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The role of hydrogen bonds in the crystals of 2-amino-4-methyl-5-nitropyridinium trifluoroacetate monohydrate and 4-hydroxybenzenesulfonate – X-ray and spectroscopic studies



I. Bryndal^{a,b,*}, M. Marchewka^c, M. Wandas^a, W. Szaśiadek^a, J. Lorenc^a, T. Lis^b, L. Dymińska^a, E. Kucharska^a, J. Hanuza^{a,c}

^a Department of Bioorganic Chemistry, Faculty of Engineering and Economics, Wrocław University of Economics, 118/120 Komandorska, 53-345 Wrocław, Poland

^b Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie, 50-383 Wrocław, Poland

^c Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

HIGHLIGHTS

- Two new organic–organic salts, AMNP-TFA and AMNP-HBS, were obtained and characterized.
- N–H···O bonds are formed between the acidic unit and pyridinium cation in both salts.
- O–H···O bonds are formed between H₂O molecules and COO[−] and NO₂ groups in AMNP-TFA.
- The SO₃[−] groups of adjacent acidic unit are linked by O–H···O bonds in AMNP-HBS.
- X-ray, IR and Raman studies and DFT calculations show the existence of intramolecular N–H···O bonds.

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ABSTRACT

Two new organic–organic salts, 2-amino-4-methyl-5-nitropyridinium trifluoroacetate monohydrate (AMNP-TFA), and 2-amino-4-methyl-5-nitropyridinium 4-hydroxybenzenesulfonate (AMNP-HBS), were obtained and characterized by means of FT-IR, FT-Raman and single crystal X-ray crystallography. In the former crystal, the cations, anions and water molecules are linked into layers by three types of hydrogen bonds, N_P–H···O, N_A–H···O and O–H···O. These layers are connected by weaker C–H···O hydrogen bonds. In the latter crystal, the cations and anions form one-dimensional structure through a number of hydrogen-bonding interactions involving the OH, NH⁺ and NH₂ groups as donors. In this case the N_P–H···O and N_A–H···O hydrogen bonds are formed. The combination of interactions between cations and anions results in the formation of columns. Additionally, there are π–π stacking interactions between the columns. The obtained X-ray structural data are related to the vibrational spectra of the studied crystals.

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Introduction

Nitrogen in a heterocyclic ring plays an important role in numerous drugs and heterocyclic compounds [1]. The nitrogen atom is an element of saturated heterocyclic rings in aliphatic heterocyclic compounds and the lone pair of electrons is accessible for a reaction with protons, e.g. piperidine. Typical pK_a values of 8–9 are representative for compounds of this type that are similar in base strength to their open-chain aliphatic analogues. Lone pairs

on the nitrogen atoms are involved in interaction with electrons of the aromatic ring in the case of aromatic heterocyclic compounds. Pyrrole is a good example; the lone pair supplies the aromatic sextet and does not react with protons. The pK_a value for pyrrole is low because pyrrole is a very weak base. Similarly, the six-membered nitrogen heterocycle pyridine is a weak base too. However, in the case of pyridine, only one electron from the nitrogen supplies the aromatic sextet. As a consequence, unshared pair of electrons can accept proton. Pyridine is basic with the pK_a value of 5.2. It seems worthwhile to mention here that this value is close to that in aromatic amines such as aniline (aminobenzene).

There is a huge number of articles dealing with pyridine derivatives starting from the paper by Pechmann and Welsh on

* Corresponding author at: Department of Bioorganic Chemistry, Faculty of Engineering and Economics, Wrocław University of Economics, 118/120 Komandorska, 53-345 Wrocław, Poland. Tel.: +48 71 368 0299; fax: +48 71 368 0292.

E-mail addresses: isai@o2.pl, ibryndal@ue.wroc.pl (I. Bryndal).

formation of pyridine derivatives from malic acid [2]. Numerous 2-aminopyridine salts with strong mineral [3–5] and organic acids are also known [6,7]. Due to complete proton transfer between acid and pyridine, pyridinium cation and acidic anion are formed. Furthermore, aromatic amino and amino-nitro systems are intensively examined in relation to their application as potentially useful non-linear optical materials. In this account, some hydrogen-bonded salts comprising 2-amino-3-nitropyridinium [8,9] or 2-amino-5-nitropyridinium cations [10–12] were also reported. Several organic–inorganic salts have been prepared in our laboratory and characterized by means of structural and spectroscopic studies [13,14]. Additionally, the crystal structures and vibrational properties of a hybrid organic–organic salt formed by 2-amino-4-methyl-3-nitropyridine with trifluoroacetic acid has also been described [15]. Some of these salts undergoes a reversible order–disorder type phase transition [15,16]. Our studies are devoted to the preparing some pyridine derivatives that exhibit potential applications in the synthesis of optically active materials. For instance, 2-amino-4-methyl-3-nitropyridine has been reported as an excellent compound that can be used in the production of functional salts with organic and inorganic acids [16].

