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4-Hydroxybenzamide 1,4-dioxane hemisolvate

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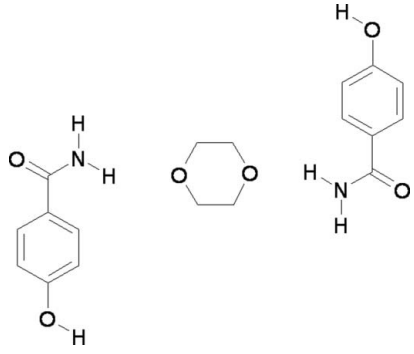
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.039; wR factor = 0.111; data-to-parameter ratio = 12.3.

The asymmetric unit of the title compound, $C_7H_7NO_2\cdot 0.5C_4H_8O_2$, is composed of one 4-hydroxybenzamide molecule and half of a 1,4-dioxane molecule. The complete dioxin molecule is generated by crystallographic inversion symmetry. The crystal has an extensive system of hydrogen bonds, in which the three donor H atoms are fully utilized: these result in amide–amide homodimers, and N—H···O(dioxane) and O—H···O(amide) links.

Related literature

For the structure and properties of 4-hydroxybenzamide and its hydrate, see: Kashino *et al.* (1991); Perlovich *et al.* (2007); Hansen *et al.* (2007).



Experimental

Crystal data

$C_7H_7NO_2\cdot 0.5C_4H_8O_2$
M_r = 181.19
Monoclinic, $P2_1/c$
a = 5.4062 (15) Å
b = 14.530 (3) Å
c = 12.027 (2) Å
β = 113.117 (10)°
V = 868.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 150 K
0.30 × 0.30 × 0.20 mm

Data collection

Rigaku Mercury375R (2x2 bin mode) diffractometer
Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)
T_{min} = 0.969, T_{max} = 0.979
9077 measured reflections
1987 independent reflections
1841 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.111
S = 1.01
1987 reflections
162 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H5···O1^{i}	0.893 (18)	2.050 (18)	2.9349 (16)	170.8 (16)
N1—H6···O3^{ii}	0.895 (19)	2.057 (19)	2.9171 (16)	161 (2)
O2—H9···O1^{iii}	0.909 (19)	1.78 (2)	2.6808 (14)	173 (2)

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

Data collection: *CrystalClear-SM Expert* (Rigaku, 2009); cell refinement: *CrystalClear-SM Expert*; data reduction: *CrystalClear-SM Expert*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1999); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2064).

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supporting information

Acta Cryst. (2012). E**68**, o2661 [doi:10.1107/S160053681203437X]

4-Hydroxybenzamide 1,4-dioxane hemisolvate

Srinu Tothadi and Gautam R. Desiraju

S1. Comment

Hydroxybenzamides and their derivates are extensively used as starting materials in the synthesis of fine chemicals and agrochemicals (Perlovich *et al.*, 2007). Their physicochemical properties are recurrently studied in environmental and biological systems in descriptions of transport and metabolism. The molecular structure of the title compound is shown in Figure 1. In the solvated crystal, molecules are linked by amide···amide homodimers and other O—H···O and N—H···O synthons. The dioxane molecules form a channel along the *a* axis. Their position in the channel is stabilized by N—H···O hydrogen-bonded synthons (Figure 2).

S2. Experimental

Crystals of the title compound were obtained by slow evaporation of a saturated solution of 4-hydroxybenzamide in 1,4-dioxane at ambient temperature. Good diffraction quality crystals were obtained after five days.

S3. Refinement

All hydrogen atoms were located from difference Fourier maps and refined isotropically.

