

A Solid Structure of 2-Pyridinesulfonic Acid

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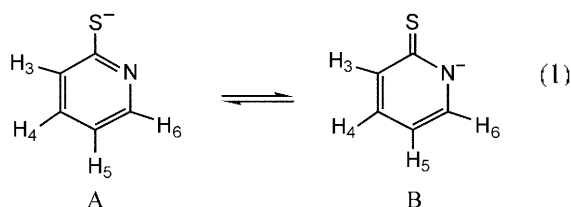
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Received September 21, 2004

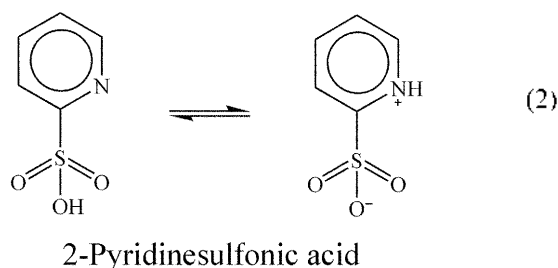
Key Words : Ambidentate ligand, Crystal structure, 2-Pyridinesulfonic acid, Tautomerism

Some tautomeric ligands and their metal complexes have been attracted owing to both biological and chemical importance.¹ In particular, tautomeric equilibria have often been scrutinized to deduce a relationship between structure and stability,²⁻⁴ and the results have been extended beyond the initial studies to such diverse areas as quantum mechanical calculations,⁵ molecular switches,⁶ tautomeric catalysts,⁷ molecular recognitions,⁸ and theories of genetic mutation.² For instance, the tautomeric equilibria of purine and pyrimidine bases have been suggested to affect RNA transcription and DNA replication in biological systems² and behaviors of nucleic acids.⁹ Tautomeric thio-bases such as thiouracil and thiocytosine are normal constituents of some *t*-RNA species.¹⁰ Among such tautomeric systems, the simplest example is pyridine-2-thiolate analogs that are capable of binding to metals as either pyridine-2-thiol (A, thiol) or pyridine-2-thione (B, thione) (eq 1).¹ Recently,



crystal structures and tautomerism of cobalt(III) and rhodium(III) complexes of pyridine-2-thiolate have been reported in our previous papers.¹¹⁻¹³

In an effort to expand the tautomeric chemistry, 2-pyridine-sulfonic acid (eq 2) has been prepared and fully characterized by X-ray crystallography. Its behaviors including the degree of dissociation in solution have been known to be strongly dependent on substituents.¹⁴ Moreover, 2-pyridine-sulfonic acid has been employed as a bidentate ligand.¹⁵



Experimental Section

Reagents and Measurements. Elemental analyses were performed by the Advanced Analysis Center at KIST. The infrared spectra in the 5000-400 cm^{-1} region were measured as KBr pellets on a Perkin Elmer 16F PC model FT-IR spectrophotometer. 2-Pyridinesulfonic acid was smoothly prepared by oxidizing 2-mercaptopyridine with nitric acid.¹⁶ ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-300 NMR spectrometer operating at 300.00 MHz (^1H) and 75.48 MHz (^{13}C), respectively. The chemical shifts were relative to SiMe_4 (^1H and ^{13}C) as an internal standard.

Crystallographic Structure Determination. A colorless crystal was wedged in a Lindemann capillary with mother solvent. X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) at ambient temperature. Unit cell dimension was based on 25 well-centered reflections by using a least-square procedure. Data were collected $\omega/2\theta$ scans within the angular range $5.2-50.0^\circ$. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ψ -scan method. The structure was solved by the SHELXS 97 and refined by SHELXL 97.¹⁷ The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated

Table 1 Crystallographic Data of 2-Pyridinesulfonic Acid

formula	$\text{C}_5\text{H}_4\text{NO}_3\text{S}$
f.w.	158.15
crystal system	orthorhombic
space group	<i>P</i> bca
<i>a</i> , \AA	8.117(1)
<i>b</i> , \AA	9.723(3)
<i>c</i> , \AA	15.640(1)
<i>V</i> , \AA^3	1234.3(4)
<i>Z</i>	8
<i>d</i> _{calc} , g cm^{-3}	1.702
μ , mm^{-1}	0.460
Data/restraints/parameters	978 / 0 / 92
R ($I > 2\sigma(I)$)	R_1 0.0400
	wR_2 0.1007

$$R_1 = \frac{\sum |F_o - F_c|}{\sum F_o}, wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w F_o^4}^{1/2}$$

positions and refined only for the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collection and structure refinement were given in Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-259642). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perlcateq/cateq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

