6-Chloronicotinic acid

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The title compound, $C_6H_4ClNO_2$, forms centrosymmetric dimers *via* intermolecular hydrogen bonds between carboxylic groups. Weak Cl···Cl interactions further bridge these dimers, leading to infinite chains. In contrast, acid-to-pyridine hydrogen-bonded catemer motifs are observed in both nicotinic acid and 2-chloronicotinic acid. Only intramolecular halogen-bonded $S(5)$ loops exist in 2-chloronicotinic acid.

Comment

As one of the most important and strongest non-covalent directional intermolecular interactions, hydrogen bonding has been a topic of intense research ever since it was discovered almost 100 years ago (Steiner, 2002). To understand hydrogen bonding in both solution and the solid state, carboxylic acids have been heavily investigated (Pauling, 1948). They have been found to exhibit robust structural diversity in crystal structures (Kuduva *et al.*, 1999). Centrosymmetric dimers and various catemers are the two major motifs formed by carboxylic acid groups in the solid state (Almarsson & Zaworotko, 2004).


(I)
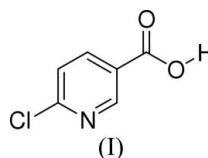
To study the effect of the substituent group on the packing of nicotinic acid, we have compared the crystal structures of nicotinic acid, 2-chloronicotinic acid and 6-chloronicotinic acid, (I). As a water-soluble vitamin, the solid-state structure of nicotinic acid was first determined in 1953 (Wright & King, 1953) and later revisited (Kutoglu & Scheringer, 1983). Both 2- and 6-chloronicotinic acid, (I) (Fig. 1), are important building blocks for agrochemicals, feed additives, animal food
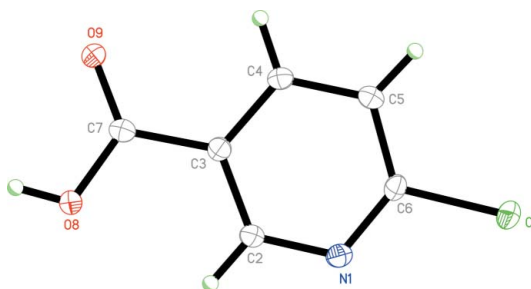
Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms).
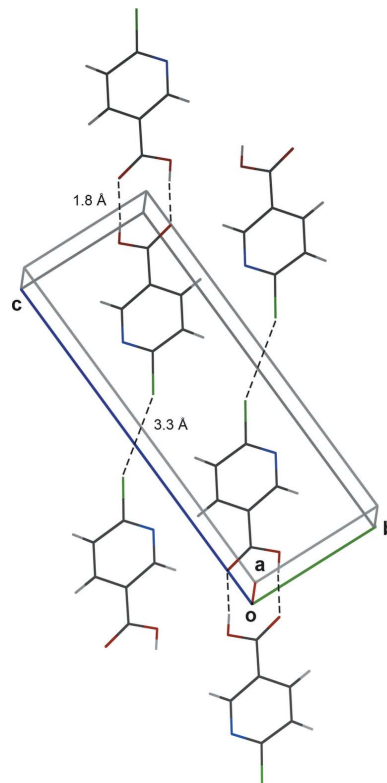
doi:10.1107/S1600536806053177
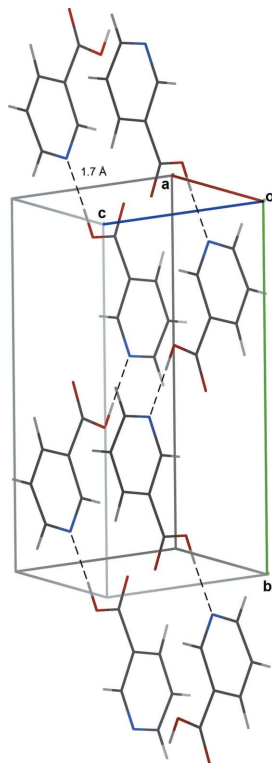
Figure 2
A packing diagram of nicotinic acid, with hydrogen bonds shown as dashed lines.
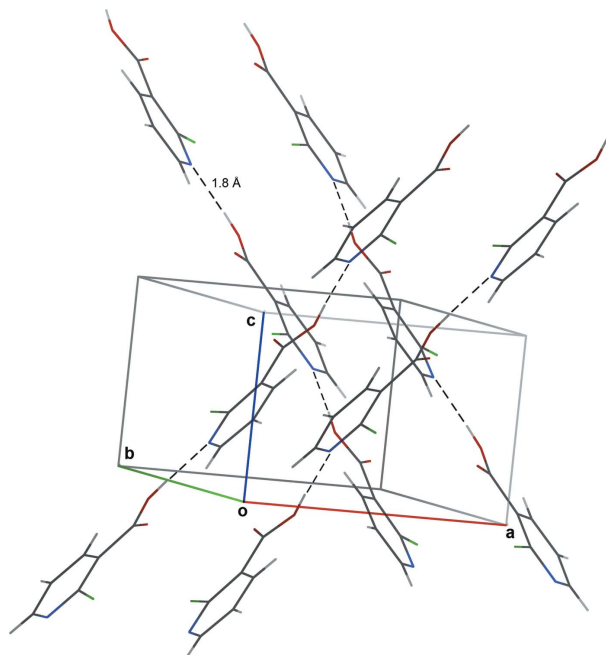
Figure 3
A packing diagram of 2-chloronicotinic acid, with hydrogen bonds shown as dashed lines.

