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(E)-Ethyl N'-(3,4-dimethoxybenzylidene)-hydrazinecarboxylate monohydrateLu-Ping Lv,^a Yong-Zhao Zhang,^a Xiao-Min Ding,^a Wei-Wei Li^a and Xian-Chao Hu^{b*}^aDepartment of Chemical Engineering, Hangzhou Vocational and Technical College, Hangzhou 310018, People's Republic of China, and ^bResearch Center of Analysis and Measurement, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

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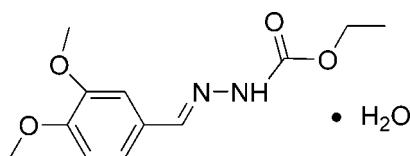
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Key indicators: single-crystal X-ray study; $T = 193$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.031; wR factor = 0.085; data-to-parameter ratio = 7.3.

In the title compound, $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_4 \cdot \text{H}_2\text{O}$, the molecular skeleton of the hydrazinecarboxylate is nearly planar [within 0.053 (3) Å]. In the crystal, chains propagating along the c axis arise, composed of alternating hydrazinecarboxylate molecules and crystalline water, which interact *via* $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds.

Related literature

For general background, see: Parashar *et al.* (1988); Hadjoudis *et al.* (1987); Borg *et al.* (1999). For a related structure, see Shang *et al.* (2007).



Experimental

Crystal data

 $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_4 \cdot \text{H}_2\text{O}$
 $M_r = 270.28$

 Orthorhombic, $Pna2_1$
 $a = 7.211$ (2) Å

 $b = 17.688$ (5) Å
 $c = 11.026$ (3) Å
 $V = 1406.3$ (7) Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 193$ (2) K
 $0.27 \times 0.25 \times 0.23$ mm

Data collection

 Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.969$, $T_{\max} = 0.976$

 7281 measured reflections
 1312 independent reflections
 1181 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.085$
 $S = 1.07$
 1312 reflections
 180 parameters
 3 restraints

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.15$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|------------|--------------|--------------|----------------|
| $\text{O1W}-\text{H1F} \cdots \text{O3}$ | 0.833 (19) | 2.14 (2) | 2.899 (3) | 151 (3) |
| $\text{N2}-\text{H2} \cdots \text{O1W}^i$ | 0.88 | 2.12 | 2.899 (3) | 148 |

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2464).

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supporting information

Acta Cryst. (2008). E64, o2196 [doi:10.1107/S1600536808034417]

(E)-Ethyl N'-(3,4-dimethoxybenzylidene)hydrazinecarboxylate monohydrate

Lu-Ping Lv, Yong-Zhao Zhang, Xiao-Min Ding, Wei-Wei Li and Xian-Chao Hu

S1. Comment

Benzaldehydhydrazone derivatives have received considerable attention for a long time due to their pharmacological activity (Parashar *et al.*, 1988) and photochromic properties (Hadjoudis *et al.*, 1987). Meanwhile, it is an important intermediate of 1,3,4-oxadiazoles, which have been reported to be compounds with versatile useful properties (Borg *et al.*, 1999). As a further investigation of this type of derivatives, we report herein the crystal structure of the title compound.

In the title compound, C₁₂H₁₆N₂O₄ (I) ·H₂O, the molecular skeleton of (I) is nearly planar. The main molecule, (I), adopts a trans configuration with respect to the C=N bond. The hydrazine carboxylic acid methyl ester group is slightly twisted away from the attached ring. The bond lengths and angles of the main molecule agree with those observed in (E)-methyl N'-(4-hydroxybenzylidene)hydrazinecarboxylate (Shang *et al.*, 2007).

