3-Carboxypyridine *N*-oxide: supramolecular aggregation through O—H···O and C—H···O interactions

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In the crystal structure of the title molecule, $C_6H_5NO_3$, weak C—H···O interactions result in dimeric units which are extended by strong O—H···O hydrogen bonds to form a two-dimensional supramolecular (4,4)-layered architecture.

Comment

Nowadays it is well known that the marked directionality of both strong O—H···O and weak C—H···O hydrogen bonds makes them useful in crystal design for the preparation of molecular materials with controlled physical properties (Desiraju, 1995; Desiraju & Steiner, 1999). Very strong intramolecular O—H···O hydrogen bonds and weak C—H···O interactions were observed (Steiner *et al.*, 2000) in the crystal structure of 2-carboxypyridine *N*-oxide (picolinic acid *N*-oxide). It can be anticipated that, when both *N*-oxide and carboxylic groups are present in a molecule, a variety of hydrogen-bonding patterns are possible. Thus, the main interest in the solid-state structure of such compounds is the determination of the hydrogen-bonding motifs. We report here the molecular and supramolecular structure of the title compound, 3-carboxypyridine *N*-oxide, (I).

(I)
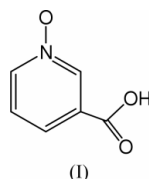
The molecular structure of (I) is shown in Fig. 1, and important bond lengths and angles are given in Table 1. In the carboxy group, the C=O and C—O bonds are clearly distinct [C=O = 1.211 (2) Å and C—O = 1.308 (2) Å]. Atoms O1 and O2 are displaced from the least-squares plane of the pyridine ring by 0.148 (2) and −0.123 (2) Å, respectively [the maximum deviation of non-H atoms from the plane is 0.006 (2) Å, while the average deviation is 0.004 (2) Å]. The N—O distance is 1.333 (2) Å, which is slightly, but significantly, elongated compared to the average value of 1.304 Å in pyridine *N*-oxides and consistent with those of other carboxypyridine *N*-oxide derivatives (Steiner *et al.*, 2000).

Analysis of the crystal packing of (I) shows that there is one classical O1—H1···O3[i] hydrogen bond and a weak C4—H4*A*···O3[ii] interaction (geometrical parameters and symmetry codes are listed in Table 2). A pair of head-to-tail intermolecular C4—H4*A*···O3[ii] interactions links adjacent molecules to form a dimer. The resulting motif, in the formalism of the graph-set analysis of hydrogen-bond patterns
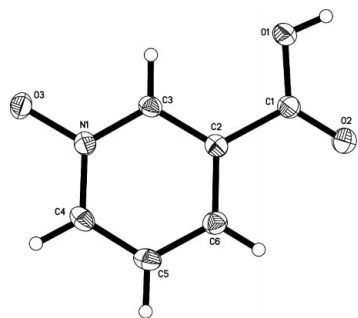
Figure 1
View of the molecule of (I), with displacement ellipsoids drawn at the 30% probability level.
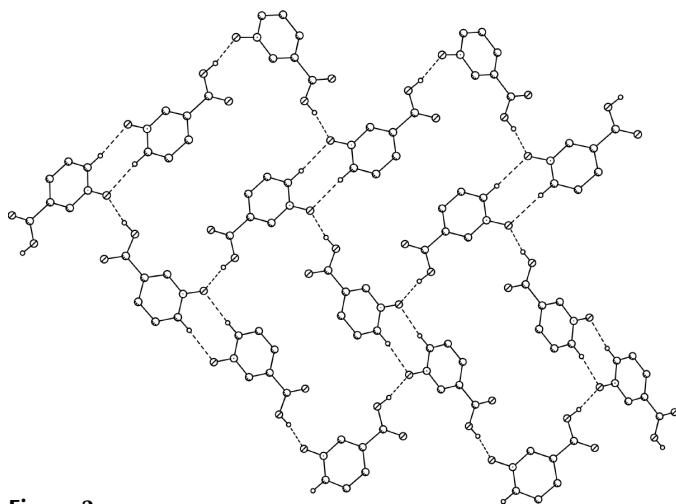

Figure 2
Part of the crystal structure of (I), showing the two-dimensional hydrogen-bonding layer containing $R_2^2(8)$ and $R_6^4(32)$ motifs.