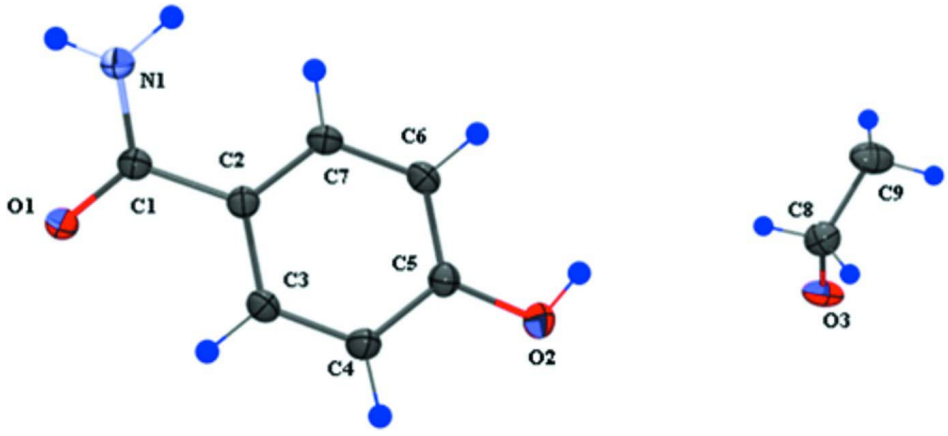

Figure 1

The structure of title the compound with atom labels and 50% probability displacement ellipsoids.

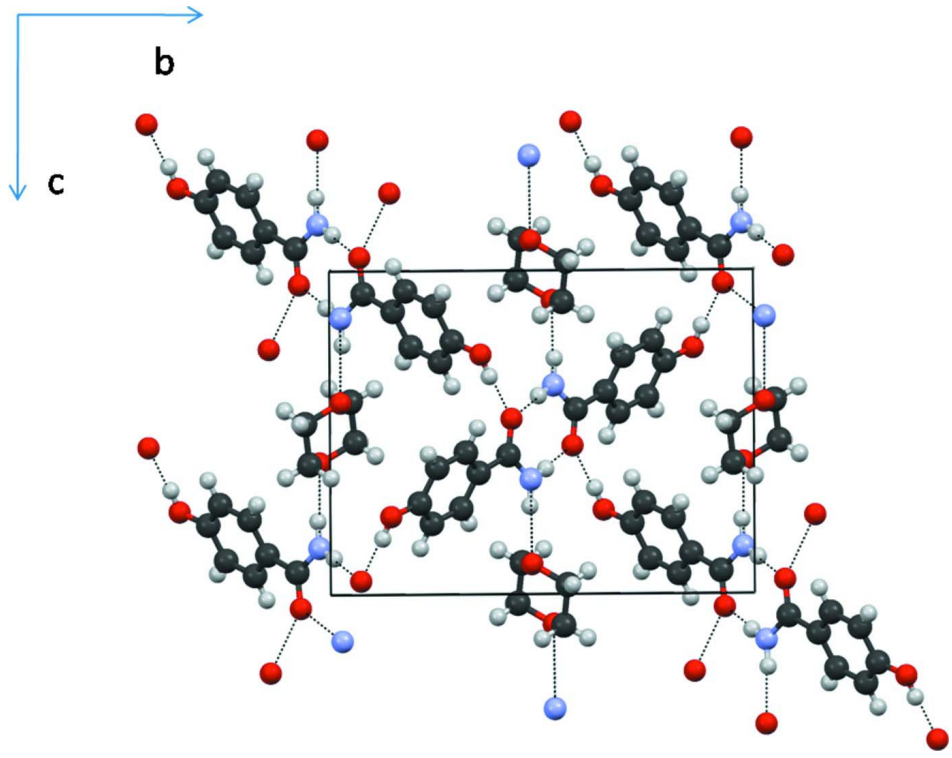

Figure 2

O—H···O, N—H···O supramolecular synthons and amide···amide homodimers in the crystal structure.

4-Hydroxybenzamide 1,4-dioxane hemisolvate

Crystal data

$C_7H_7NO_2·0.5C_4H_8O_2$
$M_r = 181.19$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 5.4062$ (15) Å
$b = 14.530$ (3) Å
$c = 12.027$ (2) Å
$\beta = 113.117$ (10)°
$V = 868.9$ (3) Å^3
$Z = 4$
$F(000) = 384$
$D_x = 1.385$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2599 reflections
$\theta = 3.4$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 150$ K
Block, colourless
0.30 × 0.30 × 0.20 mm

