Available online at www.sciencedirect.com

ScienceDirect

Journal of Molecular Structure 839 (2007) 76–83

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

Infrared spectrum, molecular structure and theoretical calculation of 2-pyridone-6-carboxylic acid

H. Arslan [a], A. Şengül [b], S. Aygün [b], N. Karadayı [c], S. Haman Bayarı [d,*]

[a] *Department of Physics, Zonguldak Karaelmas University, 67100 Zonguldak, Turkey*
[b] *Department of Chemistry, Zonguldak Karaelmas University, 67100 Zonguldak, Turkey*
[c] *Department of Physics, Ondokuz Mayıs University, 55159 Samsun, Turkey*
[d] *Department of Physics Education, Hacettepe University, Beytepe, 06800 Ankara, Turkey*

Received 27 July 2006; received in revised form 19 October 2006; accepted 24 October 2006
Available online 26 December 2006

Abstract

The X-ray and infrared spectroscopic analysis of 2-pyridone-6-carboxylic acid are reported. The crystals of investigated molecule belong to $P2_1/c$ of the monoclinic system, $a = 11.714$ Å, $b = 3.7088$Å, $c = 18.223$Å and $\beta = 123.71°$. The molecule is found in the ketonic form. Comprehensive studies of the molecular structures and vibrational frequencies and infrared intensities of the molecule have been performed by using Hartree–Fock, density functional B3LYP and second-order Moller–Plesset MP2 methods with the 6-31G+(d, p) basis set. The calculated geometrical parameters of investigated molecule in gas phase were compared with the experimental X-ray data.

Keywords: Molecular structure; X-ray; Infrared; Theoretical calculation; 6-Hydroxypicoline; 2-Pyridone-6-carboxylic acid

1. Introduction

Picolinic acid (PA) is a very interesting model, as it is a biologically important ligand incorporated into some enzymes and its molecule is an active agent in some drugs [1–3].

The ligands possessing oxygen atom or nitrogen and oxygen atoms are of great interest in the field of supramolecular chemistry [4]. 6-Hydroxypicolinic acid is characterized by enol-ketonic tautomerism [4] (ketonic form can be namely as 2-pyridone-6-carboxylic acid: PCA) as shown in Scheme 1.

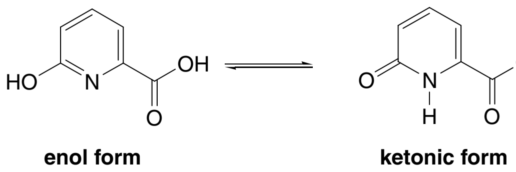
Keto–enol tautomerism has been the subject of continuous interest in chemistry. The electronic effects and the position of the substituents, pH and the solvent polarity are the major factors that influence this tautomerism [5]. In particular, the proton transfer (PT) associated with keto–enol tautomerisation has long been of much interest because such interactions may catalyze certain biochemical transformations [6]. Adjacent donor and acceptor groups within the molecules are known to form rigid dimers in the solid state. The PCA possesses complementary hydrogen-bonding sites that are adjacent to one another; the N–H and the acidic O–H groups as donors and the carbonyl C=O and the ketonic C–O groups as acceptors. A similar tautomerism occurs for 2-hydroxynicotinic acid and 2-mercaptonicotinic acid [7] and for 6-methyl-2-pyridone [5]. The tautomerisation in favor of pyridine form is greatly enhanced by the electron realizing effect of the OH group due to the basicity of the hetero aromatic nitrogen atom [5,8,9]. Supramolecular synton as an important concept in crystal engineering introduced by Desiraju, is typically applied to non-covalent interactions, such as hydrogen bonds [10]. Supramolecular synthons are the recognition motifs between self-complementary constituent functional groups (or building blocks) that can be used to propagate networks or supramolecular assemblies [11]. Hydrogen bonding is a directional interaction essential for a great

---

* Corresponding author. Tel.: +90 312 297 86 06; fax: +90 312 297 86 00.

E-mail address: bayari@hacettepe.edu.tr (S.H. Bayarı).