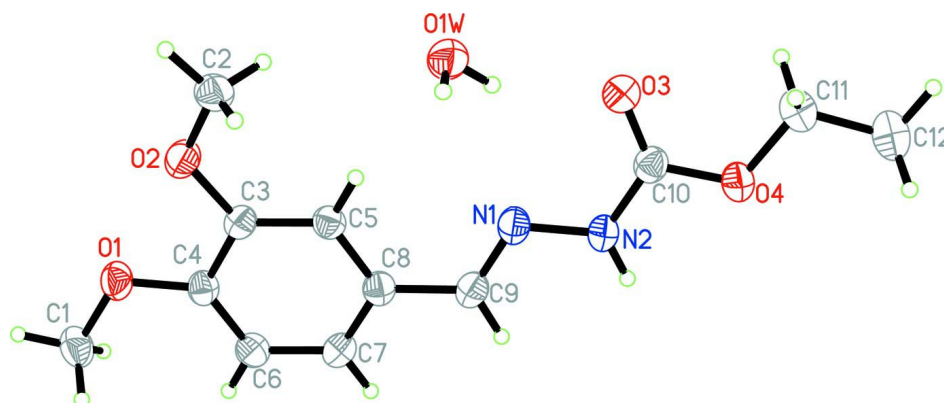
The crystal packing exhibits hydrogen-bonded chains extended along c axis and composed from alternating molecules of (I) and crystalline water, which interact via N-H···O [N···O 2.899 (3) Å] and O-H···O [O···O 2.899 (3) Å] hydrogen bonds (Table 1).

S2. Experimental

3,4-Dimethoxybenzaldehyde (1.66g, 0.01mol) and ethyl hydrazinecarboxylate(1.04g, 0.01mol) were dissolved in stirred methanol (20ml) and left for 3h at room temperature. The resulting solid was filtered off and recrystallized from ethanol to give the title compound in 90% yield. Crystals suitable for X-ray analysis were obtained by slow evaporation of a ethanol solution at room temperature (m.p. 458-460 K).

S3. Refinement

H atoms of the water molecule were located in a difference map and were refined with O-H distances restrained to 0.82 (2) Å, H atoms were included in the riding model approximation with N-H = 0.88 Å. C-bound H atoms were positioned geometrically (C-H = 0.95-0.99 Å) and refined using a riding model, with U_{iso}(H) = 1.2-1.5U_{eq}(C). In the absence of significant anomalous scatterers, the 1193 Friedel pairs were merged before the final refinement.

**Figure 1**

Molecular structure of (I), showing 30% probability displacement ellipsoids and the atomic numbering.

(E)-Ethyl N'-(3,4-dimethoxybenzylidene)hydrazinecarboxylate monohydrate

Crystal data

$C_{12}H_{16}N_2O_4 \cdot H_2O$

$M_r = 270.28$

Orthorhombic, $Pna2_1$

Hall symbol: $P\ 2c\ -2n$

$a = 7.211\ (2)\ \text{\AA}$

$b = 17.688\ (5)\ \text{\AA}$

$c = 11.026\ (3)\ \text{\AA}$

$V = 1406.3\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 576$

$D_x = 1.277\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1312 reflections

$\theta = 2.2\text{--}25.5^\circ$

$\mu = 0.10\ \text{mm}^{-1}$

$T = 193\ \text{K}$

Block, colourless

$0.27 \times 0.25 \times 0.23\ \text{mm}$

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2002)

$T_{\min} = 0.969$, $T_{\max} = 0.976$

7281 measured reflections

1312 independent reflections

1181 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -8 \rightarrow 8$

$k = -20 \rightarrow 20$

$l = -13 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.085$

$S = 1.07$

1312 reflections

180 parameters

3 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.0753P]$

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

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

$\Delta\rho_{\max} = 0.16\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.15\ \text{e \AA}^{-3}$

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.

