Crystal structure of 4-[(E)-(2-carbamothioylhydrazinylidene)methyl]benzoic acid

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The title compound, $C_9H_9N_3O_2S$, is close to planar with an r.m.s. deviation of 0.032 Å. An intramolecular N—H⋯N hydrogen bond closes an $S(5)$ ring. In the crystal, molecules are connected into inversion dimers of the $R_2^2(8)$ type by pairs of O—H⋯O interactions. The dimers are further connected by pairs of N—H⋯S interactions, which also complete $R_2^2(8)$ ring motifs. The chains of dimers are cross-linked by N—H⋯O bonds and hence $R_4^2(28)$ rings are completed. Taken together, these interactions lead to infinite sheets propagating in the (122) plane.

1. Related literature

For related structures, see: Carballo et al. (2014); Wu et al., (2009).
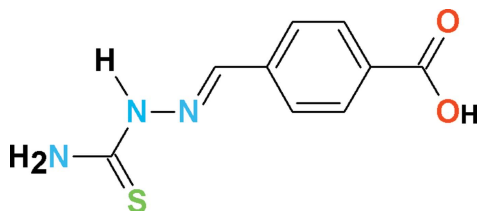
2. Experimental

2.1. Crystal data

$C_9H_9N_3O_2S$
$M_r = 223.25$

Triclinic, $P\bar{1}$
$a = 4.7454 (5)$ Å
$b = 8.5691 (10)$ Å
$c = 13.3886 (15)$ Å
$\alpha = 81.386 (6)°$
$\beta = 82.878 (6)°$
$\gamma = 79.416 (6)°$
$V = 526.52 (10)$ Å^3

$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.29$ mm^{-1}
$T = 296$ K
$0.40 \times 0.22 \times 0.16$ mm

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2005)
$T_{min} = 0.895$, $T_{max} = 0.958$

5971 measured reflections
2286 independent reflections
1566 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.146$
$S = 1.06$
2286 reflections
143 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3B⋯N1	0.86 (3)	2.28 (3)	2.600 (3)	102 (2)
O1—H1⋯O2^i	0.82	1.84	2.653 (2)	170
N2—H2⋯S1^{ii}	0.86	2.53	3.347 (2)	160
N3—H3A⋯O2^{iii}	0.85 (1)	2.14 (2)	2.918 (3)	152 (3)

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014/6 (Sheldrick, 2015); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 2012) and PLATON.

Acknowledgements

References

Bruker (2005). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Carballo, R., Pino-Cuevas, A. & Vázquez-López, E. M. (2014). Acta Cryst. E70, o970.
Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849–854.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Sheldrick, G. M. (2015). Acta Cryst. C71, 3–8.
Spek, A. L. (2009). Acta Cryst. D65, 148–155.
Wu, D.-H., Zhang, Y.-H., Li, Z.-F. & Li, Y.-H. (2009). Acta Cryst. E65, o107.

supporting information

Crystal structure of 4-[(*E*)-(2-carbamothioylhydrazinylidene)methyl]benzoic acid

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S1. Comment

The title compound (I, Fig. 1) has been synthesized for the complexation and other studies. The crystal structures of 2-(4-cyanobenzylidene)hydrazinecarbothioamide (Wu *et al.*, 2009) and 2-(4-formylbenzylidene)hydrazinecarbothioamide (Carballo *et al.*, 2014) have been published which are related to (I).

The heavy atoms of (I) i.e (C1–C9/N1/M2/M3/O1/O2/S1) are almost in a plane. The r. m. s. deviation from the mean square plane is 0.0312 Å. *S* (5) ring motif is present due to intramolecular H-interaction of N–H···N type (Table 1, Fig. 1). The molecules are dimerized due to conventional O–H···O interaction with $R_2^2(8)$ rings (Table 1, Fig. 2). These dimmers are connected from opposite ends due to N–H···S interactions and also complete $R_2^2(8)$ ring motifs. $R_4^2(28)$ rings are completed (Table 1, Fig. 2), when we consider N–H···O and O–H···O contacts (Table 1, Fig. 2). The molecules are overall stabilized in the form of a two dimensional network with base vectors [4 - 1 -1] and [2 - 1 0] in the (1 2 2) plane.

