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C—H$\cdots$O interactions. The dihedral angle between the planes of adjacent molecules in a chain is 9.77 (7)°. An intramolecular N—H$\cdots$O hydrogen bond is also present.

Comment

This is one of a series of reports on hydrogen bonding in amino-substituted N-heterocyclic carboxylic acids and follows our reports on 3-aminopyrazine-2-carboxylic acid and α- and β-4-aminoquinoline-2-carboxylic acid (Dobson & Gerkin, 1996; Burd, Dobson & Gerkin, 1997). 2-Aminonicotinic acid, (I), crystallized in the centrosymmetric space group $P2_1/c$. In this structure, the molecule occurs as a zwitterion, the carboxyl proton having been transferred to the ring N atom as shown in Fig. 1, which also presents the numbering scheme.

(I)
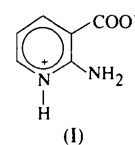
As a consequence, cyclic carboxylic acid group hydrogen-bonded dimers are not possible. However, cyclic hydrogen-bonded dimers are formed which involve the carboxylate group O atoms as acceptors and the ring and amino N atoms as donors. Since in each of these hydrogen-bonded cycles both donors are in one molecule and both acceptors are in a second, the cycles do not occur about centers of symmetry. Since each molecule contains both functionalities, zigzag chains of cyclic hydrogen-bonded molecules can occur and do so, in this case propagating along the b axis as shown in Fig. 2. Two sets of such chains result: one set involves molecules of symmetry types 1 and 2, the

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2-Aminonicotinic Acid

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Abstract

2-Aminonicotinic acid, $C_6H_6N_2O_2$, crystallized in the centrosymmetric space group $P2_1/c$ in the zwitterionic form. Intermolecular N—H$\cdots$O hydrogen bonds with N$\cdots$O distances of 2.652 (2) and 2.807 (2) Å link molecules into two sets of zigzag chains propagating along the b axis. The two sets of chains are crosslinked by
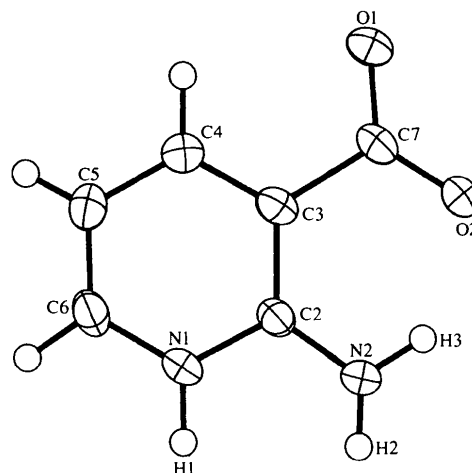
Fig. 1. *ORTEPII* (Johnson, 1976) drawing of 2-aminonicotinic acid showing our numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms for which they have been set artificially small.
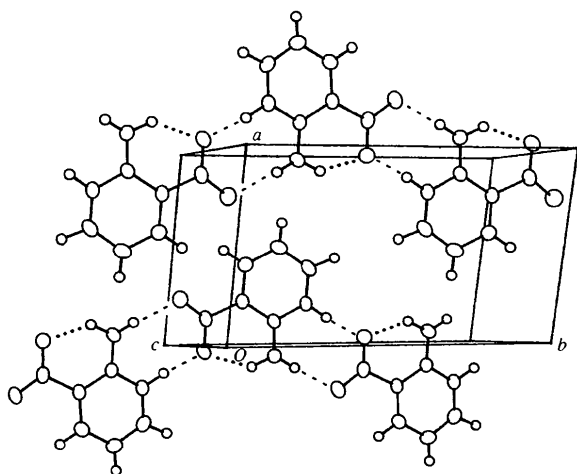
Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of 2-aminonicotinic acid. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms for which they have been set artificially small. Intermolecular hydrogen bonds are shown as dashed lines and intramolecular hydrogen bonds as dotted lines. Note that the cyclic hydrogen bonds shown do not occur about centers of symmetry.

1976), the maximum deviation of a core atom from the best-fit core plane is 0.004 Å, while the dihedral angle between the carboxyl group plane and the core plane is 2.0°. Again the degree of planarity is quite similar to that of the title acid.

Distances and angles of special interest in the title molecule are given in Table 1. In this molecule, the pyridinium C—N—C angle is 122.5 (2)°, considerably larger than the corresponding angles found in the two (inequivalent) pyridinium ions in bis(pyridinium) pamoate, 119.0 (3) and 119.9 (3)° (Blackburn, Dobson & Gerkin, 1996). On the other hand, the carboxylate C—O distances in the present molecule fall within the range of carboxylate C—O distances determined for bis-(pyridinium) pamoate.

The closest intermolecular approach, excluding pairs of atoms within directly hydrogen-bonded groups or C—H···O interactions, is between C4 and C5^v [symmetry code: (v) x, $\frac{1}{2} - y$, $\frac{1}{2} + z$] and is 0.05 Å less than the corresponding Bondi (1964) van der Waals radius sum.

other set involving molecules of symmetry types 3 and 4. These sets are not crosslinked by strong hydrogen bonds but are crosslinked by C—H···O interactions: for the home molecule as donor, these are C4—H4···O1^{ii} (symmetry type 3), C5—H5···O2^{iii} (symmetry type 4) and C6—H6···O1^{iv} (symmetry type 4). In addition to the two intermolecular N—H···O hydrogen bonds forming the cycles, there is a third N—H···O hydrogen bond, which is intramolecular. Geometric details of these bonds are given in Table 2. The results of hydrogen-bond graph set analysis (Bernstein, Davis, Shimoni & Chang, 1995) involving the three N—H···O hydrogen bonds (designated a, b and c, respectively, for this purpose) for the first- and second-level graph sets are presented in Table 3.