Data collection

Rigaku Mercury375R (2x2 bin mode) diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
profile data from ω–scans
Absorption correction: multi-scan (REQAB; Jacobson, 1998)
$T_{min} = 0.969$, $T_{max} = 0.979$
9077 measured reflections
1987 independent reflections
1841 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
$h = -7\rightarrow7$
$k = -18\rightarrow18$
$l = -15\rightarrow15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.111$
$S = 1.01$
1987 reflections
162 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 0.2987P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.028$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.80614 (16)	0.92851 (6)	1.04228 (7)	0.0225 (2)
O2	1.18374 (17)	0.64369 (6)	0.74199 (8)	0.0260 (3)
N1	0.5317 (2)	0.97339 (7)	0.85611 (9)	0.0239 (3)
C1	0.7279 (2)	0.92062 (7)	0.93018 (10)	0.0188 (3)
C2	0.8467 (2)	0.85033 (7)	0.87597 (10)	0.0188 (3)
C3	0.6951 (2)	0.80863 (8)	0.76593 (10)	0.0223 (3)
C4	0.8032 (2)	0.73933 (8)	0.71972 (10)	0.0221 (3)
C5	1.0678 (2)	0.71106 (8)	0.78283 (10)	0.0198 (3)
C6	1.2219 (2)	0.75283 (8)	0.89296 (10)	0.0233 (3)
C7	1.1109 (2)	0.82067 (8)	0.93947 (10)	0.0222 (3)
O3	0.24469 (18)	−0.02513 (7)	0.59392 (8)	0.0324 (3)
C8	0.0104 (3)	0.04862 (11)	0.40326 (13)	0.0355 (4)
C9	0.2203 (3)	0.05905 (9)	0.52870 (12)	0.0294 (4)
H5	0.442 (3)	1.0084 (12)	0.8887 (15)	0.033 (4)*
H6	0.481 (4)	0.9703 (13)	0.7759 (17)	0.043 (5)*
H7	1.217 (3)	0.8496 (11)	1.0151 (15)	0.032 (4)*
H8	1.405 (3)	0.7330 (11)	0.9349 (14)	0.032 (4)*
H9	1.060 (4)	0.6223 (13)	0.6709 (17)	0.047 (5)*
H10	0.693 (3)	0.7102 (11)	0.6426 (14)	0.029 (4)*
H11	0.513 (3)	0.8257 (11)	0.7213 (14)	0.030 (4)*
H1	−0.014 (4)	0.1061 (14)	0.3610 (17)	0.052 (5)*
H2	0.071 (4)	−0.0023 (14)	0.3589 (16)	0.044 (5)*
H3	0.173 (3)	0.1079 (13)	0.5718 (15)	0.039 (4)*
H4	0.402 (3)	0.0711 (11)	0.5297 (15)	0.033 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0245 (4)	0.0243 (4)	0.0172 (4)	0.0054 (3)	0.0067 (3)	0.0014 (3)
O2	0.0231 (4)	0.0265 (5)	0.0249 (5)	0.0029 (3)	0.0056 (3)	−0.0086 (3)
N1	0.0250 (5)	0.0264 (5)	0.0184 (5)	0.0079 (4)	0.0066 (4)	0.0017 (4)
C1	0.0186 (5)	0.0185 (5)	0.0189 (5)	−0.0008 (4)	0.0071 (4)	0.0014 (4)
C2	0.0201 (5)	0.0179 (5)	0.0187 (5)	0.0002 (4)	0.0078 (4)	0.0010 (4)
C3	0.0180 (5)	0.0255 (6)	0.0197 (5)	0.0020 (4)	0.0035 (4)	0.0002 (4)
C4	0.0207 (5)	0.0242 (6)	0.0182 (5)	−0.0010 (4)	0.0041 (4)	−0.0030 (4)
C5	0.0209 (5)	0.0181 (5)	0.0207 (5)	−0.0009 (4)	0.0085 (4)	−0.0016 (4)
C6	0.0171 (5)	0.0253 (6)	0.0234 (6)	0.0017 (4)	0.0035 (4)	−0.0037 (4)
C7	0.0198 (5)	0.0236 (6)	0.0195 (5)	−0.0004 (4)	0.0038 (4)	−0.0040 (4)
O3	0.0234 (5)	0.0407 (6)	0.0269 (5)	0.0015 (4)	0.0033 (4)	0.0110 (4)
C8	0.0300 (7)	0.0439 (8)	0.0309 (7)	−0.0002 (6)	0.0103 (5)	0.0147 (6)
C9	0.0267 (6)	0.0254 (6)	0.0347 (7)	−0.0032 (5)	0.0106 (5)	−0.0012 (5)

Geometric parameters (Å, º)

