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ORIGINAL PAPER

Hydrogen Bonding Network Assembled with 2-Amino-3-hydroxypyridium and Isonicotinate-N-oxide

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Abstract The crystal structure of the compound $(C_5H_7N_2O)\cdot(C_6H_4NO_3)\cdot H_2O$ (**1**) consisting of 2-amino-3-hydroxypyridium, isoniconate-N-oxide and lattice water was characterized by single-crystal X-ray diffraction analysis: monoclinic, $P2_1/c$, $a = 9.6905(8)$, $b = 6.0040(4)$, $c = 21.039(2)$ Å, $\beta = 101.062(8)°$, $V = 1201.34(18)$ Å^3, Z = 4. In **1**, the deprotonated isoniconate-N-oxide, the protonated 2-amino-3-hydroxypyridium and the lattice water are linked by a series of classical hydrogen bonds to form 2-D layer. Then, these 2-D sheets assemble to a 3-D network via weak hydrogen bonds.

Keywords Pyridine N-oxide · Hydrogen bond · Crystal structure · Supramolecular

Introduction

Weak intermolecular interactions, such as H-bonding, van der Waals interactions, and π–π stacking etc., play very important roles in the formation of supramolecular structures and natural sciences. Among these weak intermolecular interactions, the hydrogen bonds have attracted many chemists' attention for its wide range of existence, various appearance, and crucial effect on the properties of many materials [1]. As useful ligands, Pyridine N-oxide derivatives have been widely applied in asymmetry catalysis [2–6], and display many interesting hydrogen bond properties [7–9].

On our continuing program of design and synthesis of the Schiff base system of pyridine N-oxide, we serendipitously obtained the hydrate 2-amino-3-hydroxypyridium isoniconate-N-oxide (**1**). In this paper, we have reported the synthesis and the crystal structure of compound **1**, as well as discussed the ion hydrogen bonds.

Experiment

Physical Measurements

All chemical regents and solvents were used as received. Element analysis (C, H) was carried out with a Pekin–Elmer 2400 II analyzer. Infrared spectrum (400–4,000 cm^{-1}) was recorded from KBr pellets on a Nicolet 360 FT-IR spectrometer. The ^{1}H NMR spectrum was obtained with a Burker Avance 500 MHz spectrometer in DMSO solution.

Synthesis of the Hydrate 2-amino-3-hydroxypyridium isoniconate-N-oxide (1)

Compound **1** was prepared from 4-picoline according to the literature [6, 8, 10] and the reaction is shown in Scheme 1. The yellow block crystals of **1** were filtered off, washed with distilled water, and dried at ambient temperature, yield: 80%. FTIR (in cm^{-1}): 3410(s), 3109(m), 2460(m), 2363(m), 2028(w), 1989(w), 1683(s), 1644(m), 1613(m), 1573(s), 1536(m), 1486(m), 1438(w), 1382(s), 1297(s), 1234(s), 1217(s), 1180(m), 1142(m), 1108(w), 1045(w), 1036(w), 998(w), 891(w), 875(w), 862(m), 786(m), 783(m), 751(w), 711(w), 686(w), 662(w), 640(s),

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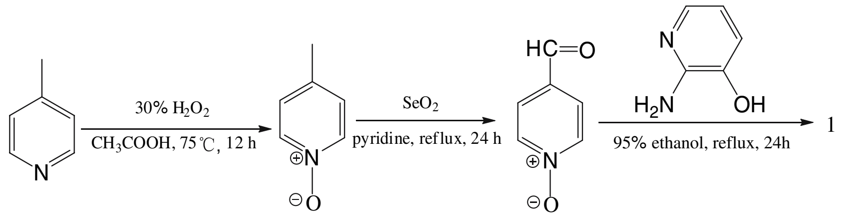
Scheme 1



611(w), 581(m), 555(w), 524(w), 507(w), 474(w), 451(w), 420(w). ^{1}H NMR (DMSO in ppm): 8.19 ~ 8.17 (d, 2H), 7.52 ~ 7.39 (d, 2H), 7.17 ~ 7.07 (m, 2H), 6.62 ~ 6.58(m, H). Element analyses, calculated for $C_{11}H_{13}N_3O_5$: C, 49.44; H, 4.90%. Found: C, 49.29; H, 4.65%.

