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## Structure Reports

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**(E)-1-(2,4,6-Trihydroxybenzylidene)-4-ethylthiosemicarbazide dihydrate**

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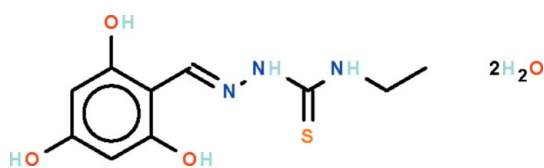
Received 1 August 2010; accepted 2 August 2010

Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.028;  $wR$  factor = 0.074; data-to-parameter ratio = 14.1.

In the title molecule,  $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_3\text{S}\cdot 2\text{H}_2\text{O}$ , the thiosemicarbazide  $=\text{N}-\text{NH}-\text{C}(=\text{S})-\text{NH}-$  fragment [torsion angle =  $0.2$  ( $1^\circ$ )] is nearly coplanar with the benzene ring [dihedral angle =  $2.4$  ( $1^\circ$ )]. The benzene ring and semicarbazide moiety are located on opposite sites of the  $\text{C}=\text{N}$  bond, showing an  $E$  configuration. The hydroxy, imino and water H atoms are engaged in extensive hydrogen bonding, forming a three-dimensional network.

## Related literature

For the crystal structure of a related compound, 1-(2,3,4-trihydroxybenzylidene)-4-ethylthiosemicarbazide, see: Shawish *et al.* (2010).



## Experimental

## Crystal data

$\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_3\text{S}\cdot 2\text{H}_2\text{O}$   
 $M_r = 291.33$   
 Monoclinic,  $P2_1$   
 $a = 4.6645$  (4) Å  
 $b = 10.4006$  (9) Å  
 $c = 13.5381$  (11) Å  
 $\beta = 98.674$  ( $1^\circ$ )

$V = 649.27$  (10) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.27$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.30 \times 0.20 \times 0.10$  mm

## Data collection

Bruker SMART APEX  
 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.923$ ,  $T_{\max} = 0.973$

6232 measured reflections  
 2937 independent reflections  
 2826 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.074$   
 $S = 1.03$   
 2937 reflections  
 208 parameters  
 12 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.19$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983), 1370 Friedel pairs  
 Flack parameter:  $-0.05$  (6)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1o}\cdots\text{N1}$	0.85 (1)	1.99 (2)	2.722 (2)	144 (2)
$\text{O2}-\text{H2o}\cdots\text{O1}^i$	0.83 (1)	2.27 (2)	2.955 (2)	140 (2)
$\text{O3}-\text{H3o}\cdots\text{O1W}$	0.85 (2)	1.76 (2)	2.598 (2)	174 (2)
$\text{O1w}-\text{H11}\cdots\text{O2w}$	0.84 (1)	1.94 (1)	2.785 (2)	177 (3)
$\text{O1w}-\text{H12}\cdots\text{O3}^{ii}$	0.84 (1)	2.22 (1)	3.002 (2)	155 (2)
$\text{O2w}-\text{H21}\cdots\text{S1}^{iii}$	0.84 (1)	2.45 (1)	3.279 (1)	169 (2)
$\text{O2w}-\text{H22}\cdots\text{S1}^{iv}$	0.84 (1)	2.49 (1)	3.292 (1)	162 (2)
$\text{N2}-\text{H2n}\cdots\text{O2w}^v$	0.86 (1)	2.13 (1)	2.965 (2)	166 (2)
$\text{N3}-\text{H3n}\cdots\text{O2}^{vi}$	0.86 (1)	2.26 (2)	2.934 (2)	136 (2)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

We thank the University of Malaya (PS354/2009) and MOHE (FRGS-FP001/2009) for supporting this study. HBS also thanks the Libyan People's Bureau in Malaysia for a scholarship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5011).

## References

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**supplementary materials**

*Acta Cryst.* (2010). E66, o2230 [ doi:10.1107/S1600536810030783 ]

## (E)-1-(2,4,6-Trihydroxybenzylidene)-4-ethylthiosemicarbazide dihydrate

H. B. Shawish, K. W. Tan, M. J. Maah and S. W. Ng

### Experimental

2,4,6-Trihydroxybenzaldehyde (1.54 g, 10 mmol) and 4-ethylthiosemicarbazide (1.19 g, 1 mmol) were heated in ethanol (20 ml) for 2 h; acetic acid (0.5 ml) was also added. A brown solid separated from the cool solution; this was recrystallized from methanol.

### Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 to 0.99 Å) and were included in the refinement in the riding model approximation, with  $U(\text{H})$  set to 1.2 to 1.5 $U(\text{C})$ .

The imino H and hydroxy H atoms were located in a difference Fourier map, and were refined with distance restraints of N—H 0.86±0.01 and O—H 0.84±0.01 Å; their temperature factors were freely refined.

### Figures

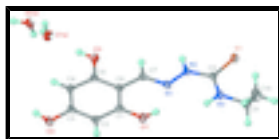


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of  $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_3\text{S}\cdot 2\text{H}_2\text{O}$  at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

## (E)-1-(2,4,6-Trihydroxybenzylidene)-4-ethylthiosemicarbazide dihydrate

### Crystal data

$\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_3\text{S}\cdot 2\text{H}_2\text{O}$

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Monoclinic,  $P2_1$

Hall symbol: P 2yb

$a = 4.6645$  (4) Å

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$c = 13.5381$  (11) Å

$\beta = 98.674$  (1)°

$V = 649.27$  (10) Å<sup>3</sup>

$Z = 2$

$F(000) = 308$

$D_x = 1.490$  Mg m<sup>-3</sup>

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

Cell parameters from 3449 reflections

$\theta = 2.5$ – $28.2$ °

$\mu = 0.27$  mm<sup>-1</sup>

$T = 100$  K

Prism, yellow

$0.30 \times 0.20 \times 0.10$  mm

### Data collection

Bruker SMART APEX  
diffractometer

2937 independent reflections

## supplementary materials

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Radiation source: fine-focus sealed tube  
graphite  
 $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.923$ ,  $T_{\max} = 0.973$   
6232 measured reflections

2826 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 1.5^\circ$   
 $h = -6 \rightarrow 5$   
 $k = -13 \rightarrow 13$   
 $l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.074$   
 $S = 1.03$   
2937 reflections  
208 parameters  
12 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 0.0466P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$   
Absolute structure: Flack (1983), 1370 Friedel pairs  
Flack parameter:  $-0.05$  (6)

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	1.52160 (9)	1.00002 (4)	0.04613 (3)	0.01642 (10)
O1	1.0480 (3)	0.82234 (12)	0.44254 (9)	0.0175 (3)
O2	0.4114 (3)	0.51122 (13)	0.53548 (9)	0.0185 (3)
O3	0.5005 (3)	0.56687 (12)	0.18897 (9)	0.0171 (3)
O1W	0.0357 (3)	0.42702 (13)	0.15044 (10)	0.0204 (3)
O2W	0.0077 (3)	0.21977 (12)	0.01907 (10)	0.0197 (3)
N1	1.1216 (3)	0.83376 (14)	0.24708 (10)	0.0136 (3)
N2	1.2187 (3)	0.87300 (14)	0.16047 (10)	0.0139 (3)
N3	1.5378 (3)	1.01558 (15)	0.24590 (10)	0.0147 (3)
C1	0.8575 (3)	0.72575 (16)	0.41274 (13)	0.0133 (3)
C2	0.7317 (4)	0.66456 (16)	0.48651 (13)	0.0152 (3)
H2	0.7859	0.6873	0.5547	0.018*
C3	0.5256 (4)	0.56959 (17)	0.45936 (12)	0.0149 (3)
C4	0.4389 (4)	0.53585 (15)	0.36022 (12)	0.0142 (3)
H4	0.2932	0.4726	0.3427	0.017*
C5	0.5697 (4)	0.59662 (15)	0.28686 (13)	0.0136 (3)
C6	0.7848 (4)	0.69196 (15)	0.31126 (13)	0.0126 (3)
C7	0.9158 (4)	0.74927 (16)	0.23201 (13)	0.0135 (3)
H7	0.8477	0.7237	0.1652	0.016*
C8	1.4257 (3)	0.96307 (15)	0.15970 (13)	0.0131 (3)
C9	1.7695 (4)	1.11131 (17)	0.25974 (13)	0.0179 (4)

