

Crystal structure of a second monoclinic polymorph of 3-methoxybenzoic acid with $Z' = 1$ Tze Shyang Chia,^{a,†} Huey Chong Kwong,^b Qin Ai Wong,^a Ching Kheng Quah^{a,§} and Md. Azharul Arafath^{c,*}^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, ^bSchool of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^cDepartment of Chemistry, Shahjalal University of Science and Technology, Sylhet, 3114, Bangladesh. *Correspondence e-mail: arafath_sustche90@yahoo.com

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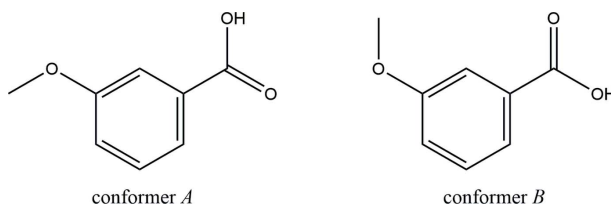
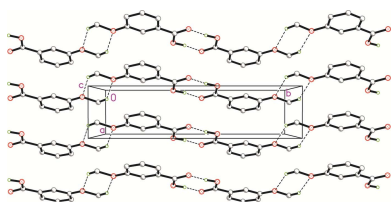
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Keywords: crystal structure; polymorph; hydrogen-bond; 3-methoxybenzoic acid.**CCDC reference:** 1448794**Supporting information:** this article has supporting information at journals.iucr.org/e

A new polymorphic form of the title compound, $C_8H_8O_3$, is described in the centrosymmetric monoclinic space group $P2_1/c$ with $Z' = 1$ as compared to the first polymorph, which crystallizes with two conformers ($Z' = 2$) in the asymmetric unit in the same space group. In the crystal of the second polymorph, inversion dimers linked by $O-H\cdots O$ hydrogen bonds occur and these are linked into zigzag chains, propagating along the b -axis direction by $C-H\cdots O$ links. The crystal structure also features a weak $\pi-\pi$ interaction, with a centroid-to-centroid distance of 3.8018 (6) Å. The second polymorph of the title compound is less stable than the reported first polymorph, as indicated by its smaller calculated lattice energy.

1. Chemical context

Methoxybenzoic acid, also called anisic acid, consists of three isomers with molecular formula $C_8H_8O_3$; the crystal structures of 2- and 4-methoxybenzoic acids with $Z' = 1$ have been reported (Parvez, 1987; Etter *et al.*, 1988; Bryan, 1967; Colapietro & Domenicano, 1978; Fausto *et al.*, 1997; Hathwar *et al.*, 2011) and polymorphism has not been observed for these two isomers in the Cambridge Structural Database (CSD) (Version 5.39, last update August 2018; Groom *et al.*, 2016) to date. In this article, we report a second polymorphic form ($I\beta$) of 3-methoxybenzoic acid with $Z' = 1$ and compare its properties with those of the previously reported first polymorphic form ($I\alpha$). Polymorph $I\alpha$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.8034$ (17) Å, $b = 5.0275$ (5) Å, $c = 21.446$ (3) Å and $\beta = 99.320$ (13)° (Raffo *et al.*, 2014; refile EFINEO). The asymmetric unit of $I\alpha$ consists of two molecules with different conformations ($Z' = 2$), which are connected into a homodimer through strong $O-H\cdots O$ hydrogen bonds. As described below, these two conformers (A and B) differ in the orientation of the methoxy group and its relative position from the $-OH$ group. DFT calculations suggest that the A conformer of $I\alpha$ is more energetically stable than the B conformer (Pereira Silva *et al.*, 2015).



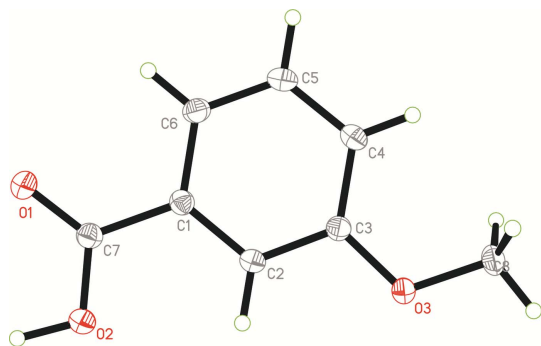


Figure 1
The molecular structure of *Iβ* with 50% probability displacement ellipsoids.

