

Ethyl *N'*-[(*E*)-4-hydroxybenzylidene]-hydrazinecarboxylate at 123 K

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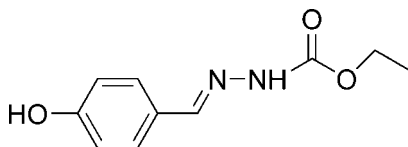
Received 19 June 2008; accepted 29 June 2008

Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.040; wR factor = 0.126; data-to-parameter ratio = 13.9.

The molecule of the title compound, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$, adopts a *trans* configuration with respect to the $\text{C}=\text{N}$ bond. The dihedral angle between the benzene ring and the hydrazinecarboxylate plane is $14.6(1)^\circ$. Molecules are linked into a three-dimensional network by $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, and by $\text{C}-\text{H}\cdots\pi$ interactions.

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

 $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$
 $M_r = 208.22$

 Orthorhombic, *Pbca*
 $a = 11.342(3)$ Å

 $b = 7.6114(17)$ Å

 $c = 24.986(5)$ Å

 $V = 2157.0(9)$ Å³
 $Z = 8$

 Mo $K\alpha$ radiation

 $\mu = 0.10$ mm⁻¹
 $T = 123(2)$ K

 $0.26 \times 0.25 \times 0.23$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

 Absorption correction: multi-scan (*SADABS*; Bruker, 2002)

 $T_{\min} = 0.965$, $T_{\max} = 0.968$

21084 measured reflections

1900 independent reflections

 1521 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.125$
 $S = 1.02$

1900 reflections

137 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 ring.

| <i>D</i> – <i>H</i> ⋯ <i>A</i> | <i>D</i> – <i>H</i> | <i>H</i> ⋯ <i>A</i> | <i>D</i> ⋯ <i>A</i> | <i>D</i> – <i>H</i> ⋯ <i>A</i> |
|--------------------------------|---------------------|---------------------|---------------------|--------------------------------|
| O1–H1⋯O2 ⁱ | 0.82 | 1.96 | 2.752 (2) | 161 |
| N2–H2A⋯O2 ⁱⁱ | 0.86 | 2.11 | 2.936 (2) | 161 |
| C9–H9B⋯O1 ⁱⁱⁱ | 0.97 | 2.57 | 3.425 (3) | 148 |
| C2–H2⋯Cg1 ^{iv} | 0.93 | 2.97 | 3.636 (2) | 130 |
| C5–H5⋯Cg1 ^v | 0.93 | 2.77 | 3.613 (2) | 151 |

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (iii) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (iv) $-x - \frac{1}{2}, y - \frac{3}{2}, z$; (v) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; 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*.

The author acknowledges financial support from Zhejiang Police College, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2620).

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supplementary materials

Acta Cryst. (2008). E64, o1396 [doi:10.1107/S1600536808019818]

Ethyl *N'*-[(*E*)-4-hydroxybenzylidene]hydrazinecarboxylate at 123 K

X.-W. Cheng

Comment

Benzaldehydehydrazone derivatives have received considerable attention for a long time due to their pharmacological activity (Parashar *et al.*, 1988) and their photochromic properties (Hadjoudis *et al.*, 1987). They are important intermediates for 1,3,4-oxadiazoles, which have been reported to be versatile compounds with many properties (Borg *et al.*, 1999). As a further investigation of this type of derivatives, the crystal structure of the title compound is reported here.

The title molecule (Fig.1) adopts a *trans* configuration with respect to the C=N bond. The hydrazine carboxylic acid ethyl ester group is slightly twisted away from the attached ring. The dihedral angle between the C1–C6 ring and the C7/C8/N1/N2/O2/O3 plane is 14.6 (1)°. The bond lengths and angles agree with those observed for *N'*-(4-methoxybenzylidene)methoxyformohydrazide (Shang *et al.*, 2007).

In the crystal structure, O—H...O, N—H...O and C—H...O hydrogen bonds and C—H... π interactions (Table 1) link the molecules into a three-dimensional network (Fig.2).

Experimental

4-Hydroxybenzaldehyde (12.2 g, 0.1 mol) and ethyl hydrazinecarboxylate (10.4 g, 0.1 mol) were dissolved in methanol (50 ml) with stirring and left for 6 h at room temperature. The resulting solid was filtered off and recrystallized from ethanol to give the title compound in 90% yield. Single crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution at room temperature (m.p. 460–462 K).

Refinement

H atoms were positioned geometrically (N—H = 0.86 Å, O—H = 0.82 Å and C—H = 0.93–0.97 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ and $1.5U_{\text{eq}}(\text{O})$.

Figures

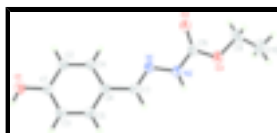


Fig. 1. Molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atomic numbering.

