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Orthorhombic polymorph of 4-[(1*H*-benzimidazol-1-yl)methyl]benzoic acid

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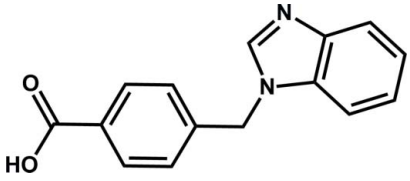
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.089; data-to-parameter ratio = 10.8.

We reported recently the first polymorph of the title compound [Kuai & Cheng (2011*a*). *Acta Cryst.*, **E67**, o2787]. A second polymorph of the title compound, $C_{15}H_{12}N_2O_2$, was unexpectedly obtained by the hydrothermal reaction of the title compound with manganese chloride in the presence of potassium hydroxide at 413 K. The benzimidazole ring system is almost planar, with a maximum deviation from the mean plane of 0.015 (2) Å. The benzimidazole and benzene rings are inclined at a dihedral angle of 79.00 (1)°. In the crystal, adjacent molecules are connected through O—H···N hydrogen bonds into a one-dimensional chain along the [001] direction.

Related literature

For the synthesis of 4-[(1*H*-benzo[*d*]imidazol-1-yl)methyl]-benzoic acid, see: Hua *et al.* (2010). For two other polymorphs of the title compound, see: Kuai & Cheng (2011*a*,*b*). For related structures, see Das & Bharadwaj (2009).



Experimental

Crystal data

$C_{15}H_{12}N_2O_2$
M_r = 252.27
Orthorhombic, $P2_12_12_1$
a = 5.6969 (15) Å
b = 12.657 (3) Å
c = 17.604 (5) Å
V = 1269.4 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.30 × 0.18 × 0.18 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.974, T_{max} = 0.984
7948 measured reflections
1786 independent reflections
1313 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.089
S = 0.99
1786 reflections
166 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.11 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H12···N12^{i}	0.82	1.84	2.649 (3)	168

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AA2024).

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supporting information

Acta Cryst. (2011). E**67**, o3014 [doi:10.1107/S1600536811042838]

Orthorhombic polymorph of 4-[(1*H*-benzimidazol-1-yl)methyl]benzoic acid

Hai-Wei Kuai and Xiao-Chun Cheng

S1. Comment

The title compound, $C_{15}H_{12}N_2O_2$ (**I**), is usually regarded as an excellent candidate for building block in molecular self-assembly engineering due to its variable conformation and coordination modes (Das & Bharadwaj, 2009). During assembly of a coordination polymer, we accidentally obtained three polymorphs of (**I**), which can be proved by different unit-cell parameters and space groups. Here, we are introducing one of them. The single crystals of (**I**) were accidentally obtained by the hydrothermal reaction at 413 K of (**I**) with manganese chloride in the presence of potassium hydroxide as alkaline medium for the deprotonation. As shown in Fig. 1, the asymmetric unit of (**I**) consists of only one molecule. Interestingly, though crystallizing from alkaline solution, (**I**) remains the intact carboxylic group in the crystal structure. The flexible benzimidazolyl arm is apt to rotate. As a result, the benzimidazolyl ring and central benzene rings are inclined at a dihedral angle of 79.00 (1) °; The torsion angles N11—C11—C1—C2 and N11—C11—C1—C6 are -61.8 (2) ° and 118.0 (2) °, respectively. Adjacent molecules are connected through O—H···N hydrogen bonds into a one-dimensional chain along [001] direction (Fig. 2, Table 1).

S2. Experimental

Reaction mixture of $MnCl_2$ (21.5 mg, 0.1 mmol), 4-((1*H*-benzo[*d*]imidazol-1-yl)methyl)benzoic acid (25.2 mg, 0.1 mmol) and KOH (5.61 mg, 0.1 mmol) in 10 ml H_2O was sealed in a 16 ml Teflon-lined stainless steel container and heated to 413 K for 3 days. After cooling to the room temperature, colorless block crystals of the title compound were obtained.