S2. Experimental

Equimolar quantities of 4-formylbenzoic acid and thiosemicarbazide were dissolved separately in methanol and then mixed. The mixture was refluxed for 3 h. The resulting solution was kept at room temperature for crystallization which afforded white needle after 48 h. m.p. 455 K

S3. Refinement

The coordinates of H-atoms of NH$_2$ group were refined with constraints. The other H-atoms were positioned geometrically (C–H = 0.93 Å, N–H = 0.86 Å, O–H = 0.82 Å) and refined as riding with $U_{iso}(H) = xU_{eq}(C, N O)$, where x = 1.5 for hydroxy and NH$_2$ groups and x = 1.2 for other H-atoms.
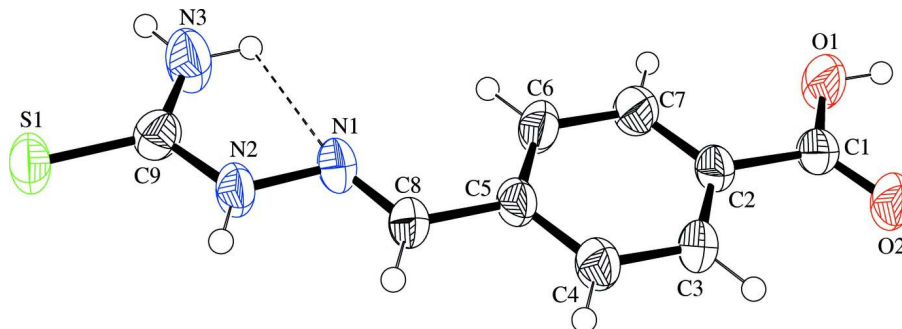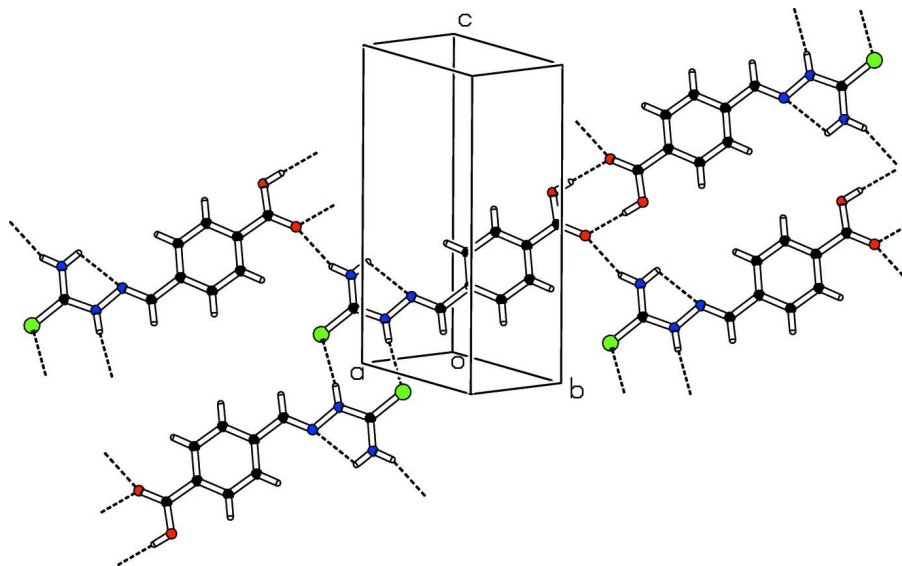

Figure 1

View of the title compound with displacement ellipsoids drawn at the 50% probability level. The dotted line indicate the intramolecular H-interaction.

Figure 2

The partial packing (*PLATON*; Spek, 2009), which shows that molecules are dimerized and form a two-dimensional network with various ring motifs.

4-[(*E*)-(2-Carbamothioylhydrazinylidene)methyl]benzoic acid

Crystal data

$C_9H_9N_3O_2S$	$Z = 2$
$M_r = 223.25$	$F(000) = 232$
Triclinic, $P\bar{1}$	$D_x = 1.408$ Mg m^{-3}
$a = 4.7454$ (5) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 8.5691$ (10) Å	Cell parameters from 1566 reflections
$c = 13.3886$ (15) Å	$\theta = 1.6$–27.0°
$\alpha = 81.386$ (6)°	$\mu = 0.29$ mm^{-1}
$\beta = 82.878$ (6)°	$T = 296$ K
$\gamma = 79.416$ (6)°	Needle, colourless
$V = 526.52$ (10) Å^3	$0.40 \times 0.22 \times 0.16$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer	5971 measured reflections
Radiation source: fine-focus sealed tube	2286 independent reflections
Graphite monochromator	1566 reflections with $I > 2\sigma(I)$
Detector resolution: 7.70 pixels mm^{-1}	$R_{int} = 0.030$
ω scans	$\theta_{max} = 27.0°$, $\theta_{min} = 1.6°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -5 \rightarrow 6$
	$k = -10 \rightarrow 10$
	$l = -17 \rightarrow 17$
$T_{min} = 0.895$, $T_{max} = 0.958$	

