Benzoic acid–2-{(E)-[(E)-2-(2-pyridyl-methylidene)hydrazin-1-ylidene]methyl}-pyridine (2/1)

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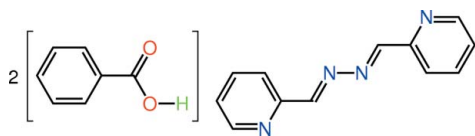
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The asymmetric unit of the title cocrystal, $C_{12}H_{10}N_4\cdot2C_7H_6O_2$, comprises a single molecule of benzoic acid and one half-molecule of 2-pyridinealdazine situated about a centre of inversion. The carboxyl group is coplanar with the benzene ring to which it is connected [O—C—C—C = −172.47 (12)°] and similarly, the 2-pyridinealdazine molecule is planar (r.m.s. deviation of the 16 non-H atoms = 0.017 Å). In the crystal, molecules are connected into a non-planar three-molecule aggregate [dihedral angle between the benzene and pyridyl ring connected by the hydrogen bond = 61.30 (7)°] with a twisted Z-shape. Layers of 2-pyridinealdazine molecules in the ab plane are sandwiched by benzoic acid molecules being connected by O—H···N and C—H···O interactions, the latter involving the carbonyl O atom so that each benzoic acid molecule links three different 2-pyridinealdazine molecules. Interdigitated layers stack along the c axis.

Related literature

For related studies on co-crystal formation involving the isomeric n-pyridinealdazines, see: Broker et al. (2008); Arman et al. (2010a,b).

Experimental

Crystal data

$C_{12}H_{10}N_4\cdot2C_7H_6O_2$	γ = 97.849 (10)°
M_r = 454.48	V = 556.16 (14) Å³
Triclinic, $P\bar{1}$	Z = 1
a = 4.4509 (7) Å	Mo $K\alpha$ radiation
b = 11.3635 (17) Å	μ = 0.09 mm⁻¹
c = 12.0612 (17) Å	T = 98 K
α = 108.985 (6)°	0.40 × 0.29 × 0.12 mm
β = 99.830 (9)°	

Data collection

Rigaku AFC12/SATURN724 diffractometer	2790 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	1935 independent reflections
T_{min} = 0.759, T_{max} = 1.000	1811 reflections with $I > 2\sigma(I)$
	R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.117	
S = 1.00	
1935 reflections	$\Delta\rho_{max}$ = 0.20 e Å⁻³
158 parameters	$\Delta\rho_{min}$ = −0.23 e Å⁻³
1 restraint	

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1o···N1	0.85 (2)	1.88 (2)	2.7269 (16)	177 (2)
C11—H11···O2[i]	0.95	2.54	3.1811 (19)	125
C12—H12···O2[ii]	0.95	2.59	3.4647 (19)	154

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

Data collection: CrystalClear (Molecular Structure Corporation & Rigaku, 2005); cell refinement: CrystalClear; data reduction: CrystalClear; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2725).

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supplementary materials

Benzoic acid-2-{(*E*)-[(*E*)-2-(2-pyridylmethylidene)hydrazin-1-ylidene]methyl}pyridine (2/1)

H. D. Arman, T. Kaulgud and E. R. T. Tiekink

Comment

Co-crystallization experiments with the isomeric n-pyridinealdazines have led to the characterization of several co-crystals (Broker *et al.*, 2008; Arman *et al.*, 2010*a*; Arman *et al.*, 2010*b*), and in continuation of these studies, the co-crystallization of benzoic acid and 2-pyridinealdazine was investigated. This lead to the isolation of the title 2/1 co-crystal, (I).

The asymmetric unit in (I) comprises a molecule of benzoic acid, Fig. 1, and half a molecule of 2-pyridinealdazine, with the latter disposed about a centre of inversion, Fig. 2. The constituents of (I) are connected by O—H···N hydrogen bonds, Table 1, to generate a centrosymmetric three molecule aggregate, Fig. 3. The benzoic acid molecule is planar as seen in the value of the O1—C1—C2—C3 torsion angle of -172.47 (12) °. Similarly, the 2-pyridinealdazine molecule is planar with the r.m.s. deviation of the 16 non-hydrogen atoms being 0.017 Å. However, the three molecule aggregate is not planar as the benzene ring forms a dihedral angle of 61.30 (7) ° with the pyridyl ring to which it is hydrogen bonded. Overall, when viewed normal to the plane through 2-pyridinealdazine, the aggregate has the shape of a twisted letter *Z*.