O1—C1	1.2498 (14)	C4—C5	1.3923 (17)
O2—C5	1.3543 (15)	C5—C6	1.3965 (16)
O2—H9	0.909 (19)	C6—C7	1.3814 (17)
O3—C9	1.4309 (17)	C3—H11	0.951 (17)
O3—C8^{i}	1.434 (2)	C4—H10	0.980 (16)
N1—C1	1.3284 (16)	C6—H8	0.962 (17)
N1—H5	0.893 (18)	C7—H7	0.961 (17)
N1—H6	0.895 (19)	C8—C9	1.498 (2)
C1—C2	1.4864 (16)	C8—H1	0.96 (2)
C2—C7	1.3973 (17)	C8—H2	1.04 (2)
C2—C3	1.3924 (16)	C9—H3	0.971 (18)
C3—C4	1.3854 (17)	C9—H4	0.993 (18)
O1···C5^{ii}	3.3571 (17)	C9···H4^{xiv}	3.060 (17)
O1···N1^{iii}	2.9349 (16)	C9···H6^{vi}	3.033 (19)
O1···C1^{iv}	3.2567 (17)	H1···C3^{xii}	2.98 (2)
O1···O2^{ii}	2.6808 (14)	H1···C4^{xii}	2.86 (2)
O1···C4^{ii}	3.2448 (17)	H2···H3^{i}	2.38 (3)
O2···O1^{v}	2.6808 (14)	H2···O2^{xv}	2.69 (2)
O3···O3^{i}	2.8184 (16)	H3···H2^{i}	2.38 (3)
O3···N1^{vi}	2.9171 (16)	H3···C5^{xvi}	2.964 (18)
O1···H7	2.632 (17)	H4···C9^{xiv}	3.060 (17)
O1···H5^{iii}	2.050 (18)	H4···H8^{xvii}	2.54 (2)
O1···H10^{ii}	2.544 (16)	H4···H4^{xiv}	2.55 (2)
O1···H9^{ii}	1.78 (2)	H5···C1^{iii}	2.868 (17)
O2···H2^{vii}	2.69 (2)	H5···H5^{iii}	2.51 (2)
O2···H7^{v}	2.806 (17)	H5···O1^{iii}	2.050 (18)
O3···H11^{vi}	2.721 (16)	H6···C3	2.64 (2)
O3···H6^{vi}	2.057 (19)	H6···C9^{ix}	3.033 (19)

N1···C8^{viii}	3.353 (2)	H6···H11	2.23 (2)
N1···O3^{ix}	2.9171 (16)	H6···C8^{viii}	2.70 (2)
N1···O1^{iii}	2.9349 (16)	H6···O3^{ix}	2.057 (19)
N1···H11	2.668 (16)	H7···O1	2.632 (17)
C1···O1^{iv}	3.2567 (17)	H7···O2^{ii}	2.806 (17)
C1···C1^{iv}	3.5941 (19)	H7···H10^{xviii}	2.58 (2)
C1···C6^{x}	3.5589 (19)	H7···H9^{ii}	2.38 (3)
C3···C6^{x}	3.5503 (19)	H8···H4^{xix}	2.54 (2)
C4···O1^{v}	3.2448 (17)	H8···H10^{xviii}	2.51 (2)
C5···O1^{v}	3.3571 (17)	H9···O1^{v}	1.78 (2)
C6···C1^{xi}	3.5589 (19)	H9···H10	2.27 (3)
C6···C3^{xi}	3.5503 (19)	H9···H7^{v}	2.38 (3)
C8···N1^{viii}	3.353 (2)	H9···C1^{v}	2.813 (19)
C1···H5^{iii}	2.868 (17)	H9···C7^{v}	3.02 (2)
C1···H9^{ii}	2.813 (19)	H10···H7^{xx}	2.58 (2)
C3···H1^{xii}	2.98 (2)	H10···H8^{xx}	2.51 (2)
C3···H6	2.64 (2)	H10···H9	2.27 (3)
C4···H1^{xii}	2.86 (2)	H10···O1^{v}	2.544 (16)
C5···H3^{xiii}	2.964 (18)	H11···H6	2.23 (2)
C7···H9^{ii}	3.02 (2)	H11···O3^{ix}	2.721 (16)
C8···H6^{viii}	2.70 (2)	H11···N1	2.668 (16)

