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Strong intramolecular O—H···O hydrogen bonds in quinaldic acid *N*-oxide and picolinic acid *N*-oxide

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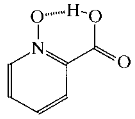
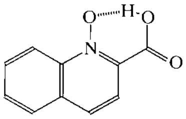
The title compounds contain very short intramolecular hydrogen bonds of the type C—O—H···O—N. The O···O distances are 2.425 (2) Å in picolinic acid *N*-oxide (2-carboxypyridine *N*-oxide), $C_6H_5NO_3$, (I), and 2.435 (2) Å in quinaldic acid *N*-oxide (2-carboxyquinoline *N*-oxide), $C_{10}H_7NO_3$, (II). In (II), this is associated with slight molecular distortion from planarity, while in (I), such an effect cannot be observed because the molecule crystallizes on a mirror plane.

Comment

There is a current revival of interest in the so-called very strong hydrogen bonds (Jeffrey, 1997). For the best studied of these hydrogen bonds, O—H···O, the majority of examples belong to a small number of chemical situations, *i.e.* the combination of acid and complementary base (O—H···O$^-$), the combination of base and complementary acid (O···H—O$^+$), and 'resonance assisted hydrogen bonding' (Hibbert & Emsley, 1990; Gilli *et al.*, 1994). It is characteristic for all these cases that proton transfer leads to a chemically identical situation (O—H···O$^-$ → $^-$O···H—O, *etc.*). Not all very strong hydrogen bonds, however, belong to one of these categories, *e.g.* the intramolecular hydrogen bonds in 2-carboxypyridine *N*-oxide (picolinic acid *N*-oxide), (I), and many of its derivatives. Although donor and acceptor groups of (I) are chemically very different, intramolecular hydrogen bonds are very short. In 6-methyl-2-carboxypyridine *N*-oxide, the intramolecular O···O distance was reported as 2.41 Å, and the H atom was found bonded to the acid group (Dideberg & Dupont, 1975). In the 6-carboxy derivative of (I), 2,6-dicarboxypyridine *N*-oxide, which crystallizes with two symmetry-independent molecules, the four independent intramolecular hydrogen bonds have O···O separations in the range 2.45–2.48 Å, and H atoms are bonded at the acid groups (Rychlewska & Gdaniec, 1977). For (I), the crystal structure was reported only with relatively low accuracy, and an intramolecular O···O distance of about 2.39 Å (Laing & Nicholson, 1971). The H-atom position in the hydrogen bond could not be located. Because the short C—O—H···O—N hydrogen bonds in (I) and derivatives of (I) are chemically unusual, and to investigate the hydrogen-bond geometry with high reliability, we have determined the low-temperature crystal structure of quinaldic acid *N*-oxide, (II), and repeated the crystal-structure determination of (I), also at low temperature. In parallel, Hadzi and coworkers have performed extensive IR spectroscopic and computational investigations of (I), (II) and related molecules (Stare *et al.*, 2000). In particular, hydrogen-bond energies are calculated around −15 kcal mol^{-1} (*in vacuo*) (1 cal = 4.184 J).


(I)


(II)

The molecular structures of (I) and (II) are shown in Fig. 1. In both molecules, very short intramolecular hydrogen bonds are formed, with O···O distances of 2.425 (2) in (I) and 2.435 (2) Å in (II). The relevant H atoms are much closer to the acid than to the *N*-oxide O atoms, so that the hydrogen bonds are of the type C—O—H···O—N (geometries in Tables 1 and 2). In the carboxyl group, the C═O and C—O bonds are clearly distinct [C═O 1.208 (2) in (I) and 1.214 (2) Å in (II); C—O 1.309 (2) in (I) and 1.305 (2) Å in (II)]. Because of stereochemical restriction of the C—O—H angle, the hydrogen bonds are relatively non-linear with O—H···O angles around 160°. The N—O distances are 1.342 (2) and 1.333 (2) Å in (I) and (II), respectively, which is

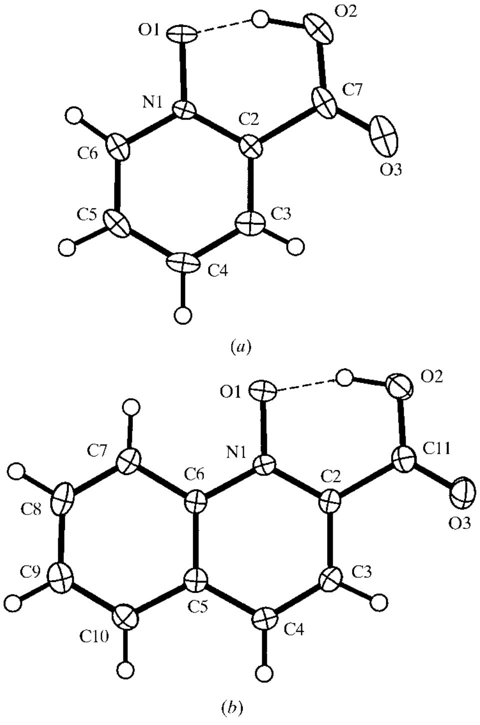


Figure 1
The molecular structures of (*a*) (I), and (*b*) (II). Displacement ellipsoids are drawn at the 50% probability level.

slightly but significantly elongated compared to the average value of 1.304 Å in pyridine *N*-oxides (Allen *et al.*, 1992; σ of sample = 0.012 Å). Because (I) crystallizes on a mirror plane, the observed geometry is restricted to be perfectly planar. Compound (II) crystallizes on a general position, so that deviations from planarity can be observed. Actually, O1 and O2 are displaced from the pyridine least-squares plane in opposite directions by +0.092 (2) and −0.049 (3) Å, respectively, and the resulting torsion angle O1—N1···C11—O2 is 3.3 (1)°. This is only a small distortion from planarity.

