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(4-Oxo-1,4-dihydropyridin-1-yl)acetic acid

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Key indicators

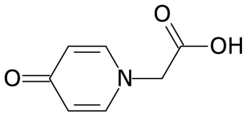
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.044
wR factor = 0.146
Data-to-parameter ratio = 9.4

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

The title compound, expected to be a betaine, 4-hydroxypyridinioacetate, $HOC_5H_4N^+CH_2CO_2^-$ or $C_7H_7NO_3$, on the basis of its synthesis by the nucleophilic displacement of chloride from the chloroacetate ion in water, exists as (4-oxo-1,4-dihydropyridin-1-yl)acetic acid. The acid H atom interacts with the oxo O atom of an adjacent molecule to form a linear helical chain [O···O = 2.451 (3) Å].

Comment

Pyridinioacetate, $C_5H_5N^+{-}CH_2{-}CO_2^-$, is a zwitterionic compound that furnishes a number of adducts with metal salts (Yang *et al.*, 2003). The betaine has been isolated as a hemihydrochloride hemihydrate (Chen & Mak, 1990). A carboxy-substituted derivative has been synthesized; the carboxy group does not retain the acid H atom but instead concedes it to the acetate unit in $C_5H_4(3\text{-}CO_2)NCH_2CO_2H$ (Chen & Mak, 1991). Our interest in the theoretical and solid-state structure of the 4-hydroxy-substituted pyridinioacetate is related to the existence of the $[O{=}C(CH{=}CH)_2N{-}CH_2{-}CO_2]^-$ anion in the hexaaquacobalt(II) (Zhang *et al.*, 2004*a*), hexaaquanickel(II) (Zhang *et al.*, 2004*b*) and hexaaquazinc(II) (Gao *et al.*, 2004) salts, whose anions possess unambiguous doubly bonded O atoms connected to the ring. The 3,5-diiodo-substituted compound, on the other hand, exists as a carboxylic acid (Cox & Hickey, 2001).



(I)

The molecules of 4-oxo-1,4-dihydropyridine-1-acetic acid, (I), are linked by a short hydrogen bond into a helical chain (Fig. 1) that propagates by a 2_1 screw axis along the c axis of

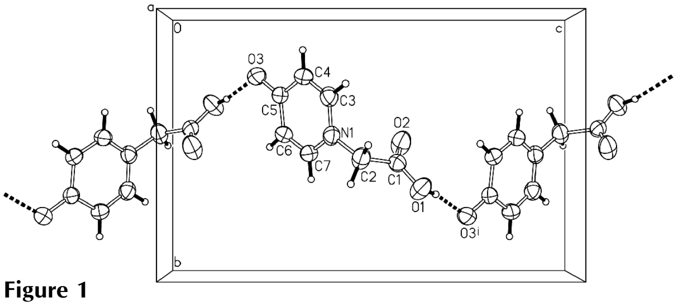


Figure 1
*ORTEP*II (Johnson, 1976) plot of a portion of the hydrogen-bonded helical chain of (I) [O1···O3^i = 2.451 (3) Å; symmetry code (i): $\frac{3}{2} - x$, $1 - y$, $\frac{1}{2} + z$.]

the unit cell. The acetate and the oxopyridine moieties are both planar, but they are aligned perpendicular to each other [dihedral angle = 89.9 (1) Å]. The aromaticity of the 4-hydroxypyridine entity is lost when it is linked to the acetic acid in the compound. The substituent is an oxo unit [C═O = 1.306 (3) Å]. Single as well as double C—C bonds are found in the ring. The isoelectronic compound with the oxo atom in the 2-position also shows these features; for 2-oxo-1,2-dihydropyridine-1-acetic acid (Rybakov *et al.*, 2002), a similarly short intermolecular hydrogen bond links the molecules into a helical chain along the *b* axis of the monoclinic unit cell. The presence of the oxo atom in the two isomeric compounds allows for the packing to differ from those of other small carboxylic acids (Beyer & Price, 2000). The two compounds feature a quinonoid-like distribution of single and double bonds; such a distribution is also found in the heterocyclic reagent that is used in the synthesis of the title compound. 4-Hydroxypyridine exists in the solid state as 4-pyridone 1.2-hydrate; the carboxy bond in the five independent molecules ranges from 1.258 (2) to 1.278 (2) Å (Jones, 2001).

A comparison of the X-ray and geometry-optimized structure (Table 1) with the structure of the hypothetical betaine, $HO-C_5H_4N^+-CH_2-CO_2^-$, shows that the acid structure is more stable.