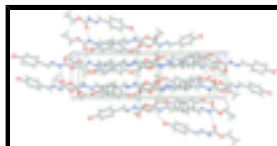


Fig. 2. Crystal packing of the title compound, viewed approximately down the *a* axis. Dashed lines indicate intermolecular hydrogen bonds.

Ethyl *N'*-[(*E*)-4-hydroxybenzylidene]hydrazinecarboxylate

Crystal data

| | |
|--------------------------------|---|
| $C_{10}H_{12}N_2O_3$ | $F_{000} = 880$ |
| $M_r = 208.22$ | $D_x = 1.282 \text{ Mg m}^{-3}$ |
| Orthorhombic, <i>Pbca</i> | Mo $K\alpha$ radiation |
| Hall symbol: -P 2ac 2ab | $\lambda = 0.71073 \text{ \AA}$ |
| $a = 11.342 (3) \text{ \AA}$ | Cell parameters from 1900 reflections |
| $b = 7.6114 (17) \text{ \AA}$ | $\theta = 1.6\text{--}25.0^\circ$ |
| $c = 24.986 (5) \text{ \AA}$ | $\mu = 0.10 \text{ mm}^{-1}$ |
| $V = 2157.0 (9) \text{ \AA}^3$ | $T = 123 (2) \text{ K}$ |
| $Z = 8$ | Block, colourless |
| | $0.26 \times 0.25 \times 0.23 \text{ mm}$ |

Data collection

| | |
|--|--|
| Bruker SMART CCD area-detector diffractometer | 1900 independent reflections |
| Radiation source: fine-focus sealed tube | 1521 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.040$ |
| $T = 123(2) \text{ K}$ | $\theta_{\text{max}} = 25.0^\circ$ |
| φ and ω scans | $\theta_{\text{min}} = 1.6^\circ$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2002) | $h = -13 \rightarrow 13$ |
| $T_{\text{min}} = 0.965$, $T_{\text{max}} = 0.968$ | $k = -8 \rightarrow 9$ |
| 21084 measured reflections | $l = -28 \rightarrow 29$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | $w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 0.4536P]$ |
| $wR(F^2) = 0.125$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.02$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 1900 reflections | $\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$ |
| 137 parameters | $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFe^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Secondary atom site location: difference Fourier map | Extinction coefficient: 0.0110 (18) |

Special details

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

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|---------------|----------------------------------|
| O2 | 0.38975 (10) | 0.12445 (15) | 0.06297 (5) | 0.0550 (4) |
| O1 | 0.10016 (11) | 0.07264 (18) | 0.38449 (5) | 0.0662 (4) |
| H1 | 0.0396 | 0.1121 | 0.3978 | 0.099* |
| O3 | 0.31948 (13) | 0.34186 (17) | 0.01045 (5) | 0.0708 (4) |
| N1 | 0.23119 (12) | 0.22542 (18) | 0.13972 (5) | 0.0472 (4) |
| N2 | 0.23619 (13) | 0.29838 (19) | 0.08895 (5) | 0.0533 (4) |
| H2A | 0.1859 | 0.3769 | 0.0794 | 0.064* |
| C4 | 0.21890 (13) | 0.1206 (2) | 0.25066 (6) | 0.0451 (4) |
| H4 | 0.2850 | 0.0839 | 0.2317 | 0.054* |
| C6 | 0.13472 (13) | 0.2248 (2) | 0.22515 (6) | 0.0422 (4) |
| C1 | 0.10857 (14) | 0.1271 (2) | 0.33239 (6) | 0.0459 (4) |
| C3 | 0.02413 (14) | 0.2324 (2) | 0.30815 (7) | 0.0493 (4) |
| H3 | -0.0410 | 0.2707 | 0.3275 | 0.059* |
| C7 | 0.14800 (14) | 0.2813 (2) | 0.16958 (7) | 0.0471 (4) |
| H7 | 0.0940 | 0.3608 | 0.1555 | 0.056* |
| C2 | 0.20628 (14) | 0.0712 (2) | 0.30315 (6) | 0.0481 (4) |
| H2 | 0.2629 | 0.0004 | 0.3192 | 0.058* |
| C5 | 0.03729 (14) | 0.2800 (2) | 0.25500 (7) | 0.0491 (4) |
| H5 | -0.0197 | 0.3501 | 0.2389 | 0.059* |
| C8 | 0.32053 (15) | 0.2449 (2) | 0.05487 (6) | 0.0489 (4) |
| C9 | 0.3972 (3) | 0.2864 (3) | -0.03288 (9) | 0.1029 (9) |
| H9A | 0.4749 | 0.2601 | -0.0188 | 0.123* |
| H9B | 0.3663 | 0.1809 | -0.0495 | 0.123* |
| C10 | 0.4055 (3) | 0.4246 (4) | -0.07193 (10) | 0.1096 (10) |
| H10A | 0.4564 | 0.3880 | -0.1005 | 0.164* |
| H10B | 0.4372 | 0.5282 | -0.0554 | 0.164* |
| H10C | 0.3285 | 0.4497 | -0.0859 | 0.164* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|------------|------------|------------|
| O2 | 0.0572 (7) | 0.0535 (7) | 0.0542 (7) | 0.0039 (6) | 0.0023 (5) | 0.0014 (5) |