enrichment and pharmaceuticals (Ross, 1967). Although both compounds are commercially available, the solid-state structure of 2-chloronicotinic acid was not reported until 2005 (de Souza *et al.*, 2005), and that of 6-chloronicotinic acid has not been determined until now.

Figure 4
A packing diagram of 6-chloronicotinic acid, (I), with hydrogen bonds shown as dashed lines.

In all three compounds, the carboxylic acid group has a *syn* conformation and is coplanar with the pyridine ring, as indicated by the dihedral angle between the carboxylic acid and the pyridine ring (>172° in all three compounds).

The molecules of niconitic acid form an infinite one-dimensional chain along the [010] direction, resulting from intermolecular O—H···N hydrogen bonds (2.666 Å and 170°) between the pyridine N atom and the carboxylic acid OH group (Fig. 2). This pattern can be designated as an acid-to-pyridine catemer motif, similar to the acid-to-keto catemer reported for other compounds with the carboxylic acid functional group present (Malak *et al.*, 2006). Since the pyridine N atom acts as the hydrogen-bond acceptor, the other hydrogen-bond acceptor of the molecule, C=O of the carboxylic acid group, is not involved in any hydrogen bonding. For 2-chloronicotinic acid, the intermolecular O—H···N hydrogen bonds (2.688 Å and 178°), *i.e.* the acid-to-pyridine catemeric arrangements, lead to infinite one-dimensional chains (Fig. 3). Because of the presence of Cl at the 2-position, an intra-molecular halogen-bonded $S(5)$ loop (Etter, 1990) forms between the Cl atom and the C=O of the carboxylic acid group (Cl···O = 2.880 Å; Metrangolo *et al.*, 2005). Consequently, the C=O of the carboxylic acid group is *cis* to the pyridine N atom in 2-chloronicotinic acid but *trans* to the N atom in niconitic acid.

In 6-chloronicotinic acid, (I), the coplanarity of the carboxylic acid group and the pyridine ring is less than in the other two compounds [−172.73 (12)° for (I), *versus* −176.03°

for nitotinic acid and 177.91° for 2-chloronicotinic acid]. The molecules form centrosymmetric dimers *via* $R_2^2(8)$ hydrogen-bonded loops (Table 1) (Etter, 1990). The hydrogen-bond acceptor pyridine does not participate in any hydrogen bonding except for a weak C—H···N interaction [3.3756 (17) Å]. In addition, weak Cl···Cl [3.325 (1) Å] interactions connect adjacent dimers, leading to infinite chains along the [021] direction (Fig. 4). As for nicotinic acid, the C=O of the carboxylic acid group is *trans* to the pyridine N atom.

In conclusion, the presence of Cl significantly changes the packing of the derivatives of nicotinic acid, probably due to the size of Cl and the associated halogen bonding.

Experimental

6-Chloronicotinic acid was purchased from Lancaster Synthesis. Single crystals were grown from a mixture of water and acetone (1:50) by slow evaporation.

Crystal data

$C_6H_4ClNO_2$	$V = 309.23\ (13)$ Å^3
$M_r = 157.55$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.692$ Mg m^{-3}
$a = 3.741\ (1)$ Å	Mo $K\alpha$ radiation
$b = 5.761\ (1)$ Å	$\mu = 0.54$ mm^{-1}
$c = 14.737\ (4)$ Å	$T = 90.0\ (2)$ K
$\alpha = 90.13\ (1)°$	Thin rod, colourless
$\beta = 90.75\ (1)°$	$0.25 \times 0.18 \times 0.08$ mm
$\gamma = 103.17\ (1)°$	

Data collection

Nonius KappaCCD area-detector diffractometer	2665 measured reflections
ω scans	1403 independent reflections
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)	1286 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.018$
$T_{min} = 0.877$, $T_{max} = 0.958$	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2 + 0.1455P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.067$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
1403 reflections	$\Delta\rho_{min} = -0.27$ e Å^{-3}
92 parameters	
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H8···O9^i	0.84	1.80	2.6382 (14)	176

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

H atoms were positioned geomterically and treated as riding, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and with O—H = 0.84 Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97* and local procedures.

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