Structural, spectroscopic and electronic properties of chosen pyridine triazoles

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Abstract

The present dissertation is focused on the characterization of several derivatives triazolo-pyridine using XRD structural investigations, infrared and Raman studies as well as theoretical quantum chemical calculations. Such compounds have important chemical and pharmaceutical applications due their biological activities. They are also used as optoelectronic materials, thermal and explosive products and helicating ligands for binding of d- and f-electron metals.

In the dissertation three problems are considered for different types of triazolopyridines. These are as follows:

1. The crystal and molecular structures of aquo 7-methyl-1H-[1,2,3]triazolo[4,5-c]pyridinium nitrate composite have been determined by X-ray diffraction and DFT quantum chemical calculations. The thermogravimetric and differential scanning calorimetric analyses were also performed. The compound crystallizes in a monoclinic structure, space group $P2_1/n$ (No. 14) with Z = 4 and the unit cell parameters: a = 7.1392(3), b =14.3163(5), c = 9.5900(4) and β = 107.330(4). The molecular structure and simulated vibrational spectra of the studied compound have been determined using B3LYP/6-311G(2d,2p) approach. The vibrational characteristics of the triazolo ring in the studied compound has been proposed. The role of the hydrogen bond in the formation of the salt composite has been discussed. The main conclusions of these studies can be generalized:

- It was described that the synthesized in this work aquo 7-methyl-1H-[1,2,3]triazolo[4,5-c]pyridinium nitrate is a hybrid material composed of 7-methyl-triazolo-pyridinium cation, nitrate anion and a water molecule in the proportion 1 : 1 : 1. It is soluble in water and therefore it can be used for binding of the d- and f-metal ions to form complex compounds.

- The thermal changes of the studied material proceeds trough progressive water evaporation and gradual decomposition at temperatures 150 - 160 ºC and above 190 ºC.
- The studied material contains the triazolopyridine skeleton that appears in a wide class of pharmaceuticals. Its DFT calculations and spectroscopic studies allowed to isolate the characteristic pattern of the bands that can be used as a diagnostic tool for identification of this double ring system in different materials. The most characteristic IR and Raman bands that allow to identify the presence of this specific double-ring system (Φ) are those observed at: 1275 cm^{-1} corresponding to in-plane asymmetric stretching $\nu(\Phi)$ vibration; 663 cm^{-1} (Raman) and 667 cm^{-1} (IR) assigned to the in-plane symmetric bending $\delta_s(\Phi)$ vibration; 513 – 521 and 204 – 209 cm^{-1} described as wagging $\gamma(\Phi)$ and twisting $\tau(\Phi)$ vibrations, respectively.
- The characteristic feature of the studied composite material is appearance of a pyridinium unit containing hydrogen proton transferred from the triazole ring. It is engaged in the hydrogen N-H···O bond with the water oxygen atom. Its formation follows from the structural XRD data as well as from the appearance of the characteristic IR patterns in the ranges 2300 – 3100 cm^{-1} and at about 1350 cm^{-1} and 720 – 765 cm^{-1}.

2. The second problem solved in the dissertation concerns the crystal and molecular structures of aquo 4,6-dimethyl-5H-[1,2,3]triazolo[4,5-c]pyridine in a zwitterionic form. X-ray diffraction and DFT quantum chemical calculations were used to define its structural properties. This compound adopts a triclinic crystal structure, space group P-1 = C_i^1 (No. 2) with Z = 2 and the unit cell parameters: a = 6.7452 Å, b =9.5292 Å, c = 9.5554 Å and α = 69.279º, β = 73.951º, γ = 74.242º. The temperature dependence of its IR and Raman spectra have been measured and discussed in terms of proton transfer dynamics. Vibrational characteristics of a triazolo-pyridinium system in the studied compound has been proposed. A role of water molecules in stabilization of the compound space structure has been considered. As a result the following conclusions were derived for this triazolopyridine derivative:

- The synthesized in this work material contains 4,6-dimethyl-5H-[1,2,3]triazolo[4,5-c]pyridine unit and lattice four water molecules in its structure. It crystallizes in a triclinic structure described by the P_i^1 space group with Z=2.
- The thermal changes of the studied material proceeds trough progressive water evaporation in the temperature range 140-190 ºC and gradual decomposition at

temperature above 200 ºC. These effects were recorded in the DSC measurements. The IR and Raman studies of this material, performed up to 130 ºC, allowed us to confirm that this compound is stable up to this