990 (2)	0.0144 (4)
C4	0.2359 (5)	0.45406 (10)	0.6259 (2)	0.0156 (4)
H4	0.163744	0.492573	0.584857	0.019*
H3	0.836 (8)	0.4252 (17)	0.929 (4)	0.025 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01408 (6)	0.01099 (7)	0.01764 (7)	−0.00031 (5)	−0.00056 (4)	−0.00134 (5)
O3	0.0173 (8)	0.0173 (8)	0.0153 (7)	0.0008 (6)	−0.0061 (6)	−0.0004 (6)
O1	0.0241 (8)	0.0104 (7)	0.0188 (8)	−0.0031 (6)	−0.0048 (6)	0.0007 (6)
O2	0.0210 (8)	0.0204 (9)	0.0211 (8)	−0.0015 (6)	−0.0083 (6)	−0.0031 (6)
C6	0.0114 (8)	0.0128 (9)	0.0138 (9)	−0.0012 (7)	0.0009 (7)	−0.0017 (7)
C7	0.0128 (9)	0.0120 (9)	0.0136 (9)	0.0008 (7)	0.0011 (7)	0.0006 (7)
C8	0.0103 (8)	0.0155 (9)	0.0105 (8)	0.0020 (7)	0.0003 (6)	0.0010 (7)
C1	0.0282 (12)	0.0114 (10)	0.0211 (11)	−0.0062 (8)	0.0005 (9)	−0.0021 (8)
C5	0.0178 (10)	0.0137 (10)	0.0158 (9)	−0.0004 (7)	−0.0061 (7)	0.0005 (7)
C3	0.0132 (9)	0.0108 (9)	0.0128 (9)	0.0003 (7)	−0.0010 (7)	0.0004 (7)
C2	0.0140 (9)	0.0152 (10)	0.0138 (9)	−0.0006 (7)	0.0007 (7)	−0.0011 (7)
C4	0.0179 (10)	0.0104 (9)	0.0177 (10)	0.0002 (7)	−0.0053 (8)	0.0012 (7)

Geometric parameters (Å, º)

I1—C6	2.101 (2)	C8—C3	1.407 (3)
O3—C8	1.357 (3)	C1—H1A	0.9800
O3—H3	0.70 (4)	C1—H1B	0.9800
O1—C1	1.447 (3)	C1—H1C	0.9800
O1—C2	1.336 (3)	C5—H5	0.9500
O2—C2	1.220 (3)	C5—C4	1.379 (3)
C6—C7	1.391 (3)	C3—C2	1.472 (3)

C6—C5	1.394 (3)	C3—C4	1.400 (3)
C7—H7	0.9500	C4—H4	0.9500
C7—C8	1.395 (3)		

C8—O3—H3	107 (3)	H1A—C1—H1C	109.5
C2—O1—C1	115.15 (18)	H1B—C1—H1C	109.5
C7—C6—I1	119.85 (16)	C6—C5—H5	121.0
C7—C6—C5	121.9 (2)	C4—C5—C6	118.0 (2)
C5—C6—I1	118.20 (15)	C4—C5—H5	121.0
C6—C7—H7	120.3	C8—C3—C2	120.44 (19)
C6—C7—C8	119.4 (2)	C4—C3—C8	118.89 (19)
C8—C7—H7	120.3	C4—C3—C2	120.63 (19)
O3—C8—C7	116.94 (19)	O1—C2—C3	113.23 (18)
O3—C8—C3	123.3 (2)	O2—C2—O1	122.9 (2)
C7—C8—C3	119.80 (19)	O2—C2—C3	123.8 (2)
O1—C1—H1A	109.5	C5—C4—C3	122.0 (2)
O1—C1—H1B	109.5	C5—C4—H4	119.0
O1—C1—H1C	109.5	C3—C4—H4	119.0
H1A—C1—H1B	109.5		

I1—C6—C7—C8	178.99 (15)	C8—C3—C2—O1	178.4 (2)
I1—C6—C5—C4	−179.01 (17)	C8—C3—C2—O2	−1.0 (3)
O3—C8—C3—C2	1.0 (3)	C8—C3—C4—C5	0.9 (3)
O3—C8—C3—C4	178.8 (2)	C1—O1—C2—O2	1.2 (3)
C6—C7—C8—O3	−178.90 (19)	C1—O1—C2—C3	−178.26 (19)
C6—C7—C8—C3	0.9 (3)	C5—C6—C7—C8	−0.8 (3)
C6—C5—C4—C3	−0.9 (4)	C2—C3—C4—C5	178.8 (2)
C7—C6—C5—C4	0.8 (3)	C4—C3—C2—O1	0.6 (3)
C7—C8—C3—C2	−178.8 (2)	C4—C3—C2—O2	−178.8 (2)
C7—C8—C3—C4	−0.9 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.70 (4)	2.05 (4)	2.670 (3)	149 (4)
O3—H3···O2^{i}	0.70 (4)	2.53 (4)	3.087 (2)	139 (4)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+2.