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Form II of adipic acid–nicotinohydrazide (1/2)

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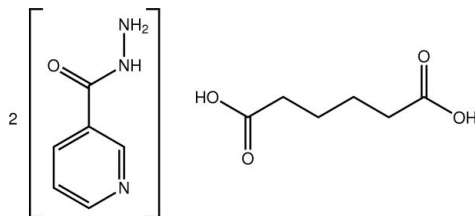
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.029; wR factor = 0.077; data-to-parameter ratio = 12.1.

The crystal structure of the title co-crystal, $2\text{C}_6\text{H}_7\text{N}_3\text{O} \cdot \text{C}_6\text{H}_{10}\text{O}_4$, is a second polymorph, designated form II, of the co-crystal formed between the two molecules [Lemmerer *et al.* (2011). *CrystEngComm*, **13**, 55–59]. The asymmetric unit comprises one molecule of nicotinic acid hydrazide, and one half-molecule of adipic acid (the entire molecule is completed by the application of a centre of inversion). In the crystal, molecules assemble into a three-dimensional network of hydrogen bonds, formed by three $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds and one $\text{O}-\text{H} \cdots \text{N}$ hydrogen bond. The $\text{O}-\text{H} \cdots \text{N}$ hydrogen bond formed between the carboxyl group and the pyridine ring is supported by a $\text{C}-\text{H} \cdots \text{O}$ hydrogen bond.

Related literature

For the first polymorph, see: Lemmerer *et al.* (2011). For experimental techniques, see: Friščić *et al.* (2009); Skovsgaard & Bond (2009); Karki *et al.* (2009). For hydrogen-bonding motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$2\text{C}_6\text{H}_7\text{N}_3\text{O} \cdot \text{C}_6\text{H}_{10}\text{O}_4$
 $M_r = 420.43$
 Monoclinic, $P2_1/c$
 $a = 15.9747$ (4) Å
 $b = 7.3309$ (2) Å

$c = 8.7451$ (2) Å
 $\beta = 103.729$ (3)°
 $V = 994.87$ (4) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.11$ mm⁻¹
 $T = 173$ K

0.32 × 0.28 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby (Gemini ultra Mo) detector
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford

Diffraction, 2006)
 $T_{\min} = 0.92$, $T_{\max} = 0.98$
 6207 measured reflections
 1845 independent reflections
 1487 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.077$
 $S = 1.02$
 1845 reflections
 153 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.14$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{O3}^{\text{i}}$	0.877 (14)	2.174 (15)	3.0409 (14)	169.7 (11)
$\text{N3}-\text{H3A} \cdots \text{O1}^{\text{ii}}$	0.934 (14)	2.129 (14)	3.0349 (14)	163.0 (12)
$\text{N3}-\text{H3B} \cdots \text{O1}^{\text{iii}}$	0.888 (15)	2.258 (16)	3.1426 (14)	173.7 (13)
$\text{O2}-\text{H2} \cdots \text{N2}$	0.950 (19)	1.671 (19)	2.6126 (13)	170.3 (16)
$\text{C2}-\text{H2A} \cdots \text{O3}$	0.95	2.73	3.3838 (14)	126

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5035).

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supporting information

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Form II of adipic acid–nicotinohydrazide (1/2)

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S1. Comment

Form **I** of the title compound was obtained by solution crystallization, where 1 equivalent of adipic acid was dissolved with two equivalents of niazid in methanol, and then the solution left to slowly evaporate over a few days (Lemmerer *et al.*, 2011). The ratio of the two starting materials was determined by the two expected primary hydrogen bond interactions, namely the two carboxylic acids hydrogen bonding to the single pyridine of two niazid molecules. Form **II** was obtained by first grinding the two starting materials in the same stoichiometric ratio as form **I** for 20 minutes, followed by conventional solution crystallization by dissolving the ground powder in methanol. Crystals were obtained after a few days from the methanol solution. Obtaining polymorphs by either grinding or solution crystallization is a focus of recent research (Friščić *et al.*, 2009; Skovsgaard & Bond, 2009; Karki *et al.*, 2009).