supplementary materials

| | | | | | | |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| O1 | 0.0693 (8) | 0.0818 (9) | 0.0475 (8) | 0.0116 (7) | 0.0088 (6) | 0.0139 (6) |
| O3 | 0.1000 (10) | 0.0651 (8) | 0.0472 (7) | 0.0138 (7) | 0.0168 (7) | 0.0131 (6) |
| N1 | 0.0533 (8) | 0.0472 (8) | 0.0412 (8) | 0.0007 (6) | 0.0011 (6) | 0.0059 (6) |
| N2 | 0.0639 (9) | 0.0534 (8) | 0.0426 (8) | 0.0116 (7) | 0.0048 (7) | 0.0112 (6) |
| C4 | 0.0428 (8) | 0.0455 (9) | 0.0469 (9) | 0.0038 (7) | 0.0050 (7) | -0.0010 (7) |
| C6 | 0.0431 (8) | 0.0387 (8) | 0.0447 (9) | -0.0018 (6) | -0.0001 (6) | 0.0012 (6) |
| C1 | 0.0508 (9) | 0.0447 (9) | 0.0421 (9) | -0.0033 (7) | 0.0001 (7) | 0.0022 (7) |
| C3 | 0.0426 (8) | 0.0528 (10) | 0.0526 (10) | 0.0030 (7) | 0.0077 (7) | 0.0009 (8) |
| C7 | 0.0495 (9) | 0.0447 (9) | 0.0471 (10) | 0.0040 (7) | -0.0013 (7) | 0.0053 (7) |
| C2 | 0.0484 (8) | 0.0478 (9) | 0.0483 (10) | 0.0063 (7) | -0.0029 (7) | 0.0024 (7) |
| C5 | 0.0437 (8) | 0.0501 (9) | 0.0534 (10) | 0.0061 (7) | 0.0001 (7) | 0.0069 (7) |
| C8 | 0.0592 (10) | 0.0455 (9) | 0.0418 (9) | -0.0046 (8) | 0.0000 (7) | 0.0011 (7) |
| C9 | 0.155 (3) | 0.0936 (18) | 0.0598 (14) | 0.0209 (17) | 0.0467 (16) | 0.0063 (12) |
| C10 | 0.107 (2) | 0.155 (3) | 0.0666 (15) | 0.0021 (19) | 0.0209 (13) | 0.0293 (16) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|---------------|-------------|
| O2—C8 | 1.224 (2) | C1—C3 | 1.388 (2) |
| O1—C1 | 1.3695 (19) | C1—C2 | 1.394 (2) |
| O1—H1 | 0.82 | C3—C5 | 1.385 (2) |
| O3—C8 | 1.3329 (19) | C3—H3 | 0.93 |
| O3—C9 | 1.458 (3) | C7—H7 | 0.93 |
| N1—C7 | 1.276 (2) | C2—H2 | 0.93 |
| N1—N2 | 1.3860 (18) | C5—H5 | 0.93 |
| N2—C8 | 1.344 (2) | C9—C10 | 1.437 (3) |
| N2—H2A | 0.86 | C9—H9A | 0.97 |
| C4—C2 | 1.372 (2) | C9—H9B | 0.97 |
| C4—C6 | 1.395 (2) | C10—H10A | 0.96 |
| C4—H4 | 0.93 | C10—H10B | 0.96 |
| C6—C5 | 1.398 (2) | C10—H10C | 0.96 |
| C6—C7 | 1.462 (2) | | |
| C1—O1—H1 | 109.5 | C4—C2—C1 | 120.03 (14) |
| C8—O3—C9 | 116.92 (16) | C4—C2—H2 | 120.0 |
| C7—N1—N2 | 115.58 (13) | C1—C2—H2 | 120.0 |
| C8—N2—N1 | 119.19 (14) | C3—C5—C6 | 121.20 (15) |
| C8—N2—H2A | 120.4 | C3—C5—H5 | 119.4 |
| N1—N2—H2A | 120.4 | C6—C5—H5 | 119.4 |
| C2—C4—C6 | 121.41 (14) | O2—C8—O3 | 123.93 (15) |
| C2—C4—H4 | 119.3 | O2—C8—N2 | 125.36 (15) |
| C6—C4—H4 | 119.3 | O3—C8—N2 | 110.71 (15) |
| C4—C6—C5 | 117.91 (15) | C10—C9—O3 | 109.4 (2) |
| C4—C6—C7 | 122.06 (14) | C10—C9—H9A | 109.8 |
| C5—C6—C7 | 119.99 (14) | O3—C9—H9A | 109.8 |
| O1—C1—C3 | 122.78 (14) | C10—C9—H9B | 109.8 |
| O1—C1—C2 | 117.48 (14) | O3—C9—H9B | 109.8 |
| C3—C1—C2 | 119.74 (15) | H9A—C9—H9B | 108.2 |
| C5—C3—C1 | 119.70 (15) | C9—C10—H10A | 109.5 |
| C5—C3—H3 | 120.1 | C9—C10—H10B | 109.5 |
| C1—C3—H3 | 120.1 | H10A—C10—H10B | 109.5 |