C5—O2—H9	108.3 (14)	C4—C3—H11	118.0 (10)
C8^{i}—O3—C9	109.51 (11)	C5—C4—H10	120.1 (10)
H5—N1—H6	120.9 (17)	C3—C4—H10	119.9 (10)
C1—N1—H5	117.6 (11)	C5—C6—H8	118.4 (9)
C1—N1—H6	121.3 (14)	C7—C6—H8	121.5 (9)
N1—C1—C2	118.11 (10)	C2—C7—H7	119.0 (10)
O1—C1—N1	120.89 (10)	C6—C7—H7	120.2 (10)
O1—C1—C2	120.98 (10)	O3^{i}—C8—C9	110.84 (12)
C1—C2—C7	119.81 (10)	O3—C9—C8	109.64 (12)
C3—C2—C7	118.63 (10)	C9—C8—H1	109.7 (12)
C1—C2—C3	121.43 (10)	C9—C8—H2	108.8 (11)
C2—C3—C4	120.93 (11)	H1—C8—H2	110.7 (16)
C3—C4—C5	120.04 (10)	O3^{i}—C8—H1	106.6 (14)
O2—C5—C4	122.57 (10)	O3^{i}—C8—H2	110.1 (12)
C4—C5—C6	119.44 (11)	O3—C9—H3	108.6 (10)
O2—C5—C6	118.00 (10)	O3—C9—H4	105.4 (9)
C5—C6—C7	120.13 (11)	C8—C9—H3	111.0 (10)
C2—C7—C6	120.80 (10)	C8—C9—H4	112.6 (10)
C2—C3—H11	121.1 (10)	H3—C9—H4	109.4 (14)

C9—O3—C8^{i}—C9^{i}	58.92 (14)	C3—C2—C7—C6	1.44 (17)
C8^{i}—O3—C9—C8	−58.20 (15)	C2—C3—C4—C5	−0.65 (18)
N1—C1—C2—C3	−30.42 (16)	C3—C4—C5—C6	0.29 (17)
N1—C1—C2—C7	153.69 (11)	C3—C4—C5—O2	180.00 (13)
O1—C1—C2—C7	−27.88 (16)	O2—C5—C6—C7	−178.77 (11)
O1—C1—C2—C3	148.02 (11)	C4—C5—C6—C7	0.93 (17)

C1—C2—C7—C6	177.45 (10)	C5—C6—C7—C2	−1.81 (18)
C1—C2—C3—C4	−176.15 (11)	O3^{i}—C8—C9—O3	58.99 (16)
C7—C2—C3—C4	−0.21 (17)		

Symmetry codes: (i) −*x*, −*y*, −*z*+1; (ii) *x*, −*y*+3/2, *z*+1/2; (iii) −*x*+1, −*y*+2, −*z*+2; (iv) −*x*+2, −*y*+2, −*z*+2; (v) *x*, −*y*+3/2, *z*−1/2; (vi) *x*, *y*−1, *z*; (vii) *x*+1, −*y*+1/2, *z*+1/2; (viii) −*x*, −*y*+1, −*z*+1; (ix) *x*, *y*+1, *z*; (x) *x*−1, *y*, *z*; (xi) *x*+1, *y*, *z*; (xii) −*x*+1, −*y*+1, −*z*+1; (xiii) −*x*+1, *y*+1/2, −*z*+3/2; (xiv) −*x*+1, −*y*, −*z*+1; (xv) *x*−1, −*y*+1/2, *z*−1/2; (xvi) −*x*+1, *y*−1/2, −*z*+3/2; (xvii) −*x*+2, *y*−1/2, −*z*+3/2; (xviii) *x*+1, −*y*+3/2, *z*+1/2; (xix) −*x*+2, *y*+1/2, −*z*+3/2; (xx) *x*−1, −*y*+3/2, *z*−1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H5···O1^{iii}	0.893 (18)	2.050 (18)	2.9349 (16)	170.8 (16)
N1—H6···O3^{ix}	0.895 (19)	2.057 (19)	2.9171 (16)	161 (2)
O2—H9···O1^{v}	0.909 (19)	1.78 (2)	2.6808 (14)	173 (2)

Symmetry codes: (iii) −*x*+1, −*y*+2, −*z*+2; (v) *x*, −*y*+3/2, *z*−1/2; (ix) *x*, *y*+1, *z*.