2-Pyridinesulfonic acid was recrystallized in a mixture of chloroform and *n*-hexane (1 : 1) to obtain single crystals suitable for X-ray crystallography. The colorless crystalline solids are soluble in polar organic solvents and are stable in solution. X-ray characterization on the single crystal has provided a confident structure. The molecular structure and packing diagram are shown in Figure 1. The compound is a discrete molecule in solid state in contrast to 3-pyridinesulfonic acid.¹⁸ The C-C and C-N bond lengths in the ring are in the range of 1.33 Å-1.38 Å, which are similar to the corresponding lengths of general aromatic compounds. The C(1)-S(1) bond length is 1.803(2) Å. All the S-O bond lengths (1.436(2) Å, 1.439(2) Å, and 1.448(2) Å) do not show significant differences, indicating that the π electrons around the S-O bonds are delocalized in solid state. Furthermore, such a fact implies that the protic H is attached to the nitrogen of 2-pyridine rather than O-H tautomer. Thus,

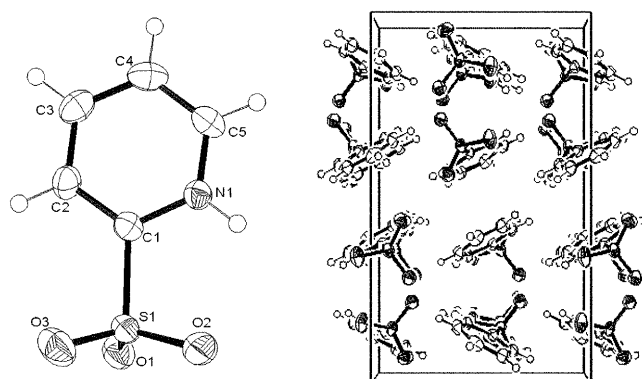
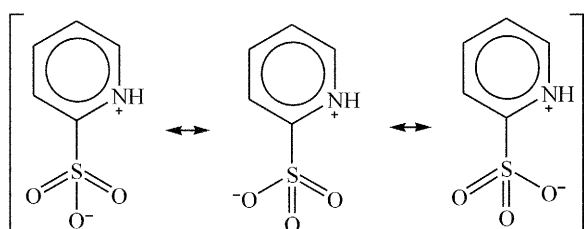
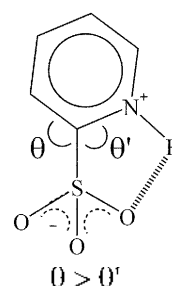


Figure 1. ORTEP view (left) and packing view (100) of 2-pyridinesulfonic acid. The ORTEP is depicted in thermal ellipsoids at the 50% level.



Scheme 1



Scheme 2

Table 2. Relevant Bond Distances and Angles of 2-Pyridinesulfonic Acid

S(1)-O(3)	1.4358(16)	N(1)-C(1)	1.346(3)
S(1)-O(2)	1.4391(18)	C(1)-C(2)	1.361(3)
S(1)-O(1)	1.4484(16)	C(2)-C(3)	1.379(3)
S(1)-C(1)	1.803(2)	C(3)-C(4)	1.383(3)
N(1)-C(5)	1.330(3)	C(4)-C(5)	1.367(3)
O(3)-S(1)-O(2)	115.57(11)	N(1)-C(1)-C(2)	119.89(19)
O(3)-S(1)-O(1)	113.04(10)	N(1)-C(1)-S(1)	115.57(15)
O(2)-S(1)-O(1)	113.86(10)	C(2)-C(1)-S(1)	124.54(17)
O(3)-S(1)-C(1)	105.13(10)	C(1)-C(2)-C(3)	118.7(2)
O(2)-S(1)-C(1)	103.23(10)	C(2)-C(3)-C(4)	120.4(2)
O(1)-S(1)-C(1)	104.37(9)	C(5)-C(4)-C(3)	118.7(2)
C(5)-N(1)-C(1)	122.39(19)	N(1)-C(5)-C(4)	119.8(2)

its structure can be summarized in the following resonance structures (Scheme 1). For the structure, an intramolecular N-H \cdots O hydrogen bond (2.33 Å; the angle of N-H \cdots O = 110.6(2) $^\circ$) exists in solid state. The hydrogen bond may result in an unsymmetrical bent conformation ($\theta > \theta'$), that is, the angle of S(1)-C(1)-N(1) (115.6(2) $^\circ$) is some or less contracted whereas the angle of S(1)-C(1)-C(2) (124.5(2) $^\circ$) is concomitantly splayed out as shown in Scheme 2. Such a bent conformation did not exist in 3-pyridinesulfonic acid.¹⁸ IR spectrum shows a strong broad band around 3000 cm^{-1} presumably owing to the N-H bond. In contrast, the corresponding band does not appear in a simple sulfonic acid without pyridine moiety.¹⁹ Furthermore, the crystal discrepancy factor (R) of N-H tautomer is more reasonable than that of O-H tautomer ($R = 0.0449$). Of course, the chemistry in solution may be different from that in the solid state.

In conclusion, the structure of 2-pyridinesulfonic acid has been fully characterized to be a N-H tautomer rather than an O-H tautomer. Thus these structural facts should be considered when this compound is treated as an ambidentate ligand in solid state and in solution.

Acknowledgment. Support for this research was provided by the University IT Research Center Project in Korea.

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