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 $F^2 > 2\sigma(F^2)$ 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.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|--------------|--------------|----------------------------------|
| C1 | 1.0427 (4) | 0.67958 (16) | 0.2893 (3) | 0.0656 (7) |
| H1A | 1.1372 | 0.7154 | 0.3172 | 0.098* |
| H1B | 0.9915 | 0.6969 | 0.2117 | 0.098* |
| H1C | 1.0989 | 0.6296 | 0.2786 | 0.098* |
| C2 | 0.4765 (4) | 0.69467 (15) | 0.6084 (3) | 0.0610 (6) |
| H2A | 0.5117 | 0.7319 | 0.6701 | 0.091* |
| H2B | 0.4388 | 0.6476 | 0.6482 | 0.091* |
| H2C | 0.3730 | 0.7144 | 0.5603 | 0.091* |
| C3 | 0.6065 (3) | 0.62962 (12) | 0.4381 (2) | 0.0458 (5) |
| C4 | 0.7529 (3) | 0.62623 (13) | 0.3535 (2) | 0.0458 (6) |
| C5 | 0.4527 (3) | 0.58339 (12) | 0.4241 (2) | 0.0462 (5) |
| H5 | 0.3536 | 0.5859 | 0.4806 | 0.055* |
| C6 | 0.7444 (3) | 0.57723 (14) | 0.2568 (2) | 0.0514 (6) |
| H6 | 0.8428 | 0.5753 | 0.1995 | 0.062* |
| C7 | 0.5889 (3) | 0.53002 (14) | 0.2433 (2) | 0.0519 (6) |
| H7 | 0.5833 | 0.4959 | 0.1769 | 0.062* |
| C8 | 0.4438 (3) | 0.53255 (13) | 0.3255 (2) | 0.0469 (5) |
| C9 | 0.2842 (3) | 0.48227 (14) | 0.3094 (3) | 0.0513 (6) |
| H9 | 0.2729 | 0.4534 | 0.2371 | 0.062* |
| C10 | -0.1176 (4) | 0.42102 (13) | 0.4535 (2) | 0.0511 (6) |
| C11 | -0.4016 (4) | 0.36234 (19) | 0.5028 (3) | 0.0719 (8) |
| H11A | -0.4699 | 0.4105 | 0.5130 | 0.086* |
| H11B | -0.3517 | 0.3471 | 0.5828 | 0.086* |
| C12 | -0.5286 (5) | 0.3030 (2) | 0.4560 (4) | 0.0882 (11) |
| H12A | -0.6307 | 0.2956 | 0.5134 | 0.132* |
| H12B | -0.4602 | 0.2555 | 0.4463 | 0.132* |
| H12C | -0.5786 | 0.3188 | 0.3773 | 0.132* |
| N1 | 0.1595 (3) | 0.47690 (10) | 0.3921 (2) | 0.0520 (5) |
| N2 | 0.0153 (3) | 0.42736 (11) | 0.3681 (2) | 0.0525 (5) |
| H2 | 0.0107 | 0.4012 | 0.3002 | 0.063* |
| O1 | 0.8976 (2) | 0.67502 (9) | 0.37704 (18) | 0.0578 (5) |
| O2 | 0.6305 (2) | 0.68036 (11) | 0.53107 (17) | 0.0620 (5) |
| O3 | -0.1179 (3) | 0.45274 (11) | 0.55163 (18) | 0.0689 (5) |
| O4 | -0.2508 (2) | 0.37243 (9) | 0.41722 (18) | 0.0582 (5) |
| O1W | 0.0397 (3) | 0.59890 (12) | 0.6111 (2) | 0.0667 (5) |