The edges of molecules (I) and (II) are constituted exclusively with O atoms and C—H groups. Therefore, it must be expected that weak C—H···O hydrogen bonds are formed in the crystal structures (Steiner, 1997; Desiraju & Steiner, 1999). Actually, there are many such interactions (Tables 1 and 2), but the geometries are all unfavourable with strongly bent angles. C—H···O hydrogen bonding does not seem to be particularly important in these compounds.

Experimental

Picolinic acid *N*-oxide, (I), was obtained from Sigma and quinaldic acid *N*-oxide was synthesized as described by Stare *et al.* (2000). Both compounds were recrystallized from MeOH.

Compound (I)

Crystal data

$C_6H_5NO_3$
$M_r = 139.11$
Monoclinic, $P2_1/m$
$a = 6.802$ (1) Å
$b = 6.066$ (2) Å
$c = 7.804$ (1) Å
$\beta = 112.61$ (1)°
$V = 297.25$ (12) Å^3
$Z = 2$

$D_x = 1.554$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
$\theta = 4.7$–18.7°
$\mu = 0.127$ mm^{-1}
$T = 125$ K
Block, colourless
0.40 × 0.25 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
2264 measured reflections
741 independent reflections
654 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.023$
$\theta_{\rm max} = 27.42°$
$h = -5 \rightarrow 8$
$k = -7 \rightarrow 7$
$l = -9 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.096$
$S = 1.117$
741 reflections
77 parameters
H atoms refined isotropically

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.0912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.07 (3)

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	1.04 (3)	1.42 (3)	2.425 (2)	159 (3)
C3—H3···O1$^{\rm i}$	0.91 (2)	2.51 (2)	3.235 (2)	138 (2)
C4—H4···O2$^{\rm ii}$	0.94 (2)	2.87 (2)	3.435 (2)	120 (2)
C5—H5···O2$^{\rm ii}$	0.99 (2)	2.66 (2)	3.328 (2)	126 (2)
C5—H5···O3$^{\rm iii}$	0.99 (2)	2.72 (2)	3.285 (2)	117 (2)
C6—H6···O3$^{\rm iii}$	0.97 (2)	2.41 (2)	3.082 (2)	126 (2)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x - 1, y, z - 1$; (iii) $x, y, z - 1$.

Compound (II)

Crystal data

$C_{10}H_7NO_3$
$M_r = 189.17$
Monoclinic, $P2_1/n$
$a = 3.821$ (3) Å
$b = 16.241$ (1) Å
$c = 13.062$ (3) Å
$\beta = 91.01$ (1)°
$V = 810.5$ (7) Å^3
$Z = 4$

$D_x = 1.550$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 reflections
$\theta = 3.3$–18.4°
$\mu = 0.117$ mm^{-1}
$T = 125$ K
Needle, yellow
0.5 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
8148 measured reflections
1829 independent reflections
1449 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.083$
$\theta_{\rm max} = 27.50°$
$h = -4 \rightarrow 4$
$k = -21 \rightarrow 19$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.115$
$S = 1.089$
1829 reflections
156 parameters
H atoms refined isotropically

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.5447P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.008 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	0.98 (3)	1.48 (3)	2.435 (2)	161 (2)
C4—H4···O2$^{\rm i}$	0.98 (2)	2.54 (2)	3.288 (2)	132 (1)
C4—H4···O3$^{\rm ii}$	0.98 (2)	2.56 (2)	3.344 (2)	137 (1)
C7—H7···O1$^{\rm iii}$	0.97 (2)	2.44 (2)	3.278 (2)	144 (1)
C7—H7···O1$^{\rm iv}$	0.97 (2)	2.83 (2)	3.322 (2)	112 (1)
C9—H9···O3$^{\rm v}$	0.96 (2)	2.83 (2)	3.395 (2)	119 (1)
C10—H10···O3$^{\rm ii}$	0.96 (2)	2.79 (2)	3.544 (2)	136 (1)

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

The area-detector data were 98.3 and 98.9% complete to $2\theta = 55°$ for (I) and (II), respectively. The H atoms were located in difference Fourier calculations and were refined isotropically. All H-atom displacement parameters refined to realistic values [H atoms bonded to C: 0.031–0.038 in (I) and 0.019–0.033 Å^2 in (II); carboxylic acid H atom: 0.072 (9) in (I) and 0.059 (8) Å^2 in (II)].

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1129). Services for accessing these data are described at the back of the journal.

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