The crystallographic asymmetric unit of the resulting crystal structure of form **II** reflects this stoichiometry, containing one niazid molecule in a general position and one half adipic acid molecule on a special position (Fig. 1). The two molecules lie approximately co-planar. The expected heterosynthon is formed between two niazid and one adipic acid molecule lying on a crystallographic center of symmetry (which requires the pyridine ring and carboxylic acid to be co-planar). The heterosynthon between the dicarboxylic acid molecule and the pyridine ring is formed by a O—H \cdots N hydrogen bond, as well as a C—H \cdots O hydrogen bond, to form a $R^2_2(7)$ ring (Bernstein *et al.*, 1995). The niazid molecules are connected by a centrosymmetric $R^2_2(10)$ ring using N—H \cdots O hydrogen bonds from one of the amine H atoms. Adjacent dimers are joined by a N—H \cdots O bond using the second amine H atom, which together with the C—H \cdots O hydrogen bond and the N—H \cdots O hydrogen bond from the amide H forms a $R^2_4(13)$ ring (Fig. 2). Hence, all four H bond donors are used to form a 3-D network. In form **I**, the same $R^2_2(7)$ ring is observed but the amide H atom forms a $C(4)$ chain to form a 2-D sheet, which is then connected into a 3-D network by the amine H atoms hydrogen bonding to adjacent sheets (Lemmerer *et al.*, 2011).

S2. Experimental

A stoichiometric amount in the ratio of 2:1 of nicotinic acid hydrazide to adipic acid was ground together in a mortar with a pestle under the drop-wise addition of methanol over 20 minutes. The resulting powder was then dissolved in 10 ml of AR-grade methanol, and the solution slowly left to evaporate to afford colourless block-like crystals after one week.

S3. Refinement

The C-bound H atoms were geometrically placed (C—H bond lengths of 0.95 (aromatic CH) and 0.99 (methylene CH₂) Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The N-bound and O-bound H atoms were located in the difference map and coordinates refined freely together with their isotropic displacement parameters.

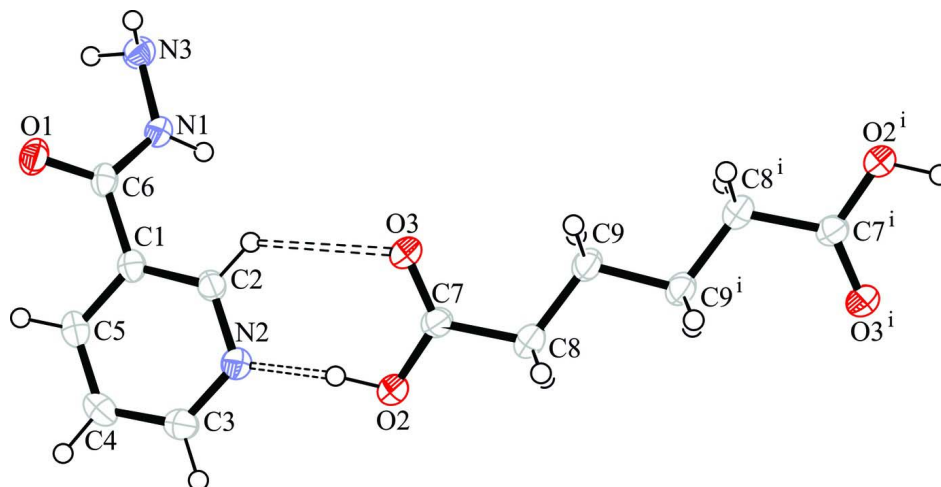


Figure 1

The asymmetric unit of (I) extended to show the entire dicarboxylic acid and showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Symmetry code: (i): $-x, -y, -z$.