Table 1 Crystal data and structure refinement for title compound

CCDC no.	CCDC 286986
Compound	$(C_5H_7N_2O)\cdot(C_6H_4NO_3)\cdot H_2O$
Color/shape	Orange/Prism
Chemical formula	$C_{11}H_{13}N_3O_5$
Formula weight	267.24
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.6905(8)
b (Å)	6.0040(4)
c (Å)	21.039(2)
β (°)	101.062(8)
Volume (Å^3)	1201.34(18)
Z	4
Density (calculated) (g cm^{-3})	1.478
Absorption coefficient (mm^{-1})	0.119
F(000)	560
Crystal size (mm)	0.58 × 0.46 × 0.32
θ range for data collection (°)	1.97 to 26.00
Limiting indices	$0 < h < 11$, $0 < k < 7$, $-25 < l < 25$
Reflections measured	2851
Independent/observed reflections	2353 (R_{int} = 0.0113)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2353 / 0 / 197
Goodness of fit on F^2	0.998
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0361$, $\omega R_2 = 0.0878$
R indices (all data)	$R_1 = 0.0574$, $\omega R_2 = 0.0941$
Extinction coefficient	0.021(2)
Largest differential peak and hole (eÅ^{-3})	0.171 and –0.140

Crystal Structure Determination

A crystal of dimensions 0.58 × 0.46 × 0.32 mm^3 was used for data collection on a Siemens $P4$ diffractometer with Mo $K\alpha$ (λ = 0.71073 Å) using ω scan method. The structure of **1** was solved by direct methods and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2. The hydrogen atoms residing on the pyridine rings 2-amino-3-hydroxypyridium and isoniconate-N-oxide(H1, H2, H3, H6, H7, H9, H10) were placed geometrically, while other hydrogen bonds (H1O, H1N, H2A, H2B, H5A, H5B) were found in difference Fourier maps.

The experimental and computations were performed on a PC computer using the programs of Bruker Smart and Bruker SHELXTL package [11, 12]. Crystallographic data are summarized in Table 1, and selected bond lengths are listed in Table 2 while selected hydrogen bond lengths and angles are presented in Table 3.

Result and Discussion

The salt of hydrate 2-amino-3-hydroxypyridium isoniconate-N-oxide was synthesized as indicated in Scheme 1

Table 2 Selected bond lengths(Å) and angle (°) for **1**

Bond lengths(Å)			
O(1)–C(4)	1.3406(18)	N(3)–C(10)	1.3456(19)
O(2)–N(3)	1.3168(16)	N(3)–C(6)	1.3502(19)
O(3)–C(11)	1.2573(18)	C(1)–C(2)	1.344(2)
O(4)–C(11)	1.2527(18)	C(2)–C(3)	1.404(2)
N(1)–C(5)	1.3409(19)	C(4)–C(5)	1.423(2)
N(1)–C(1)	1.361(2)	C(8)–C(11)	1.505(2)
N(2)–C(5)	1.331(2)		
Bond angles (°)			
O(1)–C(4)–C(3)	126.64(15)	N(1)–C(5)–C(4)	118.29(14)
O(1)–C(4)–C(5)	114.24(14)	N(2)–C(5)–C(4)	121.76(15)
O(2)–N(3)–C(10)	119.37(12)	N(2)–C(5)–N(1)	119.95(15)
O(2)–N(3)–C(6)	120.86(13)	C(3)–C(4)–C(5)	119.12(14)
O(3)–C(11)–C(8)	117.61(14)	C(7)–C(8)–C(9)	116.90(14)
O(4)–C(11)–C(8)	116.89(13)	C(7)–C(8)–C(11)	121.39(13)
O(4)–C(11)–O(3)	125.50(15)	C(9)–C(8)–C(11)	121.71(14)