In the crystal packing, the 2-pyridinealdazine molecules pack in the *ab* plane with the benzoic acid molecules sandwiching these, Fig. 4. The connections are mediated by the aforementioned O—H···N hydrogen bond as well as C—H···O interactions formed by the carbonyl-O atom; each benzoic acid molecule links three distinct 2-pyridinealdazine molecules. Inter-digitated layers stack along the *c* axis.

Experimental

Yellow crystals of (I) were isolated from the 2/1 co-crystallization of benzoic acid (Sigma Aldrich, 0.24 mmol) and 2-[(*E*)-[(*E*)-2-(pyridin-2-ylmethylidene)hydrazin-1-ylidene]methyl]pyridine (Sigma Aldrich, 0.12 mmol) in ethanol, m. pt. 351–353 K.

IR assignment (cm^{-1}): 2600 (br) ν(O—H); 1691 ν(C=O); 1627 ν(C=N); 1469, 1451, 1416 ν(C–C(aromatic)); 1627 ν(C—N); 777 δ(C—H).

Refinement

C-bound H-atoms were placed in calculated positions (C–H 0.95–0.99 Å) and were included in the refinement in the riding model approximation with U_{iso}(H) set to $1.2U_{eq}$(C). The O-bound H-atom was located in a difference Fourier map and was refined with a distance restraint of O–H 0.84±0.01 Å, and with U_{iso}(H) = $1.5U_{eq}$(O). In the final refinement a low angle reflection evidently effected by the beam stop was omitted, *i.e.* (0 $\bar{1}$ 1).
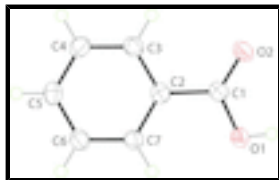
supplementary materials

Figures

Fig. 1. Molecular structure of benzoic acid found in the structure of (I) showing atom-labelling scheme and displacement ellipsoids at the 50% probability level
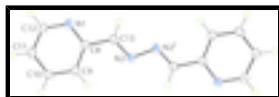

Fig. 2. Molecular structure of 2-pyridinealdazine found in the structure of (I) showing atom-labelling scheme and displacement ellipsoids at the 50% probability level. The molecule is disposed about a centre of inversion and $i = 2 - x, 1 - y, 1 - z$.
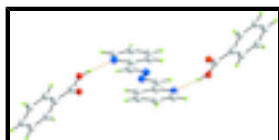

Fig. 3. The three molecule aggregate in (I) highlighting the extended chair conformation. The O—H···N hydrogen bonds are shown as orange dashed lines.
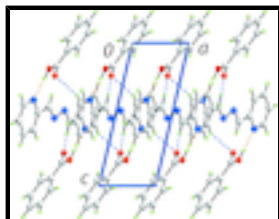

Fig. 4. A view of the supramolecular layer in (I) whereby 2-pyridinealdazine molecules are sandwiched by benzoic acid molecules. The O—H···N hydrogen bonds and C—H···O contacts are shown as orange and blue dashed lines, respectively.
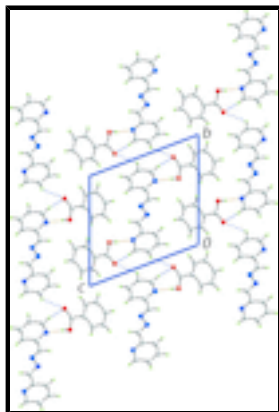
Fig. 5. A view in projection down the a axis showing the stacking of layers comprising three molecule aggregates along c. The O—H···N hydrogen bonds and C—H···O contacts are shown as orange and blue dashed lines, respectively.

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Crystal data

$C_{12}H_{10}N_4 \cdot 2C_7H_6O_2$	$Z = 1$
$M_r = 454.48$	$F(000) = 238$
Triclinic, $P\bar{1}$	$D_x = 1.357$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.4509$ (7) Å	Cell parameters from 2619 reflections
$b = 11.3635$ (17) Å	$\theta = 2.1–40.2°$
$c = 12.0612$ (17) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 108.985$ (6)°	$T = 98$ K
$\beta = 99.830$ (9)°	Block, yellow

$\gamma = 97.849\ (10)°$

$V = 556.16\ (14)\ \text{Å}^3$

0.40 × 0.29 × 0.12 mm

Data collection

Rigaku AFC12K/SATURN724 diffractometer	1935 independent reflections
Radiation source: fine-focus sealed tube	1811 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.022$
ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$h = -5\rightarrow4$
$T_{min} = 0.759$, $T_{max} = 1.000$	$k = -13\rightarrow13$
2790 measured reflections	$l = -14\rightarrow14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.117$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.0744P)^2 + 0.1759P]$ where $P = (F_o^2 + 2F_c^2)/3$
1935 reflections	$(\Delta/\sigma)_{max} < 0.001$
158 parameters	$\Delta\rho_{max} = 0.20$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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	0.6343 (3)	0.67141 (10)	0.18059 (9)	0.0287 (3)
H1o	0.584 (5)	0.692 (2)	0.2479 (12)	0.050 (6)*
O2	0.7598 (3)	0.88248 (10)	0.23009 (9)	0.0315 (3)

