Isonicotinamide–formamide (1/1)

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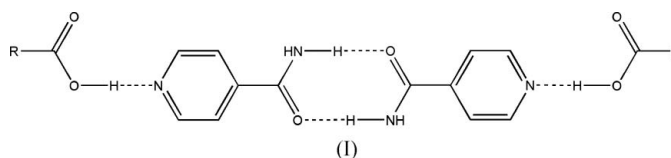
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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.122
Data-to-parameter ratio = 14.9

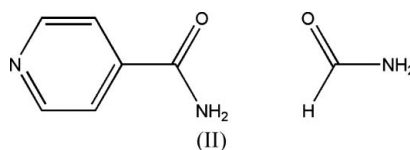For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The 1:1 co-crystal of isonicotinamide and formamide, $C_6H_6N_2O \cdot CH_3NO$, consists of hydrogen-bonded dimers, each comprising two isonicotinamide or two formamide molecules. These dimers are connected further by hydrogen bonds into sheets, which are parallel to the $(\bar{2}11)$ plane.

Comment

Isonicotinamide has been shown to crystallize with carboxylic acids in a 1:1 stoichiometry to form a robust building block or 'supermolecule', (I), consisting of two amide and two acid molecules (Aakeröy *et al.*, 2002; Oswald *et al.*, 2004). Amides contain C=O and C—NH_2 groups that could act in an analogous way to the C=O and C—OH groups of carboxylic acids. The aim of the present investigation was to assess the validity of this analogy in the case of the simplest amide, formamide.

(I)

The title co-crystal, (II), crystallizes in the monoclinic space group $P2_1/c$ with one molecule of each component in the asymmetric unit (Fig. 1). The bond distances and angles are unremarkable.
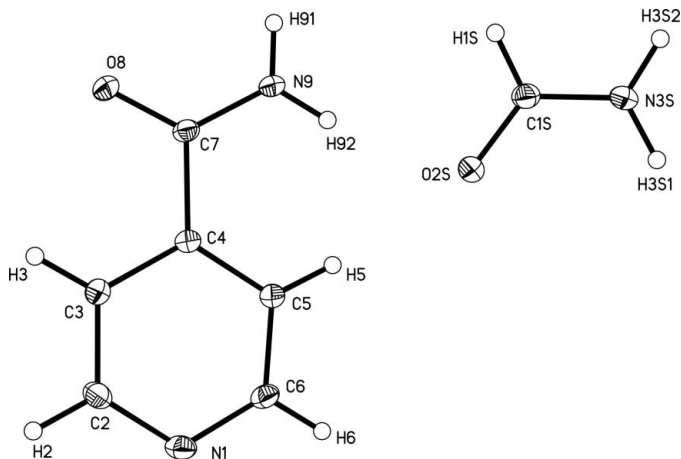

(II)

Amides characteristically form $R_2^2(8)$ (Bernstein *et al.* 1995) centrosymmetric dimers through hydrogen bonding between the NH_2 and C=O groups. This behaviour is observed in (II), where homomeric dimers are formed (i.e. formamide forms a dimer with another formamide *etc.*), the two components in each case being related by crystallographic inversion centres. The N···O distances in the $R_2^2(8)$ dimers are 2.9239 (16) Å in the case of isonicotinamide and 2.9696 (16) Å for formamide.

