



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

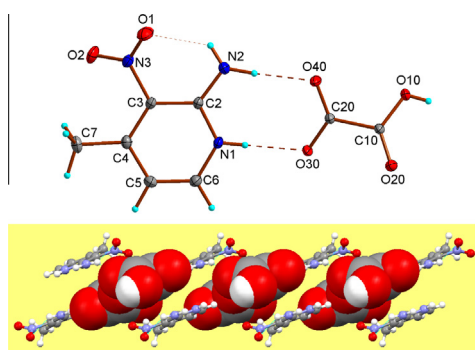
Comprehensive physicochemical studies of a new hybrid material: 2-Amino-4-methyl-3-nitropyridinium hydrogen oxalate

I. Bryndal^{a,*}, E. Kucharska^a, M. Wandas^a, J. Lorenc^a, K. Hermanowicz^b, M. Mączka^b, T. Lis^c, M. Marchewka^b, J. Hanuza^{a,b}^a Department of Bioorganic Chemistry, Institute of Chemistry and Food Technology, Faculty of Engineering and Economics, Wrocław University of Economics, 118/120 Komandorska, 53-345 Wrocław, Poland^b Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 2 Okólna, 50-422 Wrocław, Poland^c Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie, 50-383 Wrocław, Poland

HIGHLIGHTS

- A new organic–organic salt and its deuterium analogue were characterized.
- The DSC measurements exhibit that **AMNPO** undergoes a reversible phase transition at ~240 K.
- The **AMNPO** crystals are built of ions which are connected via N–H···O and O–H···O interactions.
- Combined X-ray, IR, RS and DFT methods applied to hydrogen bonds.
- The temperature dependence of hydrogen bonds band wavenumbers was analyzed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 June 2013

Received in revised form 30 July 2013

Accepted 2 August 2013

Available online 20 August 2013

Keywords:

2-Amino-4-methyl-3-nitropyridinium hydrogen oxalate
Deuterated salt
Temperature dependence
IR and Raman spectra
Crystal structure

ABSTRACT

A new organic–organic salt, 2-amino-4-methyl-3-nitropyridinium hydrogen oxalate (**AMNPO**), and its deuterium analogue have been synthesized and characterized by means of FT-IR, FT-Raman, DSC and single crystal X-ray studies. The DSC measurements and temperature dependence of the IR and Raman spectra in the range 4–295 K show that it undergoes a reversible phase transition at ~240 K. At room temperature it crystallizes in noncentrosymmetric space group $P2_1$. The unit-cell is built of the 2-amino-4-methyl-3-nitropyridinium cations and oxalate monoanions which are connected via the N–H···O and O–H···O hydrogen bonds. The geometrical and hydrogen bond parameters are similar for non-deuterated (at 120 and 293 K) and deuterated compounds (at 90 K). The phase transition is probably a consequence of order–disorder transition inside of hydrogen network. The 6-311G(2d,2p) basis set with B3LYP functional have been used to discuss the structure and vibrational spectra of the studied compound.

© 2013 Elsevier B.V. All rights reserved.

Introduction

2-Amino-4-methyl-3-nitropyridinium hydrogen oxalate (**AMNPO**) belongs to a wide family of organic–organic hybrid salts that have attracted considerable attention recently. Such materials

form a new class of compounds with prospective optical applications [1–4]. The Raman and IR spectra of some polycrystalline methyl, amino and dihalogeno substituted pyridine–oxalic acid complexes have been investigated and discussed in terms of possibility of hydrogen bonds formation [5]. Various hydrogen bonds of the N–H···O, O–H···O and O–H···N types have been distinguished and their roles in stabilization of the crystal structure have been analyzed.

* Corresponding author. Tel.: +48 71 368 0301; fax: +48 71 368 0292.

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

Several new organic–inorganic salts have been prepared in our laboratory and characterized by means of structural and spectroscopic studies [6,7]. Additionally, the crystal structures and vibrational properties of a hybrid organic–organic salt formed by 2-amino-4-methyl-3-nitropyridine and trifluoroacetic acid has also been described [8]. It was shown that it undergoes a reversible phase transition at ~ 162 K [8]. The transition is an order–disorder type. The present work continues the studies of hybrid salts built of pyridinium cations coupled with other organic ions by means of hydrogen bonds.

Experimental

Synthesis

The starting compound, 2-amino-4-methyl-3-nitropyridine, was obtained in our laboratory [9]. Crystals of **AMNPO** was prepared by dissolving a 1:1 ratio of 2-amino-4-methyl-3-nitropyridine and oxalic acid dihydrate (POCH) in hot acetone–methanol–water mixture (2:1:1) and allowing the solution to evaporate slowly after cooling to room temperature. The crystals of the deuterated analog were prepared by dissolution of non-deuterated salt in CH_3OD and slow evaporation of the solvent in the nitrogen stream. Recrystallization repeated several times from CH_3OD solution gave suitable crystals of the deuterated salt.