| | | | | |
|-----|-----------|-------------|-----------|-------------|
| H1E | 0.003 (5) | 0.6288 (18) | 0.561 (3) | 0.090 (12)* |
| H1F | 0.030 (5) | 0.5563 (13) | 0.579 (3) | 0.088 (12)* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C1 | 0.0528 (15) | 0.0662 (16) | 0.0777 (18) | -0.0115 (12) | 0.0121 (14) | -0.0002 (15) |
| C2 | 0.0693 (16) | 0.0566 (14) | 0.0570 (15) | -0.0026 (12) | 0.0121 (15) | -0.0057 (13) |
| C3 | 0.0457 (12) | 0.0442 (11) | 0.0474 (12) | 0.0005 (8) | -0.0055 (11) | -0.0020 (10) |
| C4 | 0.0389 (12) | 0.0447 (10) | 0.0537 (15) | 0.0004 (9) | -0.0033 (10) | 0.0030 (11) |
| C5 | 0.0414 (11) | 0.0506 (12) | 0.0466 (13) | -0.0001 (9) | -0.0005 (10) | 0.0029 (10) |
| C6 | 0.0456 (12) | 0.0538 (12) | 0.0548 (15) | 0.0026 (10) | 0.0029 (11) | 0.0000 (12) |
| C7 | 0.0536 (13) | 0.0510 (12) | 0.0513 (13) | 0.0004 (10) | -0.0048 (12) | -0.0061 (11) |
| C8 | 0.0430 (12) | 0.0462 (11) | 0.0515 (13) | 0.0010 (9) | -0.0065 (11) | 0.0051 (10) |
| C9 | 0.0512 (12) | 0.0483 (12) | 0.0543 (14) | -0.0020 (10) | -0.0075 (12) | -0.0013 (11) |
| C10 | 0.0553 (14) | 0.0453 (11) | 0.0526 (14) | -0.0034 (10) | -0.0067 (12) | 0.0022 (11) |
| C11 | 0.0618 (17) | 0.082 (2) | 0.0724 (19) | -0.0143 (14) | 0.0081 (15) | 0.0022 (15) |
| C12 | 0.0713 (19) | 0.097 (2) | 0.096 (3) | -0.0260 (18) | 0.004 (2) | 0.003 (2) |
| N1 | 0.0493 (11) | 0.0485 (10) | 0.0582 (13) | -0.0066 (8) | -0.0074 (11) | 0.0029 (9) |
| N2 | 0.0500 (11) | 0.0521 (11) | 0.0554 (13) | -0.0116 (8) | -0.0024 (10) | -0.0037 (9) |
| O1 | 0.0451 (9) | 0.0621 (10) | 0.0661 (11) | -0.0105 (7) | 0.0053 (9) | -0.0080 (9) |
| O2 | 0.0529 (10) | 0.0723 (10) | 0.0607 (12) | -0.0111 (8) | 0.0041 (9) | -0.0181 (10) |
| O3 | 0.0744 (12) | 0.0770 (11) | 0.0553 (11) | -0.0204 (10) | 0.0011 (10) | -0.0043 (10) |
| O4 | 0.0546 (10) | 0.0570 (9) | 0.0628 (12) | -0.0138 (7) | 0.0022 (8) | -0.0010 (9) |
| O1W | 0.0778 (13) | 0.0662 (12) | 0.0561 (12) | -0.0123 (10) | -0.0078 (11) | 0.0050 (11) |

Geometric parameters (Å, °)

| | | | |
|-----------|-----------|----------|------------|
| C1—O1 | 1.427 (3) | C7—H7 | 0.9500 |
| C1—H1A | 0.9800 | C8—C9 | 1.465 (3) |
| C1—H1B | 0.9800 | C9—N1 | 1.284 (3) |
| C1—H1C | 0.9800 | C9—H9 | 0.9500 |
| C2—O2 | 1.423 (3) | C10—O3 | 1.219 (3) |
| C2—H2A | 0.9800 | C10—N2 | 1.348 (3) |
| C2—H2B | 0.9800 | C10—O4 | 1.350 (3) |
| C2—H2C | 0.9800 | C11—O4 | 1.451 (4) |
| C3—O2 | 1.374 (3) | C11—C12 | 1.485 (5) |
| C3—C5 | 1.387 (3) | C11—H11A | 0.9900 |
| C3—C4 | 1.410 (3) | C11—H11B | 0.9900 |
| C4—C6 | 1.376 (4) | C12—H12A | 0.9800 |
| C4—O1 | 1.379 (3) | C12—H12B | 0.9800 |
| C5—C8 | 1.412 (4) | C12—H12C | 0.9800 |
| C5—H5 | 0.9500 | N1—N2 | 1.385 (3) |
| C6—C7 | 1.406 (4) | N2—H2 | 0.8800 |
| C6—H6 | 0.9500 | O1W—H1E | 0.812 (19) |
| C7—C8 | 1.385 (3) | O1W—H1F | 0.833 (19) |
| O1—C1—H1A | 109.5 | C7—C8—C9 | 119.6 (2) |