H9A	1.8548	1.1188	0.1973	0.021*
H9B	1.9242	1.0822	0.3133	0.021*
C10	1.6620 (5)	1.24156 (18)	0.28688 (17)	0.0274 (4)
H10A	1.8236	1.3028	0.2953	0.041*
H10B	1.5812	1.2350	0.3495	0.041*
H10C	1.5113	1.2715	0.2335	0.041*
H1O	1.132 (4)	0.846 (2)	0.3945 (12)	0.022 (6)*
H2O	0.280 (4)	0.462 (2)	0.5106 (17)	0.036 (7)*
H3O	0.356 (4)	0.517 (2)	0.1785 (17)	0.029 (6)*
H11	0.024 (5)	0.3659 (19)	0.1092 (18)	0.048 (8)*
H12	-0.122 (4)	0.467 (2)	0.1412 (19)	0.059 (10)*
H21	-0.127 (3)	0.1711 (18)	0.0304 (18)	0.029 (7)*
H22	0.162 (3)	0.178 (2)	0.022 (2)	0.047 (8)*
H2N	1.140 (4)	0.841 (2)	0.1046 (10)	0.020 (5)*
H3N	1.476 (4)	0.9852 (19)	0.2978 (10)	0.014 (5)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.01776 (19)	0.0203 (2)	0.01189 (19)	-0.00408 (18)	0.00442 (14)	0.00107 (17)
O1	0.0181 (6)	0.0191 (6)	0.0151 (6)	-0.0046 (5)	0.0025 (5)	-0.0017 (5)
O2	0.0223 (6)	0.0215 (6)	0.0122 (6)	-0.0044 (6)	0.0042 (5)	0.0020 (5)
O3	0.0195 (6)	0.0208 (6)	0.0113 (6)	-0.0057 (5)	0.0031 (5)	-0.0035 (5)
O1W	0.0173 (7)	0.0228 (7)	0.0204 (7)	-0.0006 (5)	0.0009 (5)	-0.0031 (5)
O2W	0.0190 (7)	0.0185 (7)	0.0215 (7)	-0.0023 (6)	0.0033 (6)	0.0019 (5)
N1	0.0141 (7)	0.0146 (6)	0.0128 (7)	0.0017 (5)	0.0042 (6)	0.0024 (5)
N2	0.0155 (7)	0.0167 (7)	0.0097 (7)	-0.0028 (5)	0.0029 (6)	0.0004 (5)
N3	0.0158 (7)	0.0176 (7)	0.0117 (6)	-0.0026 (6)	0.0052 (5)	-0.0001 (6)
C1	0.0114 (8)	0.0134 (7)	0.0150 (8)	0.0024 (6)	0.0014 (6)	-0.0002 (6)
C2	0.0165 (9)	0.0182 (8)	0.0102 (8)	0.0027 (7)	0.0001 (6)	-0.0001 (6)
C3	0.0168 (8)	0.0146 (8)	0.0142 (8)	0.0038 (7)	0.0057 (6)	0.0033 (6)
C4	0.0139 (8)	0.0136 (8)	0.0153 (8)	-0.0008 (6)	0.0033 (6)	-0.0008 (6)
C5	0.0141 (8)	0.0137 (7)	0.0133 (8)	0.0026 (6)	0.0033 (6)	0.0004 (6)
C6	0.0115 (8)	0.0129 (7)	0.0137 (8)	0.0025 (6)	0.0027 (6)	0.0011 (6)
C7	0.0150 (8)	0.0141 (8)	0.0115 (8)	0.0028 (6)	0.0020 (6)	0.0000 (6)
C8	0.0118 (8)	0.0134 (7)	0.0146 (8)	0.0019 (6)	0.0033 (6)	0.0020 (6)
C9	0.0164 (9)	0.0202 (8)	0.0171 (9)	-0.0032 (7)	0.0031 (7)	-0.0027 (7)
C10	0.0308 (11)	0.0174 (9)	0.0363 (12)	-0.0024 (8)	0.0122 (9)	0.0012 (8)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—C8	1.7085 (17)	N3—H3N	0.86 (1)
O1—C1	1.362 (2)	C1—C2	1.387 (2)
O1—H1O	0.85 (1)	C1—C6	1.409 (2)
O2—C3	1.3710 (19)	C2—C3	1.389 (2)
O2—H2O	0.83 (1)	C2—H2	0.9500
O3—C5	1.352 (2)	C3—C4	1.387 (2)
O3—H3O	0.85 (1)	C4—C5	1.393 (2)
O1W—H11	0.84 (1)	C4—H4	0.9500