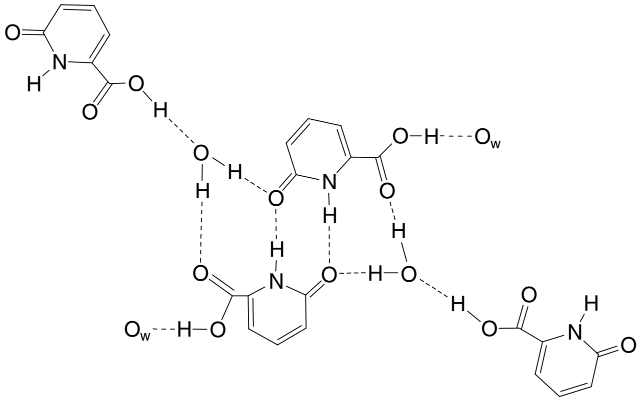
0022-2860/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2006.10.045



Scheme 1.

number of supramolecular constructions. In particular, the conventional hydrogen bonds of the type O–H···N, N–H···O (energies 20–40 kJ mol^{-1}) usually termed as the strong ones, dictate the molecular assembling in the studied class, and also prevail in drug and biological molecules [12–14]. The PT forces molecules to produce hydrated structures involving intermolecular H-bonds between the water molecules and the –COOH groups of the adjacent molecules to assemble supramolecular networks *via* hydrogen-bonded dimer synthon [15]. Hydrogen bond pattern of PCA in the solid state is given in Scheme 2. The coordinated water molecules and the amido groups of PCA can act as hydrogen bond donors, while the carboxylate groups and the carbonyl oxygen atoms of PCA can act as hydrogen bond acceptors.

In general, water prefers to accept hydrogen bonds from –OH and N–H donors in macromolecular structures [16]. The O–H group of the carboxylic acid is a very strong donor but a very poor acceptor, whereas the water molecule is a good acceptor but only a moderate donor [17]. The large difference in electronegativity between the H atom and O atoms makes the O–H bonds of water molecule inherently polar, with partial atomic charges of around +0.4 on each H atom and −0.8 on each O atom [18]. So, the inclusion of water molecules opens the possibility for a strong O–H···O_w motif due to formation of hydrogen bonding in a hierarchical fashion: best donor to best acceptor; second-best donor to second-best acceptor, etc [19]. The present supramolecular motif accords well with this criterion, in which the water molecule donates hydrogen bonds to the dimer through O_w–H···O_{oxo} and O_w–H···$O_{carbonyl}$ and accepts hydrogen bond from the adjacent dimer via O_{acid}–H···O_w. The inclusion of water, a donor-rich molecule, prevents the pyridine–carboxylic acid interactions and serves as template in assembling the molecules around it with different packing motif [20]. On the other hand, in the absence of water molecule, the title compound exists in the tautomeric equilibrium with the oxo tautomer, the latter being preferred in the solid state. Two molecules are connected by two N–H···O hydrogen bonds around an inversion centre to form cyclic dimer, and the dimers are linked in a planar fashion by O–H···O hydrogen bonds to form a sheet [21]. The carbonyl O atoms do not take part in hydrogen bonding. Engineering the carboxylic acid dimer clearly requires the absence of successful competitors (i.e. pyridine N atom or water molecule). A very recent study on carboxyl donors shows that recognition of COOH with pyridine is favored 10 times more through an O–H···N hydrogen bond compared to dimer O–H···O [18]. For example, in the crystal structure of 5-amino-2-benzoic acid, two identical acid molecules form A–A type homodimer in the absence of any competitor [22].



Scheme 2.

Due to its small size and excellent H-bond capability, water plays a critical role in many of the structures in which it is found [23]. These strong H-bonds play important role in chemical and enzymatic interaction and are, therefore, subject of great current interest to shed lights on the influence of the hydration on the stability of the tautomers in different media [23].

To perform this study, we have used both an experimental and theoretical approach. The single crystal X-ray structure of the 2-pyridone-6-carboxylic acid (PCA) has been determined.

The FT-IR spectrum of sample (crystal form) was recorded. The theoretical calculations were performed for isolated molecule using the HF, MP2 and DFT methods. A general assignment of the fundamental vibrational modes was proposed on the basis of the calculated results of ketonic form. DFT calculation of the PCA dimer also performed in this paper and is compared with the monomer PCA.

2. Experimental

2.1. Preparation of crystal

6-Hydroxypicolinic acid was purchased from Aldrich. It was dissolved in an ammonia solution and set to reflux for 1 h. After evaporation of the solution to dryness under vacuum, the brown residue was crystallized in an ethanol–water (1:1 v/v) solvent mixture to form needle shape colorless crystals of suitable for X-ray analysis [24].

2.2. X-ray analysis

X-ray diffraction data were collected on a STOE IPDS II diffractometer with graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å) at 296 K. A summary of crystallographic data, experimental details and refinement results