In co-crystals of carboxylic acids with isonicotinamide, homomeric $R_2^2(8)$ dimers are often formed between the amide groups of the isonicotinamide molecules (Aakeröy *et al.*, 2002). The two pyridyl functions at either end of the nicotinamide dimer so formed hydrogen bond to two carboxylic acid
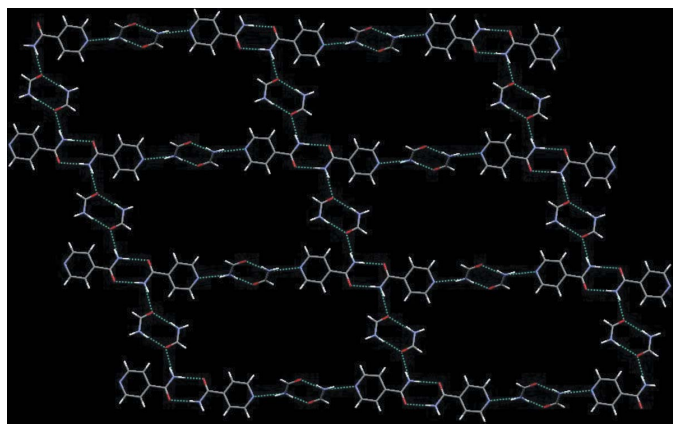
organic papers

Figure 1
The asymmetric unit of (II). Displacement ellipsoids are shown as 30% probability surfaces and H atoms are drawn as circles of arbitrary radii.

Figure 2
Formation of hydrogen-bonded layers in (II); hydrogen bonds are shown as broken lines. This view is approximately along the ($\bar{2}$11) reciprocal lattice direction.

molecules in $R_2^2(7)$ motifs comprising C—OH···N and C—H···O hydrogen bonds. Of these interactions, only the $R_2^2(8)$ dimer formation is observed in (II).

The second donor function of the isonicotinamide forms a hydrogen bond to the carbonyl O atom of the formamide; these interactions build up chains. The chains are linked together through a hydrogen bond between a symmetry-equivalent formamide dimer and the pyridine N atom of the isonicotinamide forming an open grid-like layer parallel to the ($\bar{2}$11) plane (Fig. 2). The second donor function of the formamide molecules serves to link this layer with a symmetry equivalent parallel to ($\bar{2}$11) filling in the structure.

Experimental

Isonicotinamide (0.49 g, 4.02 mmol) was dissolved in an excess of formamide (1.48 g, 32.10 mmol) and warmed until all the solid dissolved. On cooling, long colourless needles were produced, which fractured into thinner shards, degrading the crystal quality, when attempts were made to cut them to a more suitable length.

Crystal data

$C_6H_6N_2O \cdot CH_3NO$	$D_x = 1.405$ Mg m^{-3}
$M_r = 167.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1965
$a = 10.5785$ (18) Å	reflections
$b = 3.7461$ (6) Å	$\theta = 2.7-28°$
$c = 20.002$ (3) Å	$\mu = 0.11$ mm^{-1}
$\beta = 94.587$ (3)°	$T = 150$ (2) K
$V = 790.1$ (2) Å^3	Needle, colourless
$Z = 4$	$1.5 \times 0.14 \times 0.08$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	1860 independent reflections
	1554 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.022$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$\theta_{max} = 28.7°$
	$h = -13 \rightarrow 10$
$T_{min} = 0.663$, $T_{max} = 1.000$	$k = -4 \rightarrow 4$
4454 measured reflections	$l = -23 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 0.1905P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.122$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
1860 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}
125 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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

D—H···A	D—H	H···A	D···A	D—H···A
N3S—H3S2···N1^i	0.92 (2)	2.09 (2)	2.9937 (17)	167 (2)
N3S—H3S1···O2S^{ii}	0.95 (2)	2.03 (2)	2.9696 (16)	172 (2)
N9—H91···O8^{iii}	0.90 (2)	2.03 (2)	2.9239 (16)	172 (2)
N9—H92···O2S	0.89 (2)	2.08 (2)	2.9544 (17)	167 (2)
C5—H5···O2S	0.95	2.35	3.2384 (17)	156

Symmetry codes: (i) $x, -y + \frac{5}{2}, +z - \frac{1}{2}$; (ii) $-x + 2, -y + 3, -z$; (iii) $-x + 1, -y + 1, -z$.

H atoms attached to C atoms were placed in idealized positions (C—H = 0.95 Å) and allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to N atoms were located in a difference map and refined freely.