X-ray diffraction

Details of data collections, analyses and refinements for **AMNPO** are given in Table S1 (Supplementary data). Crystallographic measurements were performed at 120 and 294 K for non-deuterated salt and at 90 K for deuterium discharge form on an Oxford Diffraction Xcalibur PX κ -geometry four-circle diffractometer with graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å) radiation. The deuterated crystal for measurement at 90 K was included into a capillary. The instrument was equipped with Oxford Cryosystems cooler. Lattice parameters were determined from least-squares analysis, and reflection data were integrated using the CrysAlis software [10].

The crystal structure was solved by direct methods using SHELXS-97 program and refined on F^2 by full-matrix least squares with anisotropic thermal parameters for all non-H-atoms using SHELXL-97 [11]. The H atoms were found in difference Fourier maps. In the final refinement cycles, all C-bonded H atoms were treated as riding atoms in geometrically optimized positions, with $\text{C–H} = 0.93$ – 0.96 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{aryl}})$ or $U_{\text{iso}}(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}(\text{C})$. N-bonded H atoms were freely refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC reference numbers 802336–802337 and 943096. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (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).

DSC measurements

DSC measurements were performed in the temperature range 80–293 K on Perkin Elmer DSC 7 instrument.

IR and Raman measurements

Room temperature infrared spectra (FTIR) were measured in the 5000 – 30 cm^{-1} spectral range using a BIORAD 575 spectrophotometer with the resolution of 2 cm^{-1} . The spectra were measured

using pressed KBr and Nujol mulls techniques for the MIR region and Nujol suspension on the polyethylene plates in the FIR region.

Room temperature FT Raman spectra (RS) were measured in the 4000 – 80 cm^{-1} spectral range using a BRUKER 110/S spectrometer with the Nd:YAG excitation and 2 cm^{-1} resolution.

Low temperature studies were performed in the temperature range 4 – 293 K using a Janis ST100 Cryostat (USA). These studies were performed using KBr pressed suspension for the IR studies and a small crystal in the Raman measurements.

Quantum chemical calculations

The molecular structure of the studied compound was optimised at the DFT level using the Lee–Yang–Parr correlation functional (B3LYP) [12–14] and 6-311G(2d,2p) basis [15–20]. The Raman and IR wavenumbers as well as the band intensities were calculated at the same DFT level using the GAUSSIAN 03 W program [21]. The theoretical wavenumbers were scaled to compare them with the experimental values. The linear correlation method was applied in this procedure [22]. From the mean square deviation, the 0.965 scaling factor was derived for the 4000 – 2500 cm^{-1} and 0.985 for 2499 – 0 cm^{-1} range.

Standardized internal coordinate systems have been applied to construct a potential function. Such an approach is now commonly used for a variety of organic molecules, functional groups, and four-, five-, and six-membered rings [23]. Redundancies between the stretching and bending coordinates were eliminated by this choice. The ring deformational coordinates involve the whole ring and therefore they are non-local. Because in the present work the internal coordinate system for eight-membered ring has to be constructed, the optimization of molecular geometry of such system was performed using the method proposed by Fogarasi et al. [24] that was based on the three fundamental principles: locality, local pseudosymmetry and elimination of redundancy. For the eight-membered ring, 18° of freedom that describe 8 individual stretchings, 5 symmetrized bendings, and 5 symmetrized torsions have been applied [24].

The AniMol program [25] was used for visualisation of the vibrational normal modes and the Balga program [26] for estimation of the PED contributions of the internal coordinates to the normal modes.

Results and discussion

DSC measurements

The DSC measurements were performed in the temperature range 80 – 293 K and showed that 2-amino-4-methyl-3-nitropyridinium hydrogen oxalate undergoes a reversible phase transition at about 240 K. Fig. S1 (Supplementary data) shows the DSC curve recorded for the compound under study. The T_c point appears at 239.2 K upon cooling and at 279.1 K upon heating of the sample. The temperature hysteresis of this transition is $\Delta T = 39.9$ K. The enthalpy and entropy of this process is equal to $\Delta H = 820.21$ (J/mol) and $\Delta S = 5.03$ (J/mol K), respectively. The values of these parameters indicate that the phase transition is of order–disorder type.

Crystal structure of **AMNPO**

The crystal of **AMNPO** is built of the 2-amino-4-methyl-3-nitropyridinium cations and oxalate monoanions (Fig. S2 – Supplementary data). The pyridine ring is essentially planar (the average deviation from least-square plane is 0.005 Å) and the amino N2 and methyl C7 atoms lie approximately in the ring plane, with deviations of $0.029(5)$ and $0.040(5)$ Å, respectively. The intramolecular $\text{N–H} \cdots \text{O}$ hydrogen bond (HB) is formed between the nitro

Download English Version:

<https://daneshyari.com/en/article/7672873>

Download Persian Version:

<https://daneshyari.com/article/7672873>

[Daneshyari.com](https://daneshyari.com)