2. Structural commentary

The asymmetric unit of *Iβ* (Fig. 1) consists of a unique 3-methoxybenzoic acid molecule ($Z' = 1$). The molecule is almost planar with a maximum deviation of 0.107 (1) Å at atom O1. The molecules of *Iβ* adopt a similar conformation (overlay r.m.s.d. = 0.052 Å) as compared to the conformer *A* of *Iα* (Raffo *et al.*, 2014). The carboxyl group (O1/O2/C7/H1O2) of *Iβ* is close to coplanar with the attached phenyl ring (C1–C6) as indicated by the dihedral angle of 5.6 (7)°. The C8–O3–C3–C2 torsion angle of *Iβ* is -176.63 (7)° as compared to -176.75 (11) and -1.4 (2)° for conformers *A* and *B*, respectively, of *Iα*.

3. Supramolecular features

In the crystal of *Iβ*, two inversion-related molecules are joined into a homodimer with an $R_2^2(8)$ graph-set motif via strong pairwise O–H···O hydrogen bonds (Fig. 2, Table 1). The homodimers are linked by weak C–H···O hydrogen bonds between two methoxy groups into zigzag chains with $R_2^2(6)$ graph-set motifs, which propagate along the *b*-axis direction. The [010] chains are stacked along the *a* axis into corrugated sheets parallel to the *ab* plane via weak π – π interactions with a

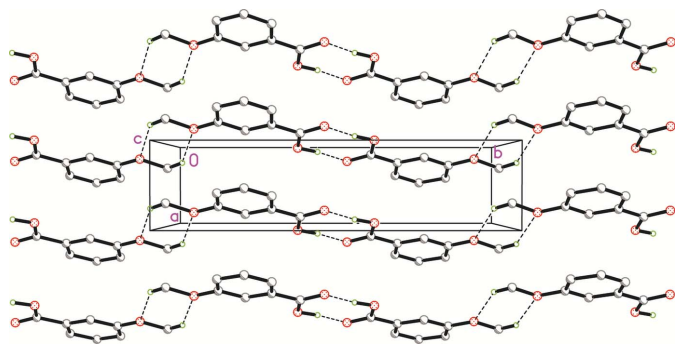


Figure 2
Partial crystal packing of *Iβ*. Dashed lines represent the hydrogen-bonds. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O2–H1O2···O1 ⁱ	1.008 (19)	1.626 (19)	2.6295 (9)	173.3 (17)
C8–H8A···O3 ⁱⁱ	0.98	2.56	3.4016 (11)	144

Symmetry codes: (i) $-x, -y + 2, -z + 2$; (ii) $-x, -y + 1, -z + 2$.

centroid-to-centroid distance of 3.8018 (6) Å (symmetry codes: $x - 1, y, z$ and $x + 1, y, z$) and slippage of 1.676 Å.

4. Hirshfeld surface analysis

The Hirshfeld surfaces mapped with normalized contact distance d_{norm} and the two-dimensional fingerprint plots for *Iβ* were generated using *CrystalExplorer17.5* (Turner *et al.*, 2017). The large and small red spots on the Hirshfeld surface mapped with d_{norm} (Fig. 3) correspond to the O2–H1O2···O1 and C8–H8A···O3 hydrogen bonds, respectively. The H···O distances are 1.09 and 0.16 Å shorter than the sum of van der Waals radii of H and O atoms (2.72 Å). The H···H contact is the most populated contact and contributes 42.3% of the total intermolecular contacts, followed by H···O/O···H (32.9%), H···C/C···H (11.4%) and C···C (8.1%) contacts (Fig. 4). The tips of pseudo-mirrored sharp spikes at $d_e + d_i \approx 1.6$ Å represent the shortest H···O/O···H contacts, corresponding to the O2–H1O2···O1 hydrogen-bond. The absence of significant C–H··· π interaction in the crystal structure of *Iβ* is indicated by the absence of characteristic ‘wings’ in the fingerprint plot of H···C/C···H contacts. The C···C contacts include the weak π – π interaction, which appears as a unique ‘triangle’ focused at $d_e \approx d_i \approx 1.8$ Å. The π – π interaction is illustrated as a unique pattern of red and blue ‘triangles’ on the shape-index surface and a flat region on the curvedness surface of the phenyl ring (see supporting Figures S1 and S2).