Table 3 Hydrogen bond lengths (Å) and bond angles (°) for **1**

Donor-H···Acceptor	ARU	D···A	D-H···A
Classical hydrogen bonds for 1-D chain			
N(1)–H(1N)···O(4)	1435	2.6610(17)	174.9(15)
O(1)–H(10)···O(5)		2.5468(18)	174(2)
N(2)–H(2A)···O(3)	1435	2.871(2)	171.5(17)
O(5)–H(5A)···O(2)		2.6646(18)	178(2)
Classical hydrogen bonds for 1-D ribbon			
N(2)–H(2B)···O(3)	3666	3.0916(19)	146.0(15)
Classical hydrogen bonds for 2-D layer			
O(5)–H(5B)···O(3)	3676	2.7942(18)	167(2)
Nonclassical hydrogen bonds for 3-D network			
C(10)–H(10)···O(4)	2645	3.1884(18)	139.46(9)

Note Translation of ARU-code to equivalent position code: [3666] = 1 – *x*, 1 – *y*, 1 – *z*; [1435] = –1 + *x*, –2 + *y*, *z*; [2645] = 1 – *x*, –1/2 + *y*, 1/2 – *z*; [3676] = 1 – *x*, 2 – *y*, 1 – *z*

with 4-picoline and 2-amino-3-hydroxylpyridine as parent reagents. Although our initial purpose of designing the reaction was to synthesize the Schiff base of pyridine N-oxide, but unexpected compound **1** was obtained because the 4-pyridincarboxaldehyde-N-oxide was oxidized under air condition.

An ORTEP diagram [13] is shown in Fig. 1. The asymmetric unit of **1** consists of one 4-carboxylpyridine-N-oxide anion, one 2-amino-3-hydroxylpyridine cation and one water molecule. In the basic unit, the protonation of 2-amino-3-hydroxylpyridine is observed (N(1)–H(1N) = 0.9919, N(1)–C(1) = 1.3614 and N(1)–C(5) = 1.3408 Å), and the dihedral angle between the pyridyl ring of 4-carboxylpyridine-N-oxide and that of 2-amino-3-hydroxylpyridine is equal to 6.97(8)°, which indicates that the two rings are almost coplanar.

As shown in Fig. 2 and 3, hydrogen bonds are the decisive factor governing the stacking pattern in the crystal lattice of **1**. According to the function of hydrogen bonds in **1**, we classify them as four types: classical hydrogen bonds for 1-D chain, classical hydrogen bonds for 1-D ribbon, classical hydrogen bonds for 2-D layer, and unclassical hydrogen bonds for 3-D network. At first, deprotonated isoniconate-N-oxide and protonated 2-amino-3-hydroxylpyridine connect with lattice water through ion hydrogen bonds [14] of O(5)–H(5A)···O(2)[2.6646(18) Å, 178(2)°] and O(1)-H(1O)···O(5)[2.5468(18) Å, 174(2)°] forming a basic building unit. Neighboring units are further connected by pairs of N$^+$–H···O$^-$ hydrogen bonds between protonated 2-amino-3-hydroxylpyridine and carboxylate group with fork-like pattern [15] [N(1)–H(1N)···O(4) 2.6610(17) Å, 174.9(15)°); N(2)–H(2A)···O(3) 2.871(2) Å, 171.5(17)°] to give rise to a infinite chain. It was worthy noting that the fork-like hydrogen bonding pattern is observed in cytosine carboxylate interactions [16–18]. Then, two antiparallel chains form a ribbon chain through the linkage of hydrogen bond of N(2)–H(2B)···O(3) [3.0916(19) Å, 146.0(15)°] (Fig. 2). Parallel ribbons are linked with each other to form a 2-D layer *via* hydrogen bond of O(5)–H(5B)···O(3)[2.7942(18) Å, 167(2)°] (Fig. 3). Finally, these 2-D layers stack in ''AB'' pattern along the *c* axis and interact through unclassical hydrogen bond of C(10)–H(10)···O(4) [3.1884(18) Å, 139.46(9)°] constructing the resulting 3-D supramolecular network. From above description, one can see that a series of classical hydrogen bonds construct the 2-D layer while the