S3. Refinement

All hydrogen atoms were located in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93–0.97, O—H = 0.82 Å and U_{iso}(H) = 1.2U_{eq}(C, or O). Absolute structure can not be determined in this case because of no heavy atoms present. Friedel-pair data are merged with the MERG 3 instruction. The number of Friedel pairs is 1229.

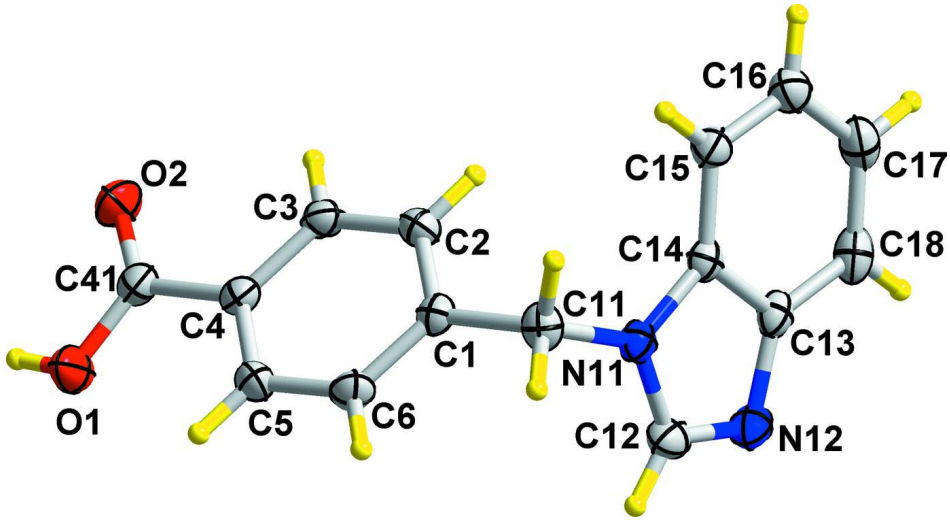

Figure 1

The crystal structure of (**I**) showing 30% probability displacement ellipsoids.

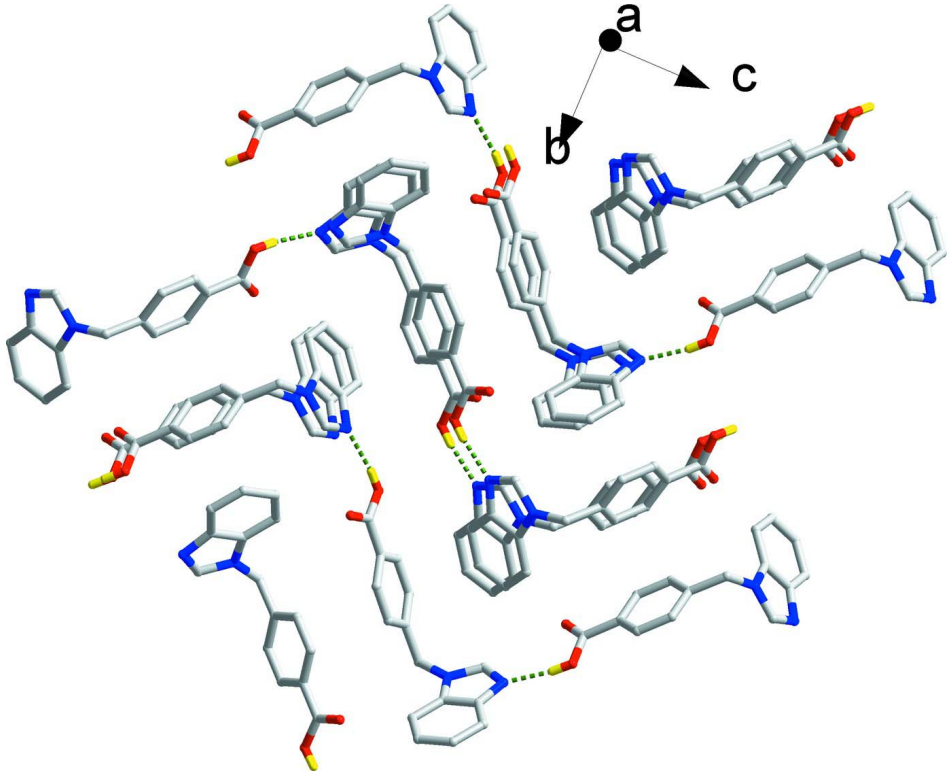

Figure 2

The packing diagram of (**I**). Hydrogen bonds are shown as dashed lines.