(Etter, 1990), is characterized as $N_2 = R_2^2(8)$. Each dimeric unit acts as a 4-connected node, linking four adjacent dimers through four strong O1—H1⋯O3^i hydrogen bonds to form a two-dimensional (4,4)-layered structure, with the repeating unit $N_6 = R_6^4(32)$ hydrogen-bonding pattern. A packing diagram of (I) in the unit cell, showing these hydrogen-bonding interactions is presented in Fig. 3. There is no evidence of any aromatic π–π stacking or C—H⋯π interactions. Examination of the structure with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids in the crystal lattice of (I).

Experimental

Well shaped colorless single crystals of the title compound, (I), suitable for X-ray diffraction were obtained by recrystallizing the commercial product (Aldrich) from a hot CH_3OH solution.

Crystal data

$C_6H_5NO_3$	$D_x = 1.578$ Mg m^{-3}
$M_r = 139.11$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3276
$a = 3.7879 (7)$ Å	reflections
$b = 10.624 (2)$ Å	$\theta = 2.4$–$28.0°$
$c = 14.674 (3)$ Å	$\mu = 0.13$ mm^{-1}
$\beta = 97.416 (3)°$	$T = 293 (2)$ K
$V = 585.6 (2)$ Å^3	Prism, colorless
$Z = 4$	$0.34 \times 0.26 \times 0.17$ mm

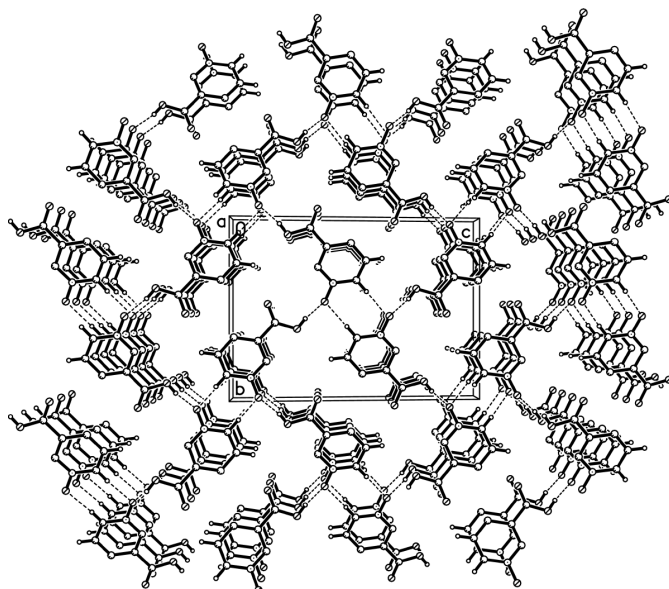**Figure 3**
A three-dimensional packing diagram of (I), showing the hydrogen-bonding interactions as dashed lines.

Data collection

Bruker SMART 1000	1397 independent reflections
diffractometer	1222 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.053$
Absorption correction: multi-scan	$\theta_{max} = 28.0°$
(*SADABS*; Sheldrick, 1997)	$h = -5 \rightarrow 4$
$T_{min} = 0.896$, $T_{max} = 0.980$	$k = -12 \rightarrow 14$
3805 measured reflections	$l = -16 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.147P]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
1397 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
91 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O3—N1	1.3332 (15)	O1—C1	1.3078 (17)
N1—C3	1.3511 (17)	O2—C1	1.2114 (18)
N1—C4	1.3516 (18)		
O3—N1—C3	119.90 (11)	C3—N1—C4	121.52 (12)
O3—N1—C4	118.56 (11)	O2—C1—O1	125.13 (13)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O3^i	0.82	1.71	2.525 (2)	169
C4—H4A⋯O3^{ii}	0.93	2.41	3.311 (2)	164

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

Although all H atoms were visible in difference maps, they were placed in geometrically calculated positions (C—H = 0.93 Å for aromatic H atoms and O—H = 0.82 Å), and included in the final

refinement in the riding-model approximation, with displacement parameters $U_{iso}(H) = 1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

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