organic compounds

3-Hydroxybenzohydrazide

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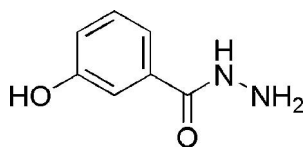Correspondence e-mail: nasimhrama@yahoo.com

The title compound, $C_7H_8N_2O_2$, is an important intermediate for the synthesis of biologically active heterocyclic compounds. The planar hydrazide group is oriented with respect to the benzene ring at a dihedral angle of 25.36 (3)°. In the crystal structure, intermolecular O—H⋯N and N—H⋯O hydrogen bonds link the molecules.

Related literature

For related literature, see: Zheng *et al.* (2003); Al-Talib *et al.* (1990); Yousif *et al.* (1986); Ahmad *et al.* (2001); Al-Soud *et al.* (2004); El-Emam *et al.* (2004); Furniss *et al.* (1978). For bond-length data, see: Allen *et al.* (1987).

Experimental

Crystal data

$C_7H_8N_2O_2$	V = 666.83 (5) Å³
M_r = 152.15	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 5.0420 (2) Å	μ = 0.11 mm^{-1}
b = 17.1970 (7) Å	T = 294 (2) K
c = 7.7020 (4) Å	$0.16 \times 0.14 \times 0.06$ mm
β = 93.113 (4)°	

Data collection

Bruker SMART CCD area-detector diffractometer	8111 measured reflections
	1491 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1299 reflections with $I > 2\sigma(I)$
T_{min} = 0.982, T_{max} = 0.994	R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.100	
S = 1.11	
1491 reflections	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
109 parameters	$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯N2^i	0.82	1.96	2.778 (2)	174
N1—H1A⋯O2^{ii}	0.86	2.10	2.8968 (13)	154
N2—H2A⋯O1^{iii}	0.90 (2)	2.32 (2)	3.192 (2)	162 (2)
N2—H2B⋯O2^{iv}	0.90 (2)	2.18 (2)	3.024 (3)	157 (2)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2378).

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supplementary materials

3-Hydroxybenzohydrazide

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Comment

Aromatic hydrazides are important intermediates in heterocyclic chemistry and have been used for the synthesis of various biologically active five-membered heterocycles such as 2,5-disubstituted-1,3,4-oxadiazoles (Zheng *et al.*, 2003; Al-Talib *et al.*, 1990) and 5-substituted-2-mercapto-1,3,4-oxadiazoles (Yousif *et al.*, 1986; Ahmad *et al.*, 2001; Al-Soud *et al.*, 2004; El-Emam *et al.*, 2004). In view of the versatility of these compounds, we have synthesized the title compound, (I), and reported its crystal structure.

In the molecule of (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The dihedral angle between the planar hydrazidic group (C7/O2/N1/N2) and the benzene ring (C1–C6) is 25.36 (3)°.

In the crystal structure, intermolecular O—H···N and N—H···O hydrogen bonds (Table 1) link the molecules (Fig. 2), in which they seem to be effective in the stabilization of the structure.

Experimental

The title compound, (I), is synthesized by the reaction of methyl ester of 3-hydroxybenzoic acid with hdyrazine hydrate using the reported procedure (Furniss *et al.*, 1978). For the preparation of (I), a mixture of methyl-3 -hydroxybenzoate (1.52 g, 10 mmol) and hydrazine hydrate (80%, 15 ml) in dry methanol (50 ml) was refluxed for 5 h at 413–423 K. The excess solvent was removed by distillation. The solid residue was filtered off, washed with water and recrystallized from ethanol (30%) to give the title compound (yield; 1.80 g, 79%, m.p. 401–402 K). Colorless single crystals of (I) were obtained by slow evaporation of an ethanol solution at room temperature.

