Vibrational Spectroscopy 75 (2014) 26–38

Contents lists available at ScienceDirect

Vibrational Spectroscopy

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

Complementary optical and neutron vibrational spectroscopy study of bromanilic acid: 2,3,5,6-tetramethylpyrazine (1:1) cocrystal

Katarzyna Łuczyńska [a,b,*], Kacper Drużbicki [b,c], Krzysztof Lyczko [a], Wojciech Starosta [a]

[a] Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland
[b] Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russian Federation
[c] Department of Radiospectroscopy, Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland

ARTICLE INFO

Article history:
Received 16 July 2014
Received in revised form 1 September 2014
Accepted 9 September 2014
Available online 16 September 2014

Keywords:
Molecular crystals
Infrared and Raman spectroscopy
Time-domain terahertz spectroscopy
Inelastic neutron scattering
Plane-wave DFT

ABSTRACT

Complementary structural and vibrational spectroscopy study of bromanilic acid:2,3,5,6-tetramethylpyrazine (BrA:TMP) 1:1 cocrystal is reported. The crystallographic structure was determined by means of single-crystal X-ray diffraction and can be described as a stacked net of hydrogen-bonded $TMPH^{+}\cdots BrA^{-}\cdots BrA^{-}\cdots TMPH^{+}$ moieties. The structural analysis was supported by ^{13}CP/MAS NMR study. The complementary vibrational analysis was performed by combining optical (infrared, Raman, terahertz) and inelastic neutron scattering spectroscopy with the state-of-the-art solid–state density functional theory (DFT) computations, which have proven to be superior to the hybrid cluster modeling approach. An excellent agreement between theoretical and experimental data was observed over the entire spectral range, allowing for deep understanding of the vibrational properties. While the primary hydrogen-bonding interactions are limited to the above quoted structural units, the system revealed very little dispersion of the phonon branches, manifested mainly in the intermolecular vibrations range. Moreover, the studied phase does not exhibit any mechanical instability, which could suggest a displacive structural transformation tendency.

1. Introduction

In recent years, a large amount of research has been focused on designing molecule-based materials, which are of growing interest for materials science. Much attention has been given to the low-weight organic ferroelectrics [1,2] following Horiuchi's discovery of molecular complexes of phenazine with chloranilic and bromanilic acid. Microscopically, the ferroelectricity can arise either from displacive or order–disorder transition and both mechanisms were encountered in the low-weight molecular systems [3]. In both cases, the hydrogen bonding forces become a fundamental issue. These specific interactions are responsible for the creation of the supramolecular units, which may be affected by the phonon-driven mechanical instabilities, leading to the molecular displacement. The order–disorder transitions, which are usually observed at higher temperature, may often be associated with the proton displacement phenomena [4].

Among the discussed systems, much attention has been given to the bromanilic acid cocrystals because of their potential polar or semiconducting properties (since the π-orbitals may overlap along the segregated stacks leading to one-dimensional conductivity). Recently, Thomas et al. have presented an extensive crystallographic view on the set of bromanilic acid:substituted-pyridine molecular complexes, proving that controlled introduction of the proton transfer may be used in a design of the supramolecular units [5]. However, the authors have concluded, that while it is possible to predict the formation of a supramolecular synthon, it does not appear to be possible to predict the relative orientations of the bromanilic acid molecule and the co-molecule. Hence, the progressive exploration of low-weight hydrogen bonded systems with potential polar or semiconducting properties becomes an important issue, allowing for future investigation of the structure–spectrum relation.

In the present work, we report the complementary structural and spectroscopic study of the system, representing the family of low-weight hydrogen bonded molecular complexes with potential polar or semiconducting properties. The low-temperature crystal structure is reported along with the complementary vibrational spectroscopy analysis, which was fully supported by the state-of-the art first principles static-DFT computations, shedding light on the molecular internal modes and the lattice-dynamics. By combining several experimental techniques, we were able to

---

* Corresponding author. Tel.: +48 225041230.
E-mail address: k.luczynska@ichtj.waw.pl (K. Łuczyńska).

http://dx.doi.org/10.1016/j.vibspec.2014.09.002
0924-2031/

present the performance of modern solid–state calculations in the description of the vibrational spectra of a middle-strength hydrogen-bonded molecular complex.

2. Experimental and computational details

2.1. Sample preparation

Bromanilic acid (2,5-dibromo-3,6-dihydroxy-*p*-quinone; BrA; $C_6H_2Br_2O_4$) and 2,3,5,6-tetramethylpyrazine (TMP; $C_8H_{12}N_2$) were used as obtained (purity > 98.0%) from TCI EUROPE N.V. The equimolar amounts of both compounds were dissolved in methanol and magnetically stirred at 30 °C. The cocrystals of ionic forms of both compounds (tetramethylpyrazinium bromanilate) were grown by slow evaporation from a violet liquid at ambient conditions. The entire process took place over a period of less than two weeks.