Data collection: *SMART* (Bruker–Nonius, 2001); temperature control: Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986); cell refinement: *SAINT* (Bruker–Nonius, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001) and *MERCURY* (Taylor & Macrae, 2001; Bruno *et al.*, 2002); software used to prepare material for publication: *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

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supporting information

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S2. Experimental

Isonicotinamide (0.49 g, 4.02 mmol) was dissolved in an excess of formamide (1.48 g, 32.10 mmol) and warmed until all the solid dissolved. On cooling, long colourless needles were produced, which fractured into thinner shards, degrading the crystal quality, when attempts were made to cut them to a more suitable length.

### S3. Refinement

H atoms attached to C atoms were placed in idealized positions (C—H = 0.95 Å) and allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to N atoms were located in a difference map and refined freely.
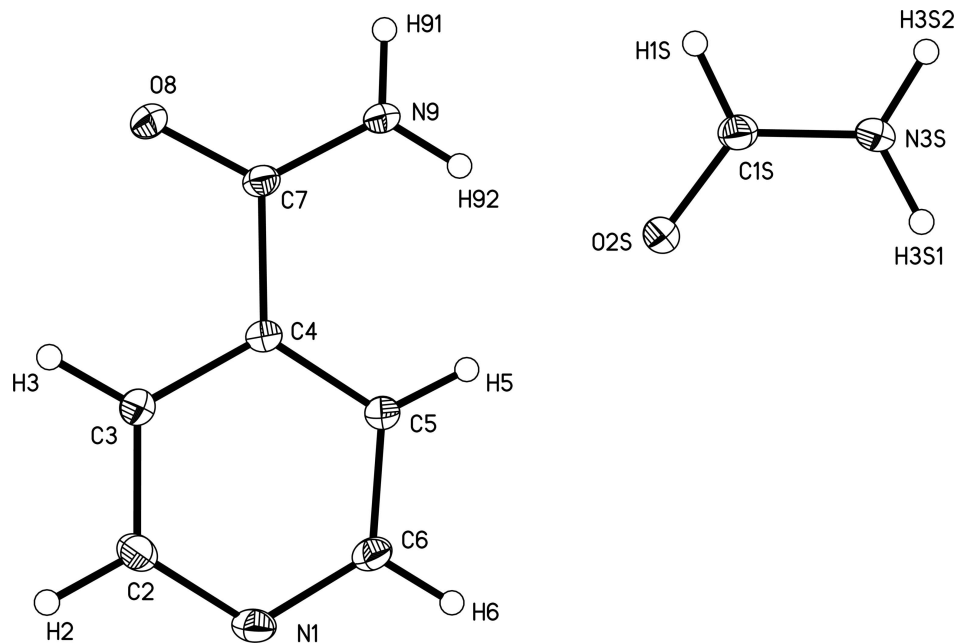
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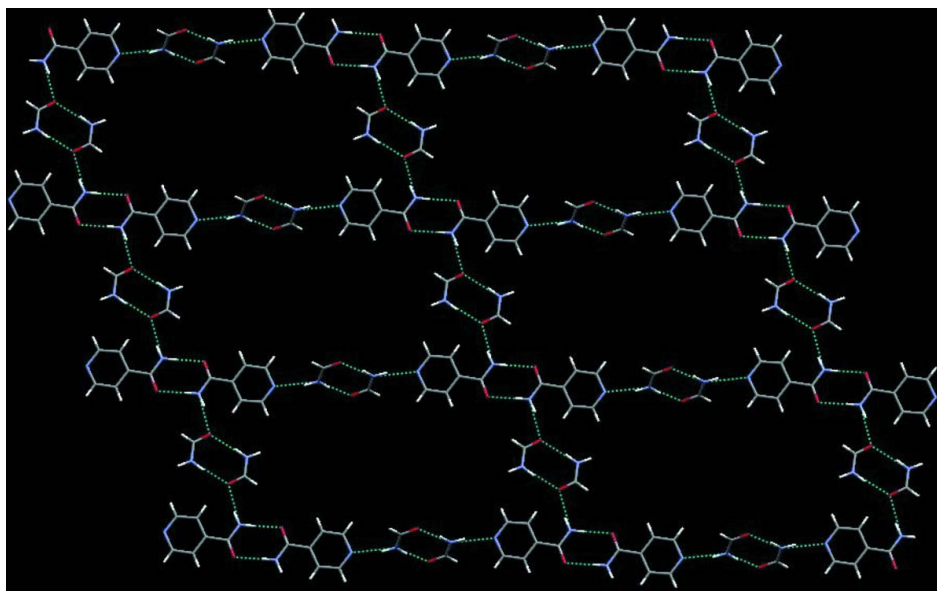
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Formation of hydrogen-bonded layers in (II). This view is approximately along the (−211) reciprocal lattice direction.