5. Lattice energy calculation

The lattice energies of polymorphs *Iα* and *Iβ* were calculated using *PIXEL* software (Gavezzotti, 2003) at default settings. The calculated lattice energy of *Iα* (107.5 kJ mol⁻¹) is larger than that of *Iβ* (98.5 kJ mol⁻¹) and this comparison is in agreement with the report of Pereira Silva *et al.* (2015), in which *Iα* is more stable than *Iβ* under ambient conditions.

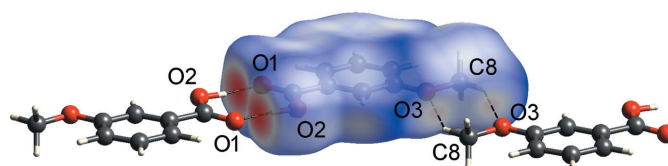


Figure 3
The Hirshfeld surface mapped over d_{norm} of the central molecule of *Iβ* hydrogen bonded to two neighbouring molecules.

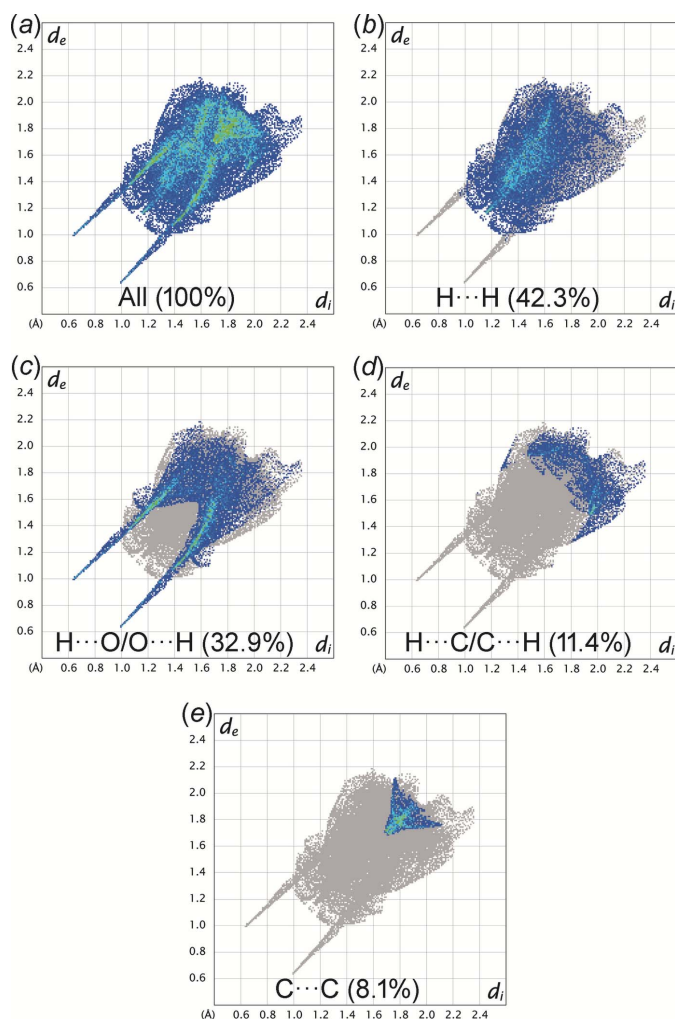


Figure 4
The two-dimensional fingerprint plots of $I\beta$ for different intermolecular contacts giving their percentages of contribution to the Hirshfeld surface. d_i and d_e are the distances from the Hirshfeld surface to the nearest atom interior and exterior, respectively, to the surface.