| | | | |
|-------------|-------------|----------------|-------------|
| O1—C1—H1B | 109.5 | C5—C8—C9 | 121.0 (2) |
| H1A—C1—H1B | 109.5 | N1—C9—C8 | 120.6 (2) |
| O1—C1—H1C | 109.5 | N1—C9—H9 | 119.7 |
| H1A—C1—H1C | 109.5 | C8—C9—H9 | 119.7 |
| H1B—C1—H1C | 109.5 | O3—C10—N2 | 125.7 (2) |
| O2—C2—H2A | 109.5 | O3—C10—O4 | 123.7 (2) |
| O2—C2—H2B | 109.5 | N2—C10—O4 | 110.6 (2) |
| H2A—C2—H2B | 109.5 | O4—C11—C12 | 108.8 (3) |
| O2—C2—H2C | 109.5 | O4—C11—H11A | 109.9 |
| H2A—C2—H2C | 109.5 | C12—C11—H11A | 109.9 |
| H2B—C2—H2C | 109.5 | O4—C11—H11B | 109.9 |
| O2—C3—C5 | 124.7 (2) | C12—C11—H11B | 109.9 |
| O2—C3—C4 | 115.30 (19) | H11A—C11—H11B | 108.3 |
| C5—C3—C4 | 120.0 (2) | C11—C12—H12A | 109.5 |
| C6—C4—O1 | 125.0 (2) | C11—C12—H12B | 109.5 |
| C6—C4—C3 | 120.4 (2) | H12A—C12—H12B | 109.5 |
| O1—C4—C3 | 114.5 (2) | C11—C12—H12C | 109.5 |
| C3—C5—C8 | 119.8 (2) | H12A—C12—H12C | 109.5 |
| C3—C5—H5 | 120.1 | H12B—C12—H12C | 109.5 |
| C8—C5—H5 | 120.1 | C9—N1—N2 | 115.9 (2) |
| C4—C6—C7 | 119.5 (2) | C10—N2—N1 | 116.9 (2) |
| C4—C6—H6 | 120.3 | C10—N2—H2 | 121.5 |
| C7—C6—H6 | 120.3 | N1—N2—H2 | 121.5 |
| C8—C7—C6 | 120.9 (2) | C4—O1—C1 | 117.5 (2) |
| C8—C7—H7 | 119.5 | C3—O2—C2 | 117.7 (2) |
| C6—C7—H7 | 119.5 | C10—O4—C11 | 114.8 (2) |
| C7—C8—C5 | 119.3 (2) | H1E—O1W—H1F | 106 (4) |
| O2—C3—C4—C6 | 179.8 (2) | C7—C8—C9—N1 | 171.3 (2) |
| C5—C3—C4—C6 | 0.0 (3) | C5—C8—C9—N1 | -8.3 (3) |
| O2—C3—C4—O1 | -0.4 (3) | C8—C9—N1—N2 | -179.5 (2) |
| C5—C3—C4—O1 | 179.8 (2) | O3—C10—N2—N1 | -3.1 (4) |
| O2—C3—C5—C8 | -179.2 (2) | O4—C10—N2—N1 | 178.61 (19) |
| C4—C3—C5—C8 | 0.5 (3) | C9—N1—N2—C10 | -179.8 (2) |
| O1—C4—C6—C7 | 179.7 (2) | C6—C4—O1—C1 | 5.4 (3) |
| C3—C4—C6—C7 | -0.5 (3) | C3—C4—O1—C1 | -174.4 (2) |
| C4—C6—C7—C8 | 0.5 (4) | C5—C3—O2—C2 | -9.6 (3) |
| C6—C7—C8—C5 | 0.0 (4) | C4—C3—O2—C2 | 170.6 (2) |
| C6—C7—C8—C9 | -179.6 (2) | O3—C10—O4—C11 | 2.3 (3) |
| C3—C5—C8—C7 | -0.5 (3) | N2—C10—O4—C11 | -179.4 (2) |
| C3—C5—C8—C9 | 179.1 (2) | C12—C11—O4—C10 | -175.3 (3) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------|----------|-------------|-------------|---------------|
| O1W—H1F \cdots O3 | 0.83 (2) | 2.14 (2) | 2.899 (3) | 151 (3) |

| | | | | |
|-------------------------------------|----------|----------|-----------|---------|
| O1 \bar{W} —H1E···O1 ⁱ | 0.81 (2) | 2.31 (2) | 3.086 (3) | 160 (4) |
| N2—H2···O1 \bar{W}^{ii} | 0.88 | 2.12 | 2.899 (3) | 148 |

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