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$\beta = 94.587\ (3)°$

$V = 790.1\ (2)$ Å^3

$Z = 4$

$F(000) = 352$

$D_x = 1.405$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1965 reflections

$\theta = 2.7–28°$

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

$T = 150$ K

Needle, colourless

$1.5 \times 0.14 \times 0.08$ mm

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    diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
    (*SADABS*; Sheldrick, 2004)

$T_{min} = 0.663$, $T_{max} = 1.000$

4454 measured reflections

1860 independent reflections

1554 reflections with $I > 2\sigma(I)$

$R_{int} = 0.022$

$\theta_{max} = 28.7°$, $\theta_{min} = 1.9°$

$h = -13\rightarrow10$

$k = -4\rightarrow4$

$l = -23\rightarrow25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.122$

$S = 1.06$

1860 reflections

125 parameters

0 restraints

Primary atom site location: structure-invariant
    direct methods

Secondary atom site location: difference Fourier
    map

Hydrogen site location: geom/difmap

H atoms treated by a mixture of independent
    and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 0.1905P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.31$ e Å^{-3}

$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Experimental. The temperature of the sample was controlled using an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986).

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.82075 (11)	0.8957 (4)	0.27104 (6)	0.0264 (3)
C2	0.70122 (14)	0.7803 (4)	0.27066 (7)	0.0271 (3)
H2	0.6668	0.7416	0.3125	0.033*
C3	0.62479 (13)	0.7142 (4)	0.21249 (7)	0.0234 (3)
H3	0.5404	0.6312	0.2149	0.028*
C4	0.67245 (12)	0.7701 (4)	0.15093 (6)	0.0190 (3)
C5	0.79641 (13)	0.8906 (4)	0.15063 (7)	0.0227 (3)
H5	0.8330	0.9331	0.1095	0.027*
C6	0.86592 (13)	0.9480 (4)	0.21147 (7)	0.0253 (3)
H6	0.9508	1.0293	0.2106	0.030*
C7	0.58927 (13)	0.6842 (4)	0.08820 (7)	0.0206 (3)
O8	0.48915 (9)	0.5197 (3)	0.09317 (5)	0.0292 (3)