4-[(1*H*-benzimidazol-1-yl)methyl]benzoic acid

Crystal data

$C_{15}H_{12}N_2O_2$
$M_r = 252.27$

Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab

a = 5.6969 (15) Å
b = 12.657 (3) Å
c = 17.604 (5) Å
V = 1269.4 (6) Å^3
Z = 4
F(000) = 528
D_x = 1.320 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1326 reflections
θ = 2.3–19.9°
μ = 0.09 mm^{-1}
T = 293 K
Block, colorless
0.30 × 0.18 × 0.18 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.974, T_{max} = 0.984

7948 measured reflections
1786 independent reflections
1313 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 28.0°, θ_{min} = 2.0°
h = −7→7
k = −14→16
l = −23→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.089
S = 0.99
1786 reflections
166 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.11 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger. Absolute structure can not be determined in this case because of no heavy atoms present. Friedel-pair data are merged with the MERG 3 instruction. The number of Friedel pairs is 1229.

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

	x	y	z	U_{iso}*/U_{eq}
O1	0.3871 (4)	0.37836 (13)	1.03801 (9)	0.0731 (6)
H12	0.3280	0.3376	1.0688	0.088*
O2	0.0975 (4)	0.48320 (13)	1.07621 (9)	0.0650 (5)
N11	0.4456 (3)	0.78681 (13)	0.75703 (9)	0.0412 (4)
N12	0.2556 (4)	0.74457 (14)	0.65069 (10)	0.053
C4	0.3625 (4)	0.54619 (16)	0.98240 (11)	0.0390 (5)
C11	0.6074 (4)	0.77548 (17)	0.82087 (11)	0.0451 (5)
H6	0.6262	0.8434	0.8456	0.054*