Refinement

H atoms of NH$_2$ group were located in difference syntheses and refined isotropically [N—H = 0.090 (2) and 0.090 (2) Å and U_{iso}(H) = 0.031 (5) and 0.031 (5) Å^2]. The remaining H atoms were positioned geometrically, with O—H = 0.82 Å (for OH), N—H = 0.86 Å (for NH) and C—H = 0.93 Å for aromatic H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = $x U_{\text{eq}}$(C,*N*,*O*), where x = 1.5 for OH H, and x = 1.2 for all other H atoms.
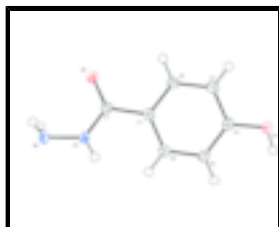
Figures

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
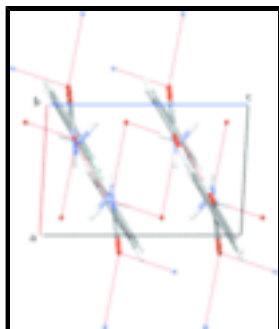
supplementary materials

Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

Fig. 3. The formation of the title compound.

3-Hydroxybenzohydrazide

Crystal data

$C_7H_8N_2O_2$	$F_{000} = 320$
$M_r = 152.15$	$D_x = 1.516$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 401(1) K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 5.0420$ (2) Å	Cell parameters from 1520 reflections
$b = 17.1970$ (7) Å	$\theta = 2.7–24.9º$
$c = 7.7020$ (4) Å	$\mu = 0.11$ mm^{-1}
$\beta = 93.113$ (4)º	$T = 294$ (2) K
$V = 666.83$ (5) Å^3	Block, colourless
$Z = 4$	$0.16 \times 0.14 \times 0.06$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	1491 independent reflections
Radiation source: fine-focus sealed tube	1299 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.055$
$T = 294(2)$ K	$\theta_{max} = 27.5º$
φ and ω scans	$\theta_{min} = 3.6º$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -6\rightarrow5$
$T_{min} = 0.982$, $T_{max} = 0.994$	$k = -22\rightarrow22$
8111 measured reflections	$l = -9\rightarrow9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.2715P]$
	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
1491 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
109 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{iso}*/U_{eq}$
O1	0.7422 (2)	0.04020 (5)	0.85439 (14)	0.0250 (3)
H1	0.6011	0.0290	0.8025	0.037*
O2	1.13499 (17)	0.39014 (5)	0.89833 (12)	0.0194 (2)
N1	0.6959 (2)	0.41043 (6)	0.84771 (15)	0.0178 (3)
H1A	0.5391	0.3906	0.8459	0.021*
N2	0.7238 (2)	0.49140 (6)	0.82153 (17)	0.0206 (3)
H2A	0.861 (4)	0.4977 (10)	0.753 (2)	0.031 (5)*
H2B	0.766 (4)	0.5145 (11)	0.924 (3)	0.031 (5)*
C1	0.8514 (2)	0.27896 (7)	0.87173 (16)	0.0146 (3)
C2	1.0320 (2)	0.22852 (7)	0.95528 (16)	0.0169 (3)
H2	1.1817	0.2486	1.0153	0.020*
C3	0.9927 (3)	0.14896 (7)	0.95055 (17)	0.0190 (3)
H3	1.1137	0.1159	1.0085	0.023*
C4	0.7709 (2)	0.11862 (7)	0.85847 (17)	0.0171 (3)
C5	0.5897 (2)	0.16851 (7)	0.77215 (17)	0.0183 (3)
H5	0.4424	0.1485	0.7094	0.022*
C6	0.6307 (2)	0.24800 (7)	0.78055 (17)	0.0177 (3)
H6	0.5085	0.2812	0.7243	0.021*
C7	0.9070 (2)	0.36367 (7)	0.87529 (16)	0.0146 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0232 (5)	0.0136 (5)	0.0374 (6)	−0.0004 (3)	−0.0059 (4)	−0.0006 (4)
O2	0.0136 (4)	0.0167 (4)	0.0277 (5)	−0.0020 (3)	−0.0015 (3)	−0.0019 (4)