N9	0.63022 (12)	0.7882 (4)	0.03055 (6)	0.0242 (3)
H91	0.5893 (19)	0.713 (5)	−0.0082 (10)	0.039 (5)*
H92	0.7035 (18)	0.904 (5)	0.0296 (9)	0.036 (5)*
C1S	0.84255 (13)	1.2871 (4)	−0.05370 (7)	0.0242 (3)
H1S	0.7674	1.2035	−0.0779	0.029*
O2S	0.85676 (9)	1.2164 (3)	0.00663 (5)	0.0283 (3)
N3S	0.92304 (12)	1.4691 (4)	−0.08733 (6)	0.0266 (3)
H3S2	0.9045 (17)	1.512 (5)	−0.1325 (10)	0.038 (5)*
H3S1	0.9983 (19)	1.561 (6)	−0.0645 (10)	0.045 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0260 (6)	0.0316 (7)	0.0207 (6)	0.0011 (5)	−0.0044 (5)	−0.0021 (5)
C2	0.0264 (7)	0.0362 (9)	0.0188 (7)	0.0022 (6)	0.0018 (5)	−0.0009 (6)
C3	0.0190 (6)	0.0296 (8)	0.0217 (7)	−0.0013 (6)	0.0022 (5)	−0.0009 (6)
C4	0.0184 (6)	0.0195 (7)	0.0188 (6)	0.0003 (5)	−0.0011 (5)	−0.0015 (5)
C5	0.0203 (6)	0.0274 (7)	0.0200 (6)	−0.0026 (6)	−0.0007 (5)	0.0020 (6)
C6	0.0198 (6)	0.0296 (8)	0.0256 (7)	−0.0031 (6)	−0.0042 (5)	−0.0002 (6)
C7	0.0182 (6)	0.0236 (7)	0.0197 (6)	−0.0007 (5)	−0.0010 (5)	−0.0040 (5)
O8	0.0228 (5)	0.0414 (7)	0.0231 (5)	−0.0120 (5)	0.0001 (4)	−0.0046 (4)
N9	0.0199 (6)	0.0338 (7)	0.0184 (6)	−0.0064 (5)	−0.0024 (5)	−0.0021 (5)
C1S	0.0209 (7)	0.0285 (8)	0.0226 (7)	−0.0002 (6)	−0.0008 (5)	−0.0004 (6)
O2S	0.0248 (5)	0.0389 (7)	0.0211 (5)	−0.0063 (4)	0.0007 (4)	0.0041 (4)
N3S	0.0259 (6)	0.0350 (7)	0.0184 (6)	−0.0033 (5)	−0.0023 (5)	0.0029 (5)

Geometric parameters (Å, º)

N1—C6	1.3332 (19)	C6—H6	0.9500
N1—C2	1.3357 (19)	C7—O8	1.2363 (17)
C2—C3	1.3851 (19)	C7—N9	1.3224 (18)
C2—H2	0.9500	N9—H91	0.90 (2)
C3—C4	1.3833 (19)	N9—H92	0.890 (19)
C3—H3	0.9500	C1S—O2S	1.2328 (17)
C4—C5	1.3873 (18)	C1S—N3S	1.3167 (19)
C4—C7	1.5086 (17)	C1S—H1S	0.9500
C5—C6	1.3873 (18)	N3S—H3S2	0.923 (19)
C5—H5	0.9500	N3S—H3S1	0.95 (2)
C6—N1—C2	116.70 (11)	N1—C6—H6	118.0
N1—C2—C3	123.46 (13)	C5—C6—H6	118.0
N1—C2—H2	118.3	O8—C7—N9	124.03 (12)
C3—C2—H2	118.3	O8—C7—C4	119.06 (12)
C4—C3—C2	119.39 (13)	N9—C7—C4	116.90 (12)
C4—C3—H3	120.3	C7—N9—H91	119.3 (13)
C2—C3—H3	120.3	C7—N9—H92	120.6 (12)
C3—C4—C5	117.72 (12)	H91—N9—H92	119.6 (17)
C3—C4—C7	118.57 (12)	O2S—C1S—N3S	125.31 (14)

C5—C4—C7	123.67 (12)	O2S—C1S—H1S	117.3
C4—C5—C6	118.78 (13)	N3S—C1S—H1S	117.3
C4—C5—H5	120.6	C1S—N3S—H3S2	119.7 (12)
C6—C5—H5	120.6	C1S—N3S—H3S1	119.6 (12)
N1—C6—C5	123.95 (13)	H3S2—N3S—H3S1	120.7 (17)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
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