6. Database survey

For the structure of 2-methoxybenzoic acid (refcodes FUFBOX and FUFBOX01, respectively), see: Parvez (1987) and Etter *et al.* (1988). For the structure of 4-methoxybenzoic acid (refcodes ANISIC, ANISIC01, ANISIC02 and ANISIC04, respectively), see: Bryan (1967), Colapietro & Domenicano (1978), Fausto *et al.* (1997) and Hathwar *et al.* (2011). For the previous structure of 3-methoxybenzoic acid (refcodes EFINEO and EFINEO01, respectively), see: Raffo *et al.* (2014) and Pereira Silva *et al.* (2015).

7. Synthesis and crystallization

Single crystals of $I\beta$ were obtained from an unsuccessful attempt of co-crystallization between 3-methoxybenzoic acid and hexamethylenetetramine. Colourless plate-like crystals were obtained from slow evaporation of a methanolic mixture

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_8O_3$
M_r	152.14
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	3.8018 (4), 15.6027 (16), 11.9755 (12)
β (°)	90.889 (2)
V (Å ³)	710.28 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.56 × 0.22 × 0.12
Data collection	
Diffractometer	Bruker SMART APEXII DUO CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2009)
T_{\min}, T_{\max}	0.881, 0.987
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9395, 2550, 2049
R_{int}	0.023
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.758
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.113, 1.04
No. of reflections	2550
No. of parameters	105
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.40, -0.27

Computer programs: APEX2 and SAINT (Bruker, 2009), SHELXS2013 and SHELXTL (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), PLATON (Spek, 2009) and publCIF (Westrip, 2010).

of 3-methoxybenzoic acid and hexamethylenetetramine in equimolar ratio at room temperature.

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The O-bound H atom was located from the difference-Fourier map and refined freely [$O2-H1O2 = 1.01$ (2) Å]. The remaining H atoms were positioned geometrically [$C-H = 0.95$ and 0.98 Å] and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$. A rotating group model (AFIX 137) was applied to the methyl group.

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Crystal structure of a second monoclinic polymorph of 3-methoxybenzoic acid with $Z' = 1$

Tze Shyang Chia, Huey Chong Kwong, Qin Ai Wong, Ching Kheng Quah and Md. Azharul Arafath

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE* (Bruker, 2009); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

3-Methoxybenzoic acid

Crystal data

$C_8H_8O_3$

$M_r = 152.14$

Monoclinic, $P2_1/c$

$a = 3.8018$ (4) Å

$b = 15.6027$ (16) Å

$c = 11.9755$ (12) Å

$\beta = 90.889$ (2)°

$V = 710.28$ (13) Å³

$Z = 4$

$F(000) = 320$

$D_x = 1.423$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3889 reflections

$\theta = 2.6$ – 32.4 °

$\mu = 0.11$ mm⁻¹

$T = 100$ K

Plate, colourless

$0.56 \times 0.22 \times 0.12$ mm

Data collection

Bruker SMART APEXII DUO CCD diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2009)

$T_{\min} = 0.881$, $T_{\max} = 0.987$

9395 measured reflections

2550 independent reflections

2049 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 32.6$ °, $\theta_{\min} = 2.1$ °

$h = -5 \rightarrow 5$

$k = -21 \rightarrow 23$

$l = -18 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.113$

$S = 1.04$

2550 reflections

105 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 0.1229P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$$