H5	0.7598	0.7537	0.8019	0.054*
C13	0.1428 (4)	0.83025 (16)	0.68400 (11)	0.0417 (5)
C14	0.2622 (4)	0.85805 (15)	0.75045 (11)	0.0372 (5)
C6	0.6520 (4)	0.60602 (17)	0.89316 (11)	0.0458 (5)
H4	0.7940	0.5954	0.8682	0.055*
C5	0.5733 (4)	0.53174 (17)	0.94491 (11)	0.0473 (6)
H3	0.6627	0.4717	0.9545	0.057*
C41	0.2678 (5)	0.46665 (17)	1.03690 (11)	0.0472 (6)
C15	0.1919 (4)	0.94228 (17)	0.79536 (12)	0.0462 (6)
H8	0.2725	0.9610	0.8393	0.055*
C1	0.5221 (4)	0.69567 (16)	0.87823 (11)	0.0374 (5)
C17	−0.1262 (5)	0.9687 (2)	0.70573 (13)	0.0572 (7)
H10	−0.2587	1.0071	0.6920	0.069*
C12	0.4308 (5)	0.72183 (17)	0.69610 (12)	0.0510 (6)
H7	0.5348	0.6665	0.6873	0.061*
C16	−0.0036 (5)	0.99675 (19)	0.77139 (13)	0.0557 (6)
H9	−0.0557	1.0541	0.7998	0.067*
C2	0.3115 (4)	0.71014 (16)	0.91701 (11)	0.0437 (5)
H1	0.2224	0.7704	0.9081	0.052*
C3	0.2344 (4)	0.63641 (15)	0.96819 (11)	0.0426 (5)
H2	0.0936	0.6474	0.9937	0.051*
C18	−0.0555 (4)	0.88605 (18)	0.66126 (13)	0.0526 (6)
H11	−0.1370	0.8678	0.6174	0.063*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0997 (15)	0.0514 (10)	0.0681 (10)	0.0157 (11)	0.0362 (11)	0.0196 (8)
O2	0.0673 (13)	0.0707 (11)	0.0571 (9)	0.0034 (10)	0.0240 (10)	0.0109 (8)
N11	0.0449 (11)	0.0390 (9)	0.0396 (9)	−0.0030 (9)	−0.0010 (8)	0.0024 (8)
N12	0.072	0.044	0.042	−0.007	−0.005	−0.002
C4	0.0435 (13)	0.0422 (11)	0.0313 (10)	0.0001 (10)	0.0020 (10)	−0.0025 (8)
C11	0.0395 (13)	0.0473 (12)	0.0484 (12)	−0.0053 (11)	−0.0046 (11)	0.0069 (10)
C13	0.0494 (14)	0.0382 (11)	0.0375 (10)	−0.0108 (10)	−0.0017 (10)	0.0050 (9)
C14	0.0382 (12)	0.0354 (10)	0.0379 (10)	−0.0067 (9)	0.0022 (10)	0.0054 (9)
C6	0.0354 (13)	0.0556 (13)	0.0462 (12)	0.0063 (11)	0.0079 (11)	0.0022 (11)
C5	0.0509 (15)	0.0467 (12)	0.0442 (12)	0.0138 (11)	0.0048 (11)	0.0069 (10)
C41	0.0569 (15)	0.0505 (14)	0.0341 (10)	0.0001 (12)	0.0032 (12)	0.0005 (10)
C15	0.0542 (16)	0.0442 (12)	0.0404 (11)	−0.0009 (11)	−0.0001 (11)	0.0002 (10)
C1	0.0360 (12)	0.0400 (11)	0.0363 (10)	−0.0036 (9)	−0.0045 (9)	−0.0012 (9)
C17	0.0488 (15)	0.0614 (15)	0.0613 (15)	0.0054 (13)	−0.0005 (13)	0.0225 (13)
C12	0.0672 (17)	0.0371 (12)	0.0487 (12)	−0.0035 (12)	0.0066 (12)	−0.0026 (10)
C16	0.0621 (16)	0.0493 (13)	0.0557 (14)	0.0082 (12)	0.0102 (14)	0.0079 (11)
C2	0.0441 (14)	0.0394 (12)	0.0476 (11)	0.0064 (10)	0.0007 (11)	0.0004 (10)
C3	0.0395 (12)	0.0478 (12)	0.0403 (11)	0.0048 (10)	0.0054 (11)	−0.0039 (10)
C18	0.0535 (16)	0.0557 (14)	0.0487 (13)	−0.0134 (13)	−0.0128 (12)	0.0152 (12)

Geometric parameters (Å, º)