N1	0.0131 (5)	0.0124 (5)	0.0277 (6)	−0.0015 (4)	0.0000 (4)	0.0004 (4)
N2	0.0195 (5)	0.0114 (5)	0.0308 (7)	0.0006 (4)	−0.0005 (5)	−0.0004 (4)
C1	0.0150 (6)	0.0148 (6)	0.0141 (6)	−0.0002 (4)	0.0029 (4)	−0.0010 (4)
C2	0.0149 (6)	0.0185 (6)	0.0170 (6)	−0.0005 (4)	−0.0018 (4)	−0.0011 (4)
C3	0.0185 (6)	0.0182 (6)	0.0200 (7)	0.0031 (5)	−0.0018 (5)	0.0008 (5)
C4	0.0187 (6)	0.0137 (6)	0.0191 (6)	−0.0006 (4)	0.0031 (5)	−0.0015 (4)
C5	0.0153 (6)	0.0170 (6)	0.0222 (7)	−0.0020 (4)	−0.0021 (5)	−0.0030 (5)
C6	0.0152 (6)	0.0169 (6)	0.0207 (6)	0.0015 (5)	−0.0020 (5)	0.0004 (5)
C7	0.0151 (5)	0.0152 (6)	0.0136 (6)	−0.0007 (4)	0.0009 (4)	−0.0011 (4)

Geometric parameters (Å, °)

O2—C7	1.2404 (15)	C3—C4	1.3929 (18)
O1—C4	1.3565 (15)	C3—H3	0.9300
O1—H1	0.8200	N2—H2A	0.90 (2)
C1—C6	1.3895 (17)	N2—H2B	0.90 (2)
C1—C2	1.3900 (17)	C5—C6	1.3834 (17)
C1—C7	1.4834 (16)	C5—C4	1.3951 (18)
N1—C7	1.3416 (16)	C5—H5	0.9300
N1—N2	1.4151 (15)	C2—H2	0.9300
N1—H1A	0.8600	C6—H6	0.9300
C3—C2	1.3828 (17)		
C4—O1—H1	109.5	N1—N2—H2B	109.3 (12)
C6—C1—C2	118.78 (11)	H2A—N2—H2B	108.0 (17)
C6—C1—C7	122.07 (11)	C6—C5—C4	119.55 (11)
C2—C1—C7	119.08 (11)	C6—C5—H5	120.2
C7—N1—N2	121.86 (10)	C4—C5—H5	120.2
C7—N1—H1A	119.1	C3—C2—C1	121.05 (11)
N2—N1—H1A	119.1	C3—C2—H2	119.5
C2—C3—C4	119.61 (11)	C1—C2—H2	119.5
C2—C3—H3	120.2	O1—C4—C3	117.75 (11)
C4—C3—H3	120.2	O1—C4—C5	122.30 (11)
O2—C7—N1	121.60 (11)	C3—C4—C5	119.94 (11)
O2—C7—C1	122.39 (11)	C5—C6—C1	121.05 (11)
N1—C7—C1	116.00 (10)	C5—C6—H6	119.5
N1—N2—H2A	106.7 (12)	C1—C6—H6	119.5

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯N2[i]	0.82	1.96	2.778 (2)	174
N1—H1A⋯O2[ii]	0.86	2.10	2.8968 (13)	154
N2—H2A⋯O1[iii]	0.90 (2)	2.32 (2)	3.192 (2)	162 (2)
N2—H2B⋯O2[iv]	0.90 (2)	2.18 (2)	3.024 (3)	157 (2)

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

Fig. 1

Fig. 2

Fig. 3

3-hydroxybenzoic acid → CH₃OH / H⁺ → methyl 3-hydroxybenzoate → NH₂-NH₂. H₂O → 3-hydroxybenzohydrazide