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.20200 (18)	0.96657 (4)	0.88546 (5)	0.02247 (16)
O2	-0.04494 (18)	0.88699 (4)	1.01876 (5)	0.02142 (16)
H1O2	-0.091 (5)	0.9451 (12)	1.0523 (16)	0.068 (5)*
O3	0.17686 (17)	0.58676 (4)	0.92170 (5)	0.01959 (15)
C1	0.2204 (2)	0.81461 (6)	0.86862 (7)	0.01512 (16)
C2	0.1573 (2)	0.73618 (6)	0.91952 (7)	0.01515 (16)
H2A	0.0504	0.7341	0.9906	0.018*
C3	0.2516 (2)	0.66069 (5)	0.86565 (7)	0.01517 (16)
C4	0.4082 (2)	0.66360 (6)	0.76109 (7)	0.01698 (17)
H4A	0.4738	0.6121	0.7245	0.020*
C5	0.4674 (2)	0.74261 (6)	0.71099 (7)	0.01847 (18)
H5A	0.5727	0.7447	0.6396	0.022*
C6	0.3755 (2)	0.81821 (6)	0.76329 (7)	0.01759 (17)
H6A	0.4169	0.8718	0.7283	0.021*
C7	0.1244 (2)	0.89573 (6)	0.92491 (7)	0.01636 (17)
C8	0.2877 (2)	0.50822 (6)	0.87173 (7)	0.01985 (18)
H8A	0.2229	0.4601	0.9198	0.030*
H8B	0.5434	0.5091	0.8628	0.030*
H8C	0.1726	0.5017	0.7984	0.030*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0301 (3)	0.0151 (3)	0.0223 (3)	-0.0001 (2)	0.0063 (2)	0.0011 (2)
O2	0.0285 (3)	0.0176 (3)	0.0184 (3)	0.0009 (2)	0.0077 (2)	-0.0004 (2)
O3	0.0254 (3)	0.0134 (3)	0.0202 (3)	0.0012 (2)	0.0073 (2)	0.0000 (2)
C1	0.0147 (3)	0.0151 (4)	0.0156 (3)	0.0003 (3)	0.0006 (2)	-0.0005 (3)
C2	0.0151 (3)	0.0165 (4)	0.0139 (3)	0.0002 (3)	0.0018 (2)	-0.0004 (3)
C3	0.0146 (3)	0.0150 (4)	0.0159 (3)	0.0000 (3)	0.0013 (2)	0.0001 (3)
C4	0.0161 (3)	0.0190 (4)	0.0160 (3)	0.0008 (3)	0.0025 (3)	-0.0026 (3)
C5	0.0175 (4)	0.0231 (4)	0.0149 (4)	-0.0005 (3)	0.0035 (3)	-0.0001 (3)
C6	0.0182 (4)	0.0183 (4)	0.0164 (4)	-0.0009 (3)	0.0023 (3)	0.0021 (3)
C7	0.0164 (3)	0.0170 (4)	0.0157 (3)	0.0006 (3)	0.0008 (3)	0.0001 (3)
C8	0.0217 (4)	0.0141 (4)	0.0238 (4)	0.0017 (3)	0.0033 (3)	-0.0029 (3)

Geometric parameters (Å, °)

O1—C7	1.2394 (10)	C3—C4	1.3956 (12)
O2—C7	1.3110 (10)	C4—C5	1.3909 (12)
O2—H1O2	1.01 (2)	C4—H4A	0.9500
O3—C3	1.3666 (10)	C5—C6	1.3829 (12)
O3—C8	1.4301 (10)	C5—H5A	0.9500
C1—C2	1.3896 (12)	C6—H6A	0.9500
C1—C6	1.4019 (11)	C8—H8A	0.9800
C1—C7	1.4823 (12)	C8—H8B	0.9800
C2—C3	1.3925 (12)	C8—H8C	0.9800
C2—H2A	0.9500		
C7—O2—H1O2	109.8 (11)	C6—C5—H5A	119.4
C3—O3—C8	116.94 (7)	C4—C5—H5A	119.4
C2—C1—C6	120.52 (8)	C5—C6—C1	119.09 (8)
C2—C1—C7	120.47 (7)	C5—C6—H6A	120.5
C6—C1—C7	119.01 (8)	C1—C6—H6A	120.5
C1—C2—C3	119.62 (7)	O1—C7—O2	122.85 (8)
C1—C2—H2A	120.2	O1—C7—C1	121.76 (7)
C3—C2—H2A	120.2	O2—C7—C1	115.39 (7)
O3—C3—C2	115.43 (7)	O3—C8—H8A	109.5
O3—C3—C4	124.26 (7)	O3—C8—H8B	109.5
C2—C3—C4	120.31 (8)	H8A—C8—H8B	109.5
C5—C4—C3	119.34 (8)	O3—C8—H8C	109.5
C5—C4—H4A	120.3	H8A—C8—H8C	109.5
C3—C4—H4A	120.3	H8B—C8—H8C	109.5
C6—C5—C4	121.13 (8)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H1O2 \cdots O1 ⁱ	1.008 (19)	1.626 (19)	2.6295 (9)	173.3 (17)
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Symmetry codes: (i) $-x, -y+2, -z+2$; (ii) $-x, -y+1, -z+2$.