C1	0.7523 (3)	0.77587 (13)	0.16270 (12)	0.0235 (3)
C2	0.8828 (3)	0.74881 (14)	0.05272 (12)	0.0227 (3)
C3	1.0455 (3)	0.85068 (14)	0.03269 (13)	0.0278 (4)
H3	1.0702	0.9349	0.0878	0.033*
C4	1.1716 (4)	0.82926 (15)	−0.06766 (14)	0.0311 (4)
H4	1.2846	0.8987	−0.0809	0.037*
C5	1.1331 (4)	0.70640 (15)	−0.14890 (13)	0.0289 (4)
H5	1.2192	0.6919	−0.2178	0.035*
C6	0.9695 (4)	0.60477 (15)	−0.12974 (13)	0.0294 (4)
H6	0.9428	0.5208	−0.1856	0.035*
C7	0.8444 (3)	0.62603 (14)	−0.02863 (13)	0.0263 (3)
H7	0.7326	0.5564	−0.0152	0.032*
N1	0.4834 (3)	0.73022 (11)	0.39929 (10)	0.0214 (3)
N2	0.9261 (3)	0.54922 (10)	0.52702 (10)	0.0211 (3)
C8	0.6169 (3)	0.69350 (12)	0.48783 (12)	0.0190 (3)
C9	0.6033 (3)	0.75148 (13)	0.60760 (12)	0.0219 (3)
H9	0.7002	0.7236	0.6683	0.026*
C10	0.4469 (3)	0.85009 (13)	0.63643 (12)	0.0233 (3)
H10	0.4365	0.8918	0.7175	0.028*
C11	0.3052 (3)	0.88738 (13)	0.54546 (13)	0.0231 (3)
H11	0.1932	0.9541	0.5627	0.028*
C12	0.3304 (3)	0.82529 (13)	0.42883 (13)	0.0230 (3)
H12	0.2344	0.8515	0.3668	0.028*
C13	0.7833 (3)	0.58938 (13)	0.45006 (12)	0.0209 (3)
H13	0.7846	0.5516	0.3674	0.025*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0405 (6)	0.0251 (6)	0.0230 (5)	0.0084 (5)	0.0124 (5)	0.0085 (4)
O2	0.0457 (7)	0.0254 (6)	0.0247 (6)	0.0126 (5)	0.0110 (5)	0.0070 (5)
C1	0.0261 (7)	0.0244 (7)	0.0208 (7)	0.0084 (6)	0.0028 (5)	0.0093 (6)
C2	0.0231 (7)	0.0261 (7)	0.0200 (7)	0.0083 (6)	0.0018 (5)	0.0098 (6)
C3	0.0333 (8)	0.0248 (8)	0.0231 (7)	0.0064 (6)	0.0035 (6)	0.0070 (6)
C4	0.0336 (8)	0.0315 (8)	0.0299 (8)	0.0025 (7)	0.0065 (6)	0.0151 (7)
C5	0.0302 (8)	0.0372 (8)	0.0238 (7)	0.0118 (6)	0.0087 (6)	0.0135 (6)
C6	0.0349 (8)	0.0277 (8)	0.0262 (8)	0.0103 (6)	0.0091 (6)	0.0075 (6)
C7	0.0314 (8)	0.0236 (7)	0.0259 (7)	0.0084 (6)	0.0081 (6)	0.0098 (6)
N1	0.0212 (6)	0.0202 (6)	0.0235 (6)	0.0037 (5)	0.0055 (5)	0.0088 (5)
N2	0.0200 (6)	0.0203 (6)	0.0242 (6)	0.0063 (5)	0.0077 (5)	0.0073 (5)
C8	0.0165 (6)	0.0182 (6)	0.0232 (7)	0.0018 (5)	0.0060 (5)	0.0087 (5)
C9	0.0205 (7)	0.0234 (7)	0.0231 (7)	0.0037 (5)	0.0059 (5)	0.0100 (6)
C10	0.0251 (7)	0.0223 (7)	0.0230 (7)	0.0036 (6)	0.0100 (6)	0.0069 (6)
C11	0.0214 (7)	0.0183 (7)	0.0312 (8)	0.0052 (5)	0.0092 (6)	0.0091 (6)
C12	0.0220 (7)	0.0217 (7)	0.0272 (7)	0.0050 (5)	0.0040 (5)	0.0117 (6)
C13	0.0194 (6)	0.0204 (7)	0.0237 (7)	0.0036 (5)	0.0076 (5)	0.0078 (6)