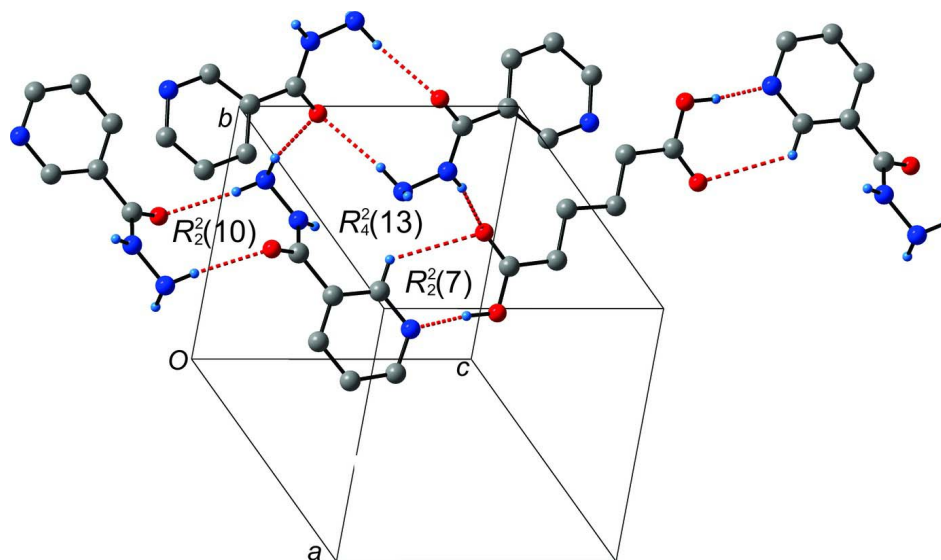


Figure 2

Hydrogen bonding diagram of (I), Form **II**, showing the various ring shaped hydrogen bonding motifs. Intermolecular N—H \cdots N, O—H \cdots N and C—H \cdots O hydrogen bonds are shown as dashed red lines.

adipic acid–nicotinohydrazide (1/2)

Crystal data

$2C_6H_7N_3O \cdot C_6H_{10}O_4$

$M_r = 420.43$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 15.9747(4) \text{ \AA}$

$b = 7.3309(2) \text{ \AA}$

$c = 8.7451(2) \text{ \AA}$

$\beta = 103.729(3)^\circ$

$V = 994.87(4) \text{ \AA}^3$

$Z = 2$

$F(000) = 444$

$D_x = 1.403 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3572 reflections

$\theta = 3.1\text{--}28.5^\circ$

$\mu = 0.11 \text{ mm}^{-1}$

$T = 173$ K
Block, colourless

$0.32 \times 0.28 \times 0.04$ mm

Data collection

Oxford Diffraction Xcalibur
diffractometer with a Ruby (Gemini ultra Mo)
detector

1845 independent reflections
1487 reflections with $I > 2\sigma(I)$

ω scans
Absorption correction: multi-scan
(*CrysAlis PRO*; Oxford Diffraction, 2006)
 $T_{\min} = 0.92$, $T_{\max} = 0.98$
6207 measured reflections

$R_{\text{int}} = 0.020$
 $\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 3.1^\circ$
 $h = -13 \rightarrow 19$
 $k = -8 \rightarrow 8$
 $l = -10 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.077$
 $S = 1.02$
1845 reflections
153 parameters
0 restraints

H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.14 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0095 (18)

Special details

Experimental. Absorption corrections were made using the program *CrysAlis Empirical* absorption correction using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm in *CrysAlisPro*.