As an extension of our searches for new hybrid salts exhibiting nonlinear second order coefficients, we prepared of 2-amino-4-methyl-5-nitropyridinium trifluoroacetate monohydrate (AMNP-TFA), and 2-amino-4-methyl-5-nitropyridinium 4-hydroxybenzenesulfonate (AMNP-HBS), by a direct reaction of 2-amino-4-methyl-5-nitropyridine with trifluoroacetic and 4-hydroxybenzenesulfonic acids in an aqueous solution. Another reason for preparing the present salts is to better understand the role of N–H···N, N–H···O and O–H···O hydrogen bonds (HBs) and π ··· π or C–H··· π interactions leading to an association of ions in the crystal structures. Unfortunately, both present salts are centrosymmetric and therefore do not generate the second harmonic generation. In spite of this it seemed to be worthwhile to characterize AMNP-TFA and AMNP-HBS by the single X-ray diffraction, spectroscopic studies and quantum chemical calculations, as well as to discuss in terms of possibility of hydrogen bonds formation.

Experimental

Synthesis

The starting compound, 2-amino-4-methyl-5-nitropyridine (AMNP), was obtained in our laboratory [17,18]. The title salts were prepared by mixing 2-amino-4-methyl-5-nitropyridine and trifluoroacetic acid (Fluka, >98%) or 4-hydroxybenzenesulfonic acid (Aldrich, 65 wt.% in H₂O, 99.95%) in the stoichiometric ratio 1:1.

Trifluoroacetic acid was dissolved in water and this solution was added to the aqueous solution of 2-amino-4-methyl-5-nitropyridine. The mixture was then slowly evaporated at room temperature within a few days until good quality colorless AMNP-TFA crystals (m.p. 185(1) °C) were formed.

Dissolved 4-hydroxybenzenesulfonic acid in water was added to the solution of 2-amino-4-methyl-5-nitropyridine. The solution was slowly evaporated during a few days at room temperature. Crystals of AMNP-HBS (m.p. >330 °C (dec.)), suitable for X-ray diffraction studies, were obtained by re-crystallization from methanol–water mixture (2:1 v/v).

X-ray studies and data collection

Details of the data collections, analyses and refinements for 2-amino-4-methyl-5-nitropyridinium trifluoroacetate monohydrate (AMNP-TFA) and 2-amino-4-methyl-5-nitropyridinium 4-hydroxybenzenesulfonate (AMNP-HBS) are given in Table S1

(Supplementary data). Crystallographic measurements were performed at 100 K, using graphite-monochromated Mo K α (λ = 0.71073 Å) radiation on Oxford Xcalibur PX κ -geometry diffractometer (ω -scan). The instrument was equipped with Oxford Cryosystems low-temperature devices. Lattice parameters were determined from least-squares analysis, and reflection data were integrated using the CrysAlis software [19]. For AMNP-TFA and AMNP-HBS, no absorption correction was applied; only Lorentz and polarization effects were taken into account.

The structures were solved by direct methods and refined on F^2 by full-matrix least squares with anisotropic thermal parameters for all non-H-atoms using SHELXL-97 [20]. The H atoms bound to C atoms were included in geometrically calculated positions, with the C–H distances of 0.95–0.98 Å, and refined using riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{aryl}})$ and $U_{\text{iso}}(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}(\text{C})$. The H atoms bonded N and O atoms were located from difference Fourier maps and were freely refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ and $1.5U_{\text{eq}}(\text{O})$, respectively. The structures were drawn using XP program [21].

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre [Ref. CCDC 802342 and 802343]. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

IR and Raman measurements

IR spectra were recorded at room temperature in Nujol suspension in the 4000–50 cm⁻¹ range and potassium bromide pellet in the 4000–400 cm⁻¹ range. The spectra were measured using a FTIR Biorad 575C spectrometer with the resolution of 2.0 cm⁻¹.

Raman spectra were measured in back scattering geometry in the 4000–80 cm⁻¹ range using a FT-Raman Bruker 110/S spectrometer. The resolution was 2.0 cm⁻¹. The YAG:Nd³⁺ laser was used as an excitation source: excitation wavelength was 1064 nm.

Quantum chemical calculations

The geometry optimization of the molecular structures of the studied compounds was performed using the Gaussian 03 programme package [22]. All calculations were accomplished by density functional three-parameters hybrid (B3LYP) methods [23–25] with the 6-31G(d,p) basis set [26,27]. The calculated and experimental values were compared using scaling factors to correct the evaluated wavenumbers for vibrational anharmonicity and deficiencies inherent to the applied computational level. The Potential Energy Distribution (PED) of the normal modes among the respective internal coordinates was calculated for the all studied compounds using the BALGA [28] program.

The vector displacements of the atoms from their equilibrium positions during the vibration and the pictures of these displacements were prepared using Chemcraft program that also visualizes particular modes in an animated way [29].

The theoretical Raman intensities were calculated using the RAINTE computer program [30] reported in [31].

Results and discussion

Crystal structure of 2-amino-4-methyl-5-nitropyridinium trifluoroacetate monohydrate

The determination of the crystal structure of AMNP-TFA shows that it crystallizes in the monoclinic P2₁/m space group. The

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