| | | | |
|-------------|--------------|---------------|--------------|
| N1—C7—C6 | 122.24 (15) | C9—C10—H10C | 109.5 |
| N1—C7—H7 | 118.9 | H10A—C10—H10C | 109.5 |
| C6—C7—H7 | 118.9 | H10B—C10—H10C | 109.5 |
| C7—N1—N2—C8 | -179.28 (15) | C3—C1—C2—C4 | 0.2 (2) |
| C2—C4—C6—C5 | 0.9 (2) | C1—C3—C5—C6 | -0.3 (3) |
| C2—C4—C6—C7 | 178.80 (15) | C4—C6—C5—C3 | -0.3 (2) |
| O1—C1—C3—C5 | -178.91 (15) | C7—C6—C5—C3 | -178.25 (15) |
| C2—C1—C3—C5 | 0.4 (2) | C9—O3—C8—O2 | 7.1 (3) |
| N2—N1—C7—C6 | -176.50 (13) | C9—O3—C8—N2 | -173.16 (19) |
| C4—C6—C7—N1 | 6.8 (3) | N1—N2—C8—O2 | 6.4 (3) |
| C5—C6—C7—N1 | -175.38 (15) | N1—N2—C8—O3 | -173.41 (14) |
| C6—C4—C2—C1 | -0.9 (2) | C8—O3—C9—C10 | -166.9 (2) |
| O1—C1—C2—C4 | 179.54 (14) | | |

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

| <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> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1—H1 \cdots O2 ⁱ | 0.82 | 1.96 | 2.752 (2) | 161 |
| N2—H2A \cdots O2 ⁱⁱ | 0.86 | 2.11 | 2.936 (2) | 161 |
| C9—H9B \cdots O1 ⁱⁱⁱ | 0.97 | 2.57 | 3.425 (3) | 148 |
| C2—H2 \cdots Cg1 ^{iv} | 0.93 | 2.97 | 3.636 (2) | 130 |
| C5—H5 \cdots Cg1 ^v | 0.93 | 2.77 | 3.613 (2) | 151 |

Symmetry codes: (i) $x-1/2, y, -z+1/2$; (ii) $-x+1/2, y+1/2, z$; (iii) $-x+1/2, -y, z-1/2$; (iv) $-x-1/2, y-3/2, z$; (v) $-x, y+1/2, -z+1/2$.

Fig. 1

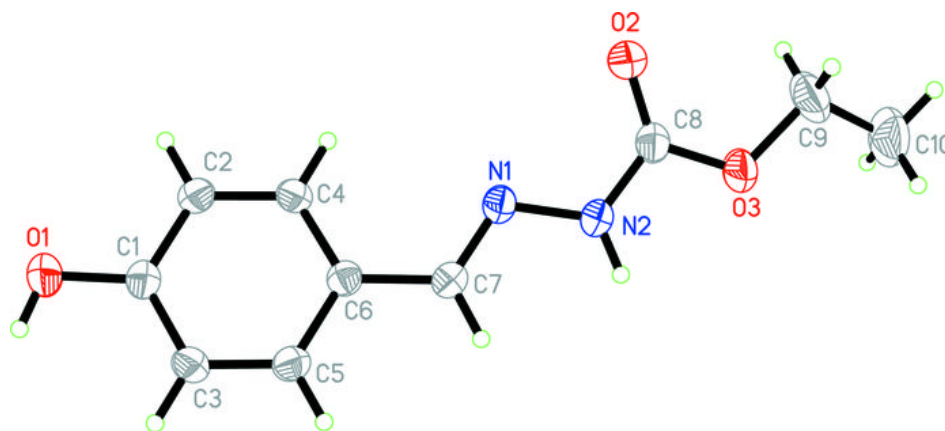


Fig. 2