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.16016 (7)	0.37907 (15)	0.35826 (13)	0.0237 (3)
C2	0.22411 (7)	0.44813 (15)	0.47997 (13)	0.0248 (3)
H2A	0.2294	0.5767	0.4922	0.03*
C3	0.27134 (8)	0.16066 (15)	0.56223 (15)	0.0296 (3)
H3	0.3105	0.0841	0.6326	0.036*
C4	0.20920 (8)	0.08110 (15)	0.44526 (15)	0.0317 (3)
H4	0.2056	-0.0479	0.4355	0.038*
C5	0.15231 (8)	0.19064 (16)	0.34265 (14)	0.0291 (3)
H5	0.1082	0.1384	0.2622	0.035*
C6	0.09817 (8)	0.49832 (15)	0.24735 (13)	0.0243 (3)
N1	0.13026 (7)	0.65323 (12)	0.20370 (11)	0.0259 (2)
H1	0.1859 (9)	0.6738 (17)	0.2300 (15)	0.030 (3)*
N2	0.27881 (6)	0.34156 (13)	0.58100 (11)	0.0276 (3)
N3	0.07997 (7)	0.77311 (15)	0.09121 (13)	0.0303 (3)
H3A	0.0389 (9)	0.8250 (17)	0.1382 (16)	0.036 (4)*
H3B	0.0508 (9)	0.7022 (19)	0.0145 (18)	0.042 (4)*

O1	0.02225 (5)	0.45309 (11)	0.19861 (10)	0.0327 (2)
C7	0.38377 (7)	0.67377 (15)	0.82289 (13)	0.0259 (3)
C8	0.45756 (8)	0.75709 (16)	0.94010 (16)	0.0352 (3)
H8A	0.5119	0.7085	0.9206	0.042*
H8B	0.4543	0.7172	1.0467	0.042*
C9	0.46178 (7)	0.96301 (15)	0.93861 (14)	0.0281 (3)
H9A	0.4079	1.0133	0.9588	0.034*
H9B	0.466	1.0045	0.833	0.034*
O2	0.39428 (6)	0.49783 (11)	0.80455 (11)	0.0341 (2)
O3	0.32068 (5)	0.75783 (10)	0.75195 (11)	0.0353 (2)
H2	0.3478 (12)	0.449 (2)	0.727 (2)	0.069 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0214 (6)	0.0264 (6)	0.0251 (6)	-0.0031 (5)	0.0090 (5)	-0.0026 (5)
C2	0.0240 (6)	0.0226 (6)	0.0279 (7)	-0.0018 (5)	0.0062 (5)	-0.0018 (5)
C3	0.0293 (7)	0.0270 (7)	0.0342 (7)	0.0028 (5)	0.0105 (6)	0.0043 (5)
C4	0.0374 (8)	0.0216 (6)	0.0387 (7)	-0.0023 (5)	0.0144 (6)	-0.0018 (5)
C5	0.0280 (7)	0.0281 (6)	0.0317 (7)	-0.0065 (5)	0.0083 (5)	-0.0057 (5)
C6	0.0221 (7)	0.0279 (6)	0.0231 (6)	-0.0031 (5)	0.0055 (5)	-0.0062 (4)
N1	0.0207 (6)	0.0276 (6)	0.0280 (6)	-0.0013 (4)	0.0030 (5)	0.0001 (4)
N2	0.0245 (6)	0.0274 (6)	0.0301 (6)	-0.0012 (4)	0.0048 (4)	0.0009 (4)
N3	0.0284 (6)	0.0319 (6)	0.0290 (6)	0.0001 (5)	0.0038 (5)	0.0023 (5)
O1	0.0232 (5)	0.0372 (5)	0.0346 (5)	-0.0062 (4)	0.0010 (4)	0.0019 (4)
C7	0.0228 (7)	0.0276 (7)	0.0266 (6)	0.0012 (5)	0.0042 (5)	0.0027 (5)
C8	0.0291 (7)	0.0348 (8)	0.0350 (7)	0.0021 (5)	-0.0058 (6)	-0.0030 (5)
C9	0.0206 (7)	0.0321 (7)	0.0292 (7)	0.0011 (5)	0.0014 (5)	-0.0023 (5)
O2	0.0296 (5)	0.0276 (5)	0.0382 (6)	0.0027 (4)	-0.0059 (4)	-0.0015 (4)
O3	0.0244 (5)	0.0306 (5)	0.0444 (5)	0.0030 (4)	-0.0047 (4)	0.0000 (4)

Geometric parameters (Å, °)