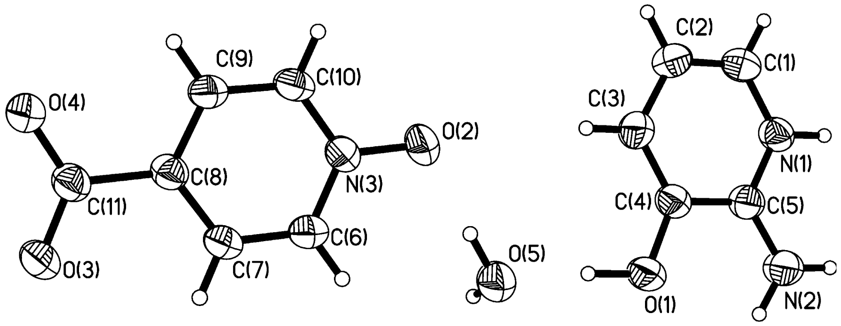


Fig. 1 An ORTEP drawing of title compound (50% probability ellipsoids)

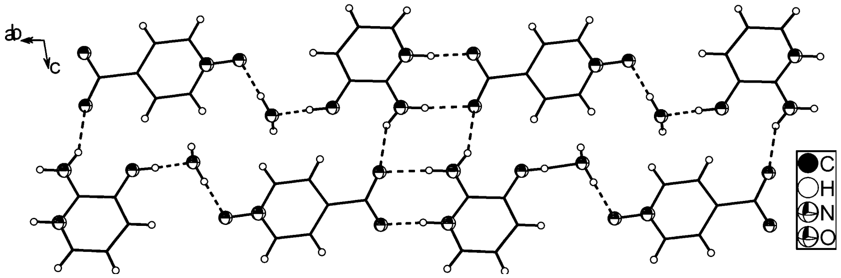


Fig. 2 One-dimensional ribbon structures connected by hydrogen bonds

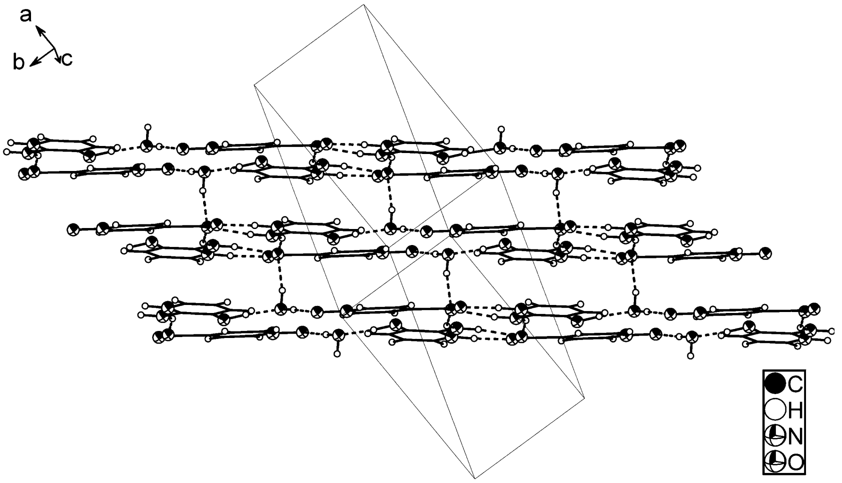


Fig. 3 View of the 2-D hydrogen bonding layer constructed by 1-D ribbons

unclassical hydrogen bond maintains the 3-D network of compound **1**.

Supplementary Material

CCDC-286986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK; fax: C44(0)1223–336033; e-mail: deposit@ccdc.cam.ac.uk.

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