Experimental

An aqueous solution of 4-hydroxypyridine (9.55 g, 0.10 mol) and sodium hydroxide (4.00 g, 0.10 mol) was reacted with an aqueous solution of chloroacetic acid (14.18 g, 0.10 mol) that had been neutralized with sodium hydroxide (6.00 g, 0.15 mol). The pH of the mixture was approximately 9–10. The mixture was refluxed for 5 h. The cooled solution was treated with hydrochloric acid to a pH of 2–3. The solution was then filtered. Colorless crystals were obtained after several days. Analysis calculated for $C_7H_7NO_3$: C 54.90, H 4.61, N 9.15%; found: C 54.72, H 4.49, N 9.27%.

For the geometry-optimization calculations with *HyperChem* (Hypercube Inc., 2000), the starting structure was taken from the X-ray structure, and this was optimized at the *PM*3 level. The heat of formation was computed to be −93.78 kcal mol^{-1}; that of the hypothetical zwitterionic structure, $HOC_5H_4N^+CH_2CO_2^-$, was computed to be −60.74 kcal mol^{-1} (*i.e.* not as stable).

Crystal data

$C_7H_7NO_3$
$M_r = 153.14$
Orthorhombic, $P2_12_12_1$
$a = 4.7413$ (17) Å
$b = 9.595$ (5) Å
$c = 15.069$ (7) Å
$V = 685.5$ (5) Å^3
$Z = 4$
$D_x = 1.484$ Mg m$^{-3$}

Mo *Kα* radiation
Cell parameters from 6039 reflections
$\theta = 4.5$–27.3°
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.32 × 0.25 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.963$, $T_{max} = 0.977$
6046 measured reflections

945 independent reflections
857 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 27.5°$
$h = -6 \rightarrow 5$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.146$
$S = 1.11$
945 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2 + 0.1698P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{i}	0.82	1.66	2.451 (3)	163

Symmetry code: (i) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$.

Table 2
Bond distances (Å) and angles (°) from the experimental $O{=}C(CH{=}CH)_2N-CH_2-CO_2H$ structure and the geometry-optimized $O{=}C(CH{=}CH)_2N-CH_2-CO_2H$ structure.

Bond	X-ray	Geometry-optimized
O1—C1	1.276 (3)	1.350
O2—C1	1.215 (4)	1.217
O3—C5	1.306 (3)	1.223
N1—C2	1.473 (4)	1.476
N1—C3	1.360 (4)	1.416
N1—C7	1.351 (4)	1.416
C1—C2	1.533 (4)	1.519
C3—C4	1.356 (4)	1.348
C4—C5	1.414 (4)	1.472
C5—C6	1.417 (4)	1.472
C6—C7	1.359 (4)	1.348
C2—N1—C3	120.9 (3)	119.0
C2—N1—C7	119.2 (2)	118.9
C3—N1—C7	119.7 (3)	119.1
O1—C1—O2	127.1 (3)	116.2
O1—C1—C2	113.2 (2)	117.6
O2—C1—C2	119.6 (2)	126.3
N1—C2—C1	112.1 (2)	117.0
N1—C3—C4	121.2 (3)	121.1
C3—C4—C5	120.5 (2)	121.4
O3—C5—C4	120.4 (2)	122.4
O3—C5—C6	122.8 (3)	122.4
C4—C5—C6	116.8 (3)	115.2
C5—C6—C7	119.9 (3)	121.4
N1—C7—C6	121.9 (2)	121.1

The H atoms were placed in calculated positions [aromatic C—H = 0.93 Å and aliphatic C—H = 0.97 Å; $U_{iso}(H) = 1.2U_{eq}(C)$], and were included in the refinement in the riding-model approximation. The acid H atom was initially located in a difference Fourier map. It is situated midway between the single-bond carboxyl O atom and the oxo O atom of the symmetry-related molecule, with O···H *ca* 1.25 Å. An attempt to refine this atom as a disordered atom occupying two sites was not successful. If the H atom was an 'acid hydrogen', then it would be midway between the two O atoms, but its presence should also lead to a significant lengthening of the C═O double bond in the oxopyridine fragment. The atom was then refined by allowing the O—H bond to rotate so as to fit the maximum electron density [O—H = 0.82 Å and $U_{iso}(H) = 1.2U_{eq}(O)$]. Although the compound crystallizes in a non-centrosymmetric space group, the molecule is not chiral, and neither are there heavy atoms that would permit the absolute structure to be calculated. Friedel pairs were merged.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick,

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1997); 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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