O1—C41	1.308 (3)	C6—C1	1.380 (3)
O1—H12	0.8200	C6—C5	1.384 (3)
O2—C41	1.210 (3)	C6—H4	0.9300
N11—C12	1.354 (3)	C5—H3	0.9300
N11—C14	1.385 (3)	C15—C16	1.376 (3)
N11—C11	1.461 (3)	C15—H8	0.9300
N12—C12	1.311 (3)	C1—C2	1.392 (3)
N12—C13	1.390 (3)	C17—C18	1.367 (3)
C4—C3	1.378 (3)	C17—C16	1.396 (3)
C4—C5	1.382 (3)	C17—H10	0.9300
C4—C41	1.492 (3)	C12—H7	0.9300
C11—C1	1.509 (3)	C16—H9	0.9300
C11—H6	0.9700	C2—C3	1.369 (3)
C11—H5	0.9700	C2—H1	0.9300
C13—C18	1.391 (3)	C3—H2	0.9300
C13—C14	1.398 (3)	C18—H11	0.9300
C14—C15	1.386 (3)		
C41—O1—H12	109.5	O2—C41—C4	122.8 (2)
C12—N11—C14	106.40 (18)	O1—C41—C4	113.5 (2)
C12—N11—C11	126.09 (19)	C16—C15—C14	116.4 (2)
C14—N11—C11	127.18 (16)	C16—C15—H8	121.8
C12—N12—C13	105.42 (18)	C14—C15—H8	121.8
C3—C4—C5	118.88 (19)	C6—C1—C2	118.50 (19)
C3—C4—C41	119.0 (2)	C6—C1—C11	120.3 (2)
C5—C4—C41	122.1 (2)	C2—C1—C11	121.2 (2)
N11—C11—C1	112.17 (17)	C18—C17—C16	121.4 (2)
N11—C11—H6	109.2	C18—C17—H10	119.3
C1—C11—H6	109.2	C16—C17—H10	119.3
N11—C11—H5	109.2	N12—C12—N11	113.4 (2)
C1—C11—H5	109.2	N12—C12—H7	123.3
H6—C11—H5	107.9	N11—C12—H7	123.3
N12—C13—C18	130.5 (2)	C15—C16—C17	122.1 (2)
N12—C13—C14	108.94 (19)	C15—C16—H9	119.0
C18—C13—C14	120.5 (2)	C17—C16—H9	119.0
N11—C14—C15	132.13 (19)	C3—C2—C1	120.6 (2)
N11—C14—C13	105.84 (17)	C3—C2—H1	119.7
C15—C14—C13	122.0 (2)	C1—C2—H1	119.7
C1—C6—C5	120.7 (2)	C2—C3—C4	121.0 (2)
C1—C6—H4	119.7	C2—C3—H2	119.5
C5—C6—H4	119.7	C4—C3—H2	119.5
C4—C5—C6	120.4 (2)	C17—C18—C13	117.6 (2)
C4—C5—H3	119.8	C17—C18—H11	121.2
C6—C5—H3	119.8	C13—C18—H11	121.2
O2—C41—O1	123.8 (2)		

C12—N11—C11—C1	−80.9 (3)	N11—C14—C15—C16	−179.6 (2)
C14—N11—C11—C1	91.6 (2)	C13—C14—C15—C16	0.6 (3)
C12—N12—C13—C18	−178.9 (2)	C5—C6—C1—C2	0.7 (3)
C12—N12—C13—C14	1.0 (2)	C5—C6—C1—C11	−179.09 (19)
C12—N11—C14—C15	−179.4 (2)	N11—C11—C1—C6	118.0 (2)
C11—N11—C14—C15	7.0 (3)	N11—C11—C1—C2	−61.8 (2)
C12—N11—C14—C13	0.4 (2)	C13—N12—C12—N11	−0.7 (2)
C11—N11—C14—C13	−173.21 (18)	C14—N11—C12—N12	0.2 (2)
N12—C13—C14—N11	−0.9 (2)	C11—N11—C12—N12	173.93 (19)
C18—C13—C14—N11	179.04 (18)	C14—C15—C16—C17	0.4 (3)
N12—C13—C14—C15	179.0 (2)	C18—C17—C16—C15	−0.9 (4)
C18—C13—C14—C15	−1.1 (3)	C6—C1—C2—C3	−0.7 (3)
C3—C4—C5—C6	−1.0 (3)	C11—C1—C2—C3	179.11 (19)
C41—C4—C5—C6	178.2 (2)	C1—C2—C3—C4	−0.2 (3)
C1—C6—C5—C4	0.1 (3)	C5—C4—C3—C2	1.0 (3)
C3—C4—C41—O2	−9.2 (3)	C41—C4—C3—C2	−178.2 (2)
C5—C4—C41—O2	171.7 (2)	C16—C17—C18—C13	0.3 (3)
C3—C4—C41—O1	171.1 (2)	N12—C13—C18—C17	−179.5 (2)
C5—C4—C41—O1	−8.0 (3)	C14—C13—C18—C17	0.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H12···N12^{i}	0.82	1.84	2.649 (3)	168

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