Refinement

Refinement on F^2	2286 reflections
Least-squares matrix: full	143 parameters
$R[F^2 > 2\sigma(F^2)] = 0.051$	3 restraints
$wR(F^2) = 0.146$	Primary atom site location: structure-invariant
$S = 1.06$	direct methods

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.105P]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: inferred from neighbouring sites	$(\Delta/\sigma)_{max} < 0.001$
H atoms treated by a mixture of independent and constrained refinement	$\Delta\rho_{max} = 0.55$ e Å^{-3}
	$\Delta\rho_{min} = -0.23$ e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	1.16213 (14)	−0.24283 (8)	0.07250 (5)	0.0516 (3)
O1	−0.7098 (4)	0.3266 (3)	0.50791 (14)	0.0659 (6)
H1	−0.8389	0.3791	0.5417	0.099*
O2	−0.8294 (4)	0.5276 (2)	0.38826 (14)	0.0598 (6)
N1	0.4804 (4)	0.0209 (2)	0.19255 (16)	0.0417 (5)
N2	0.7068 (4)	−0.0327 (2)	0.12477 (16)	0.0426 (5)
H2	0.7307	0.0194	0.0651	0.051*
N3	0.8427 (6)	−0.2352 (3)	0.24762 (19)	0.0635 (7)
H3A	0.951 (6)	−0.321 (3)	0.270 (2)	0.095*
H3B	0.702 (5)	−0.199 (4)	0.289 (2)	0.095*
C1	−0.6710 (5)	0.4042 (3)	0.41755 (19)	0.0443 (6)
C2	−0.4179 (5)	0.3333 (3)	0.35245 (19)	0.0409 (6)
C3	−0.3616 (5)	0.4082 (3)	0.2550 (2)	0.0426 (6)
H3	−0.4830	0.5005	0.2308	0.051*
C4	−0.1243 (5)	0.3456 (3)	0.1935 (2)	0.0434 (6)
H4	−0.0858	0.3969	0.1282	0.052*
C5	0.0572 (4)	0.2066 (3)	0.22859 (19)	0.0380 (6)
C6	−0.0038 (5)	0.1310 (3)	0.3255 (2)	0.0488 (7)
H6	0.1146	0.0372	0.3493	0.059*
C7	−0.2402 (5)	0.1942 (3)	0.3875 (2)	0.0495 (7)
H7	−0.2795	0.1430	0.4527	0.059*
C8	0.3065 (5)	0.1441 (3)	0.16108 (19)	0.0406 (6)
H8	0.3370	0.1949	0.0952	0.049*
C9	0.8922 (5)	−0.1683 (3)	0.15277 (19)	0.0415 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0457 (4)	0.0493 (4)	0.0491 (4)	0.0093 (3)	0.0097 (3)	−0.0059 (3)
O1	0.0503 (11)	0.0888 (16)	0.0404 (11)	0.0235 (10)	0.0101 (8)	−0.0059 (11)