The pyridine core is almost planar: the maximum deviation of a core atom from the best-fit plane describing the core is 0.018 (2) Å, while the average deviation is 0.012 (2) Å. The dihedral angle between the core plane and the carboxylate group plane is 5.0 (1)°, while that between the core plane and the amino group plane is 2 (2)°; the dihedral angle between the carboxylate group plane and the amino group plane is 6 (2)°. Thus, the entire molecule is approximately planar. The dihedral angle between the core planes of adjacent molecules in a hydrogen-bonded chain is 9.77 (7)°. For comparison, in nicotinic acid (Kutoglu & Scheringer, 1983), the maximum deviation of a core atom from the best-fit core plane is 0.005 (2) Å, while the dihedral angle between the carboxyl group plane and the core plane is 4.5° (our calculation). Thus, although the nicotinic acid core is more nearly planar, the degree of planarity is quite similar for the entire molecules. For further comparison, in isonicotinic acid (Takusagawa & Shimada,

Experimental

Crystal data

C₆H₆N₂O₂	Mo $K\alpha$ radiation
$M_r = 138.13$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 7.446 (1)$ Å	$\theta = 15.0–17.4°$
$b = 12.1722 (6)$ Å	$\mu = 0.119$ mm^{-1}
$c = 6.9261 (7)$ Å	$T = 296$ K
$\beta = 108.93 (1)°$	Cut rod
$V = 593.8 (1)$ Å^3	$0.39 \times 0.31 \times 0.27$ mm
$Z = 4$	Pale yellow
$D_x = 1.545$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-5S diffractometer	$\theta_{max} = 27.5°$
ω scans	$h = -9 \rightarrow 9$
Absorption correction: none	$k = -15 \rightarrow 0$
1545 measured reflections	$l = 0 \rightarrow 8$
1434 independent reflections	6 standard reflections
1165 reflections with	every 150 reflections
$I > 0.1\sigma(I)$	intensity decay: 5.0%
$R_{int} = 0.025$	

Refinement

Refinement on F	Extinction correction:
$R = 0.062$	Zachariasen (1963, 1968)
$wR = 0.057$	Extinction coefficient:
$S = 1.74$	3.9 (6) $\times$ 10^{-6}

1165 reflections
116 parameters
All H atoms refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Scattering factors from
Stewart, Davidson &
Simpson (1965) (H)
and Creagh & McAuley
(1992) (C, N, O)

Table 1. Selected geometric parameters (Å, °)

O1—C7	1.234 (2)	C2—C3	1.423 (2)
O2—C7	1.266 (2)	C3—C4	1.374 (3)
N1—C2	1.360 (2)	C3—C7	1.514 (2)
N1—C6	1.348 (2)	C4—C5	1.398 (3)
N2—C2	1.322 (2)	C5—C6	1.355 (3)
C2—N1—C6	122.5 (2)	O1—C7—C3	117.4 (2)
O1—C7—O2	125.6 (2)	O2—C7—C3	116.9 (2)

Table 2. Hydrogen bonds and significant C—H···O interactions in 2-aminonicotinic acid at 296 K (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^i	0.96 (2)	1.70 (2)	2.652 (2)	174 (2)
N2—H2···O1^i	0.88 (2)	1.93 (2)	2.807 (2)	173 (2)
N2—H3···O2	0.94 (3)	1.88 (3)	2.651 (2)	137 (2)
C4—H4···O1^{ii}	0.97 (2)	2.87 (2)	3.713 (2)	146 (1)
C5—H5···O2^{iii}	0.91 (2)	3.18 (2)	3.847 (3)	131 (2)
C6—H6···O1^{iv}	1.02 (2)	3.28 (2)	3.506 (3)	94 (1)

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

Table 3. First- and second-level graph-set descriptors involving hydrogen bonds designated a–c as described in the text

	a	b	c
a	C(6)	$C_2^2(6)$ [$R_2^2(8)$]	$C_2^1(6)$
b		C(6)	$C_2^2(6)$
c			S(6)

Scan widths were $(1.50 + 0.35\tan\theta)°$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry indicated space group $P2_1/c$ (No. 14) and since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions. Refined C—H and N—H distances are given in Table 2; U_{iso} for H atoms ranged from 0.038 (6) to 0.055 (7) Å^2. The maximum effect of extinction was 13.1% of F_o for 002. The maximum positive residual peak was located near the midpoint of the C3—C7 bond; the maximum negative peak was located near the center of the pyridine ring.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Polysulfonylamines. LXXXVII.† Bis-(benzenesulfonamido) Sulfone–Dichloromethane (1/0.5)

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Abstract

Bis(benzenesulfonamido) sulfone, $C_{12}H_{12}N_2O_6S_3$, forms strands in the solid state that are made up from two independent molecules linked by four independent N—H···O hydrogen bonds. In addition, the structure displays numerous C—H···O interactions. The bond

† Part LXXXVI: Weitze, Blaschette & Jones (1997).