C1—C2	1.3845 (16)	N1—H1	0.877 (14)
C1—C5	1.3908 (15)	N3—H3A	0.934 (14)
C1—C6	1.4932 (16)	N3—H3B	0.888 (15)
C2—N2	1.3371 (15)	C7—O3	1.2180 (13)
C2—H2A	0.95	C7—O2	1.3154 (13)
C3—N2	1.3382 (15)	C7—C8	1.4965 (17)
C3—C4	1.3747 (18)	C8—C9	1.5113 (16)
C3—H3	0.95	C8—H8A	0.99
C4—C5	1.3744 (17)	C8—H8B	0.99
C4—H4	0.95	C9—C9 ⁱ	1.522 (2)
C5—H5	0.95	C9—H9A	0.99
C6—O1	1.2317 (14)	C9—H9B	0.99
C6—N1	1.3383 (15)	O2—H2	0.950 (19)
N1—N3	1.4178 (14)		

C2—C1—C5	118.13 (10)	C2—N2—C3	118.21 (10)
C2—C1—C6	122.68 (10)	N1—N3—H3A	106.8 (8)
C5—C1—C6	119.16 (10)	N1—N3—H3B	105.7 (9)
N2—C2—C1	122.79 (10)	H3A—N3—H3B	105.8 (12)
N2—C2—H2A	118.6	O3—C7—O2	123.24 (11)
C1—C2—H2A	118.6	O3—C7—C8	124.36 (10)
N2—C3—C4	122.64 (11)	O2—C7—C8	112.40 (10)
N2—C3—H3	118.7	C7—C8—C9	115.55 (10)
C4—C3—H3	118.7	C7—C8—H8A	108.4
C5—C4—C3	119.13 (11)	C9—C8—H8A	108.4
C5—C4—H4	120.4	C7—C8—H8B	108.4
C3—C4—H4	120.4	C9—C8—H8B	108.4
C4—C5—C1	119.08 (11)	H8A—C8—H8B	107.5
C4—C5—H5	120.5	C8—C9—C9 ⁱ	112.33 (12)
C1—C5—H5	120.5	C8—C9—H9A	109.1
O1—C6—N1	122.82 (11)	C9 ⁱ —C9—H9A	109.1
O1—C6—C1	120.92 (10)	C8—C9—H9B	109.1
N1—C6—C1	116.25 (10)	C9 ⁱ —C9—H9B	109.1
C6—N1—N3	122.12 (10)	H9A—C9—H9B	107.9
C6—N1—H1	120.3 (8)	C7—O2—H2	110.9 (10)
N3—N1—H1	116.6 (8)		
C5—C1—C2—N2	0.84 (16)	C5—C1—C6—N1	-143.68 (10)
C6—C1—C2—N2	178.88 (10)	O1—C6—N1—N3	-3.28 (17)
N2—C3—C4—C5	0.17 (17)	C1—C6—N1—N3	175.83 (10)
C3—C4—C5—C1	1.15 (17)	C1—C2—N2—C3	0.45 (15)
C2—C1—C5—C4	-1.61 (15)	C4—C3—N2—C2	-0.97 (15)
C6—C1—C5—C4	-179.73 (10)	O3—C7—C8—C9	-14.84 (18)
C2—C1—C6—O1	-142.57 (11)	O2—C7—C8—C9	165.28 (10)
C5—C1—C6—O1	35.46 (15)	C7—C8—C9—C9 ⁱ	179.74 (12)
C2—C1—C6—N1	38.30 (15)		

Symmetry code: (i) $-x+1, -y+2, -z+2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O3 ⁱⁱ	0.877 (14)	2.174 (15)	3.0409 (14)	169.7 (11)
N3—H3A \cdots O1 ⁱⁱⁱ	0.934 (14)	2.129 (14)	3.0349 (14)	163.0 (12)
N3—H3B \cdots O1 ^{iv}	0.888 (15)	2.258 (16)	3.1426 (14)	173.7 (13)
O2—H2 \cdots N2	0.950 (19)	1.671 (19)	2.6126 (13)	170.3 (16)
C2—H2A \cdots O3	0.95	2.73	3.3838 (14)	126

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