2.2. Single-crystal X-ray diffraction

Diffraction measurements were performed at 100 K with Agilent Technologies SuperNova (Dual Source) single-crystal diffractometer, equipped with an EOS CCD detector, using mirror-monochromated CuK_α radiation ($\lambda = 1.54184$ Å) from a micro-focused Nova X-ray source. Data collection (ω-scans) and processing (cell refinement, data reduction and empirical absorption correction) were performed with the CrysAlis Pro program package. The structure was solved by direct methods and refined by full-matrix least squares method on F^2 data using SHELXTL programs [6]. All non-hydrogen atoms were refined anisotropically. The methyl H atoms were placed in calculated positions with C—H = 0.98 Å and refined isotropically using riding model with $U_{iso}(H) = 1.5U_{eq}(C)$. The two remaining hydrogen atoms attached to heteroatoms were found in a difference Fourier map. The first one, bonded to a nitrogen atom, was freely refined while the second one, from the hydroxyl group, was restrained with O—H = 0.82 Å and refined with $U_{iso}(H)$ set to $1.5U_{eq}(O)$. Crystal graphics were generated by SHELXTL and VESTA programs [7]. The crystallographic data and structural refinement parameters are summarized in Table 1.

The crystallographic data for this paper are deposited at the Cambridge Crystallographic Data Center (CCDC 10004464). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

2.3. Solid-state nuclear magnetic resonance (^{13}C CP/MAS NMR)

Cross-polarization magic angle spinning (CP/MAS NMR) ^{13}C NMR spectrum was acquired at room temperature, using a Bruker Avance III spectrometer (16.5 T), operating at ^1H Larmor frequency of 700.27 MHz and ^{13}C Larmor frequency of 176.08 MHz. The powdered sample was placed in a 3 mm diameter zirconia rotor and spun at the frequency of 18 kHz. 640 scans were accumulated with a cross-polarization contact time of 2.5 μs and a recycle delay of 6 s. The ^{13}C chemical shifts were referenced to the 38.3 ppm carbon signal of adamantane with respect to tetramethylsilane (TMS).

2.4. Optical vibrational spectroscopy (FT-IR, FT-RS, TDs-THz)

All of the optical vibrational spectroscopy measurements were performed on powdered samples at room temperature. The middle-FT-IR spectroscopy studies were performed both in absorption and attenuated total reflectance (ATR) modes, with a spectral resolution of 2 cm^{-1}. The absorption spectrum was recorded with a Bruker Equinox 55 FT-IR spectrometer, working with a deuterated triglycine sulfate (DTGS) detector and a silicon carbide (globar) source. The spectrum was recorded using a KBr pellet, by collecting 200 scans in the range of 4000–400 cm^{-1}. The ATR measurements were performed by collecting 64 scans with a Nicolet iS10 FT-IR spectrometer, equipped with a diamond crystal, globar source and a DTGS detector. The far-infrared absorption measurements were carried out using a Bruker Vertex v70 vacuum spectrometer, equipped with a polyethylene detector and globar source. The sample was suspended in Apiezon N grease and placed on a polyethylene disc. The measurements were made at the same resolution, also by the accumulation of 64 scans.

The FT-Raman spectroscopy measurements were performed using a Bruker Raman FRA 106/S module, equipped with a germanium detector and the 1064 nm excitation line of a Nd:YAG laser. The laser power of 350 mW, spectral resolution of 2 cm^{-1}, and accumulation of 2000 scans were chosen as the experimental conditions. The spectrum was recorded in the wavenumber range of 4000–50 cm^{-1}.

The time-domain terahertz (TDs-THz) spectroscopy study was performed in the transmission mode, using Teraview TPS 3000 unit. The quoted setup works with the pulses generated by the 800 nm line of a Ti:sapphire femtosecond laser. The ultrashort laser beam is split into the pump and probe beams and directed throughout the system of mirrors to the emitter and detector, which are both based on the low-temperature grown GaAs dipole antennas. The pump beam is focused on the biased emitter antenna to generate the THz pulses through the photoconductive phenomenon. Such pulses last near 1 ps and have the broadband spectrum, which usually covers the range of ~3–100 cm^{-1}. The sample was ground using a mortar and pestle in order to reduce the particle size and avoid the scattering loss. A mixture containing 10% of the sample and 90% of high-density polyethylene (HDPE) was prepared to obtain 400 mg pellet. A pure polyethylene sample was used as a reference. The spectrum was acquired by accumulation of 1800 scans.

Table 1
The crystallographic data and structure refinement parameters for the BrA:TMP (1:1) cocrystal.

Molecular formula	$C_{14}H_{14}Br_2N_2O_4$
Formula weight	434.09
Temperature (K)	100 (2)
$\lambda[CuK\alpha]$ (Å)	1.54184
Crystal system	Triclinic
Space group	$P\bar{1}\left(C_i^1\right)$
Unit cell dimensions	
a (Å)	8.5060 (6)
b (Å)	8.8205 (7)
c (Å)	11.5307 (7)
α (°)	81.043 (6)
β (°)	72.489 (6)
γ (°)	67.099 (7)
Volume (Å)	759.26 (10)
Z	2
D_c (g cm^{-3})	1.899
μ (mm^{-1})	6.962
F (000)	428
Crystal size (mm)	0.20 × 0.12 × 0.10
θ range for data collection (°)	4.0 to 72.1
Reflections collected	5974
Independent reflections	2957
R_{int}	0.0119
Absorption correction	Multi-scan
Transmission, T_{min}/T_{max}	0.76043/1.0000
Data/restraints/parameters	2957/1/210
Goodness of fit on F^2	1.129
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0194$; $wR_2 = 0.0500$
R indices (all data)	$R_1 = 0.0198$; $wR_2 = 0.0503$
Largest diff. peak/hole (e Å^{-3})	0.388/−0.424