O2	0.0497 (11)	0.0690 (13)	0.0463 (11)	0.0202 (10)	0.0079 (8)	−0.0087 (10)
N1	0.0345 (10)	0.0446 (12)	0.0429 (12)	−0.0032 (9)	0.0093 (9)	−0.0108 (10)
N2	0.0366 (10)	0.0457 (12)	0.0378 (12)	0.0032 (9)	0.0092 (8)	−0.0041 (9)
N3	0.0702 (17)	0.0557 (16)	0.0458 (15)	0.0152 (12)	0.0145 (12)	0.0054 (12)
C1	0.0340 (13)	0.0574 (17)	0.0390 (15)	0.0029 (12)	−0.0009 (10)	−0.0133 (13)
C2	0.0306 (12)	0.0519 (15)	0.0393 (14)	0.0012 (10)	0.0003 (10)	−0.0160 (12)
C3	0.0330 (12)	0.0452 (14)	0.0461 (15)	0.0034 (10)	0.0014 (10)	−0.0115 (12)
C4	0.0381 (13)	0.0483 (15)	0.0402 (14)	−0.0027 (11)	0.0046 (10)	−0.0069 (12)
C5	0.0273 (11)	0.0465 (14)	0.0407 (14)	−0.0036 (10)	0.0014 (9)	−0.0143 (11)
C6	0.0382 (13)	0.0536 (16)	0.0466 (16)	0.0088 (11)	0.0018 (11)	−0.0060 (13)
C7	0.0419 (14)	0.0632 (18)	0.0359 (14)	0.0025 (12)	0.0048 (11)	−0.0039 (13)
C8	0.0324 (12)	0.0458 (14)	0.0406 (14)	0.0007 (10)	0.0023 (10)	−0.0094 (12)
C9	0.0382 (13)	0.0395 (14)	0.0444 (15)	−0.0050 (10)	−0.0033 (10)	−0.0007 (12)

Geometric parameters (Å, º)

S1—C9	1.664 (2)	C2—C3	1.383 (4)
O1—C1	1.299 (3)	C2—C7	1.383 (3)
O1—H1	0.8200	C3—C4	1.383 (3)
O2—C1	1.222 (3)	C3—H3	0.9300
N1—C8	1.268 (3)	C4—C5	1.392 (3)
N1—N2	1.375 (3)	C4—H4	0.9300
N2—C9	1.357 (3)	C5—C6	1.383 (4)
N2—H2	0.8600	C5—C8	1.466 (3)
N3—C9	1.325 (3)	C6—C7	1.386 (3)
N3—H3A	0.853 (10)	C6—H6	0.9300
N3—H3B	0.851 (10)	C7—H7	0.9300
C1—C2	1.484 (3)	C8—H8	0.9300
C1—O1—H1	109.5	C3—C4—H4	119.7
C8—N1—N2	116.9 (2)	C5—C4—H4	119.7
C9—N2—N1	119.5 (2)	C6—C5—C4	119.1 (2)
C9—N2—H2	120.3	C6—C5—C8	122.0 (2)
N1—N2—H2	120.3	C4—C5—C8	118.8 (2)
C9—N3—H3A	120 (2)	C5—C6—C7	120.4 (2)
C9—N3—H3B	124 (2)	C5—C6—H6	119.8
H3A—N3—H3B	116 (3)	C7—C6—H6	119.8
O2—C1—O1	122.6 (2)	C2—C7—C6	120.1 (2)
O2—C1—C2	122.2 (2)	C2—C7—H7	119.9
O1—C1—C2	115.2 (2)	C6—C7—H7	119.9
C3—C2—C7	119.9 (2)	N1—C8—C5	120.0 (2)
C3—C2—C1	118.9 (2)	N1—C8—H8	120.0
C7—C2—C1	121.2 (2)	C5—C8—H8	120.0
C4—C3—C2	119.9 (2)	N3—C9—N2	115.3 (2)
C4—C3—H3	120.0	N3—C9—S1	123.1 (2)
C2—C3—H3	120.0	N2—C9—S1	121.62 (19)
C3—C4—C5	120.5 (2)		

C8—N1—N2—C9	−177.0 (2)	C4—C5—C6—C7	−0.9 (4)
O2—C1—C2—C3	−0.8 (4)	C8—C5—C6—C7	179.5 (2)
O1—C1—C2—C3	179.8 (2)	C3—C2—C7—C6	0.9 (4)
O2—C1—C2—C7	179.5 (3)	C1—C2—C7—C6	−179.5 (2)
O1—C1—C2—C7	0.1 (4)	C5—C6—C7—C2	0.3 (4)
C7—C2—C3—C4	−1.3 (4)	N2—N1—C8—C5	179.0 (2)
C1—C2—C3—C4	179.0 (2)	C6—C5—C8—N1	−2.9 (4)
C2—C3—C4—C5	0.7 (4)	C4—C5—C8—N1	177.6 (2)
C3—C4—C5—C6	0.5 (4)	N1—N2—C9—N3	−2.7 (4)
C3—C4—C5—C8	180.0 (2)	N1—N2—C9—S1	177.48 (17)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
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