Geometric parameters (Å, °)

O1—C1	1.3292 (18)	N1—C12	1.3381 (18)
O1—H1o	0.846 (9)	N1—C8	1.3449 (18)
O2—C1	1.2117 (17)	N2—C13	1.2757 (18)
C1—C2	1.496 (2)	N2—N2^i	1.408 (2)
C2—C7	1.388 (2)	C8—C9	1.3949 (19)
C2—C3	1.391 (2)	C8—C13	1.4698 (18)
C3—C4	1.384 (2)	C9—C10	1.380 (2)
C3—H3	0.9500	C9—H9	0.9500
C4—C5	1.388 (2)	C10—C11	1.386 (2)
C4—H4	0.9500	C10—H10	0.9500
C5—C6	1.385 (2)	C11—C12	1.385 (2)
C5—H5	0.9500	C11—H11	0.9500
C6—C7	1.390 (2)	C12—H12	0.9500
C6—H6	0.9500	C13—H13	0.9500
C7—H7	0.9500		
C1—O1—H1o	109.1 (15)	C6—C7—H7	120.0
O2—C1—O1	123.44 (13)	C12—N1—C8	117.83 (12)
O2—C1—C2	123.29 (14)	C13—N2—N2^i	111.87 (13)
O1—C1—C2	113.26 (12)	N1—C8—C9	122.45 (12)
C7—C2—C3	119.91 (13)	N1—C8—C13	115.34 (12)
C7—C2—C1	121.78 (14)	C9—C8—C13	122.20 (12)
C3—C2—C1	118.31 (13)	C10—C9—C8	118.85 (13)
C4—C3—C2	119.96 (14)	C10—C9—H9	120.6
C4—C3—H3	120.0	C8—C9—H9	120.6
C2—C3—H3	120.0	C9—C10—C11	119.04 (12)
C3—C4—C5	120.05 (14)	C9—C10—H10	120.5
C3—C4—H4	120.0	C11—C10—H10	120.5
C5—C4—H4	120.0	C10—C11—C12	118.57 (12)
C6—C5—C4	120.19 (14)	C10—C11—H11	120.7
C6—C5—H5	119.9	C12—C11—H11	120.7
C4—C5—H5	119.9	N1—C12—C11	123.25 (13)
C5—C6—C7	119.84 (14)	N1—C12—H12	118.4
C5—C6—H6	120.1	C11—C12—H12	118.4
C7—C6—H6	120.1	N2—C13—C8	120.75 (12)
C2—C7—C6	120.06 (14)	N2—C13—H13	119.6
C2—C7—H7	120.0	C8—C13—H13	119.6
O2—C1—C2—C7	−173.81 (14)	C12—N1—C8—C9	−0.65 (19)
O1—C1—C2—C7	7.72 (19)	C12—N1—C8—C13	−179.57 (11)
O2—C1—C2—C3	6.0 (2)	N1—C8—C9—C10	0.1 (2)
O1—C1—C2—C3	−172.47 (12)	C13—C8—C9—C10	178.93 (12)
C7—C2—C3—C4	−0.7 (2)	C8—C9—C10—C11	0.8 (2)
C1—C2—C3—C4	179.52 (13)	C9—C10—C11—C12	−1.0 (2)
C2—C3—C4—C5	0.6 (2)	C8—N1—C12—C11	0.4 (2)
C3—C4—C5—C6	−0.2 (2)	C10—C11—C12—N1	0.5 (2)
C4—C5—C6—C7	−0.2 (2)	N2^i—N2—C13—C8	−179.13 (12)

C3—C2—C7—C6	0.3 (2)		N1—C8—C13—N2	178.03 (12)
C1—C2—C7—C6	−179.93 (13)		C9—C8—C13—N2	−0.9 (2)
C5—C6—C7—C2	0.2 (2)			

Symmetry codes: (i) −x+2, −y+1, −z+1.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1o⋯N1	0.85 (2)	1.88 (2)	2.7269 (16)	177 (2)
C11—H11⋯O2[ii]	0.95	2.54	3.1811 (19)	125
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Symmetry codes: (ii) −x+1, −y+2, −z+1; (iii) x−1, y, z.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5