## supplementary materials

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O1W—H12	0.84 (1)	C5—C6	1.414 (2)
O2W—H21	0.84 (1)	C6—C7	1.442 (2)
O2W—H22	0.84 (1)	C7—H7	0.9500
N1—C7	1.294 (2)	C9—C10	1.509 (3)
N1—N2	1.3809 (19)	C9—H9A	0.9900
N2—C8	1.346 (2)	C9—H9B	0.9900
N2—H2N	0.86 (1)	C10—H10A	0.9800
N3—C8	1.323 (2)	C10—H10B	0.9800
N3—C9	1.461 (2)	C10—H10C	0.9800
C1—O1—H1O	110.3 (16)	O3—C5—C4	121.98 (15)
C3—O2—H2O	108.4 (17)	O3—C5—C6	116.47 (15)
C5—O3—H3O	111.8 (16)	C4—C5—C6	121.55 (15)
H11—O1W—H12	107.8 (15)	C1—C6—C5	117.44 (15)
H21—O2W—H22	109.8 (15)	C1—C6—C7	123.77 (15)
C7—N1—N2	113.40 (14)	C5—C6—C7	118.80 (15)
C8—N2—N1	122.67 (15)	N1—C7—C6	123.43 (15)
C8—N2—H2N	118.4 (15)	N1—C7—H7	118.3
N1—N2—H2N	118.9 (15)	C6—C7—H7	118.3
C8—N3—C9	125.54 (14)	N3—C8—N2	117.97 (15)
C8—N3—H3N	115.7 (14)	N3—C8—S1	125.35 (13)
C9—N3—H3N	118.6 (14)	N2—C8—S1	116.68 (13)
O1—C1—C2	116.95 (15)	N3—C9—C10	112.11 (15)
O1—C1—C6	121.56 (15)	N3—C9—H9A	109.2
C2—C1—C6	121.46 (15)	C10—C9—H9A	109.2
C1—C2—C3	119.14 (15)	N3—C9—H9B	109.2
C1—C2—H2	120.4	C10—C9—H9B	109.2
C3—C2—H2	120.4	H9A—C9—H9B	107.9
O2—C3—C4	121.71 (16)	C9—C10—H10A	109.5
O2—C3—C2	116.61 (15)	C9—C10—H10B	109.5
C4—C3—C2	121.67 (15)	H10A—C10—H10B	109.5
C3—C4—C5	118.68 (16)	C9—C10—H10C	109.5
C3—C4—H4	120.7	H10A—C10—H10C	109.5
C5—C4—H4	120.7	H10B—C10—H10C	109.5
C7—N1—N2—C8	178.00 (15)	O3—C5—C6—C1	179.15 (15)
O1—C1—C2—C3	176.95 (15)	C4—C5—C6—C1	-1.5 (2)
C6—C1—C2—C3	-1.2 (2)	O3—C5—C6—C7	-0.6 (2)
C1—C2—C3—O2	179.17 (15)	C4—C5—C6—C7	178.74 (15)
C1—C2—C3—C4	-1.1 (2)	N2—N1—C7—C6	178.51 (14)
O2—C3—C4—C5	-178.27 (15)	C1—C6—C7—N1	2.9 (3)
C2—C3—C4—C5	2.0 (2)	C5—C6—C7—N1	-177.42 (15)
C3—C4—C5—O3	178.64 (15)	C9—N3—C8—N2	177.96 (15)
C3—C4—C5—C6	-0.6 (2)	C9—N3—C8—S1	-2.1 (2)
O1—C1—C6—C5	-175.63 (14)	N1—N2—C8—N3	-0.2 (2)
C2—C1—C6—C5	2.5 (2)	N1—N2—C8—S1	179.78 (12)
O1—C1—C6—C7	4.1 (3)	C8—N3—C9—C10	110.57 (19)
C2—C1—C6—C7	-177.80 (15)		

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>
O1—H1o···N1	0.85 (1)	1.99 (2)	2.722 (2)	144 (2)
O2—H2o···O1 <sup>i</sup>	0.83 (1)	2.27 (2)	2.955 (2)	140 (2)
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O2w—H21···S1 <sup>iii</sup>	0.84 (1)	2.45 (1)	3.279 (1)	169 (2)
O2w—H22···S1 <sup>iv</sup>	0.84 (1)	2.49 (1)	3.292 (1)	162 (2)
N2—H2n···O2w <sup>v</sup>	0.86 (1)	2.13 (1)	2.965 (2)	166 (2)
N3—H3n···O2 <sup>vi</sup>	0.86 (1)	2.26 (2)	2.934 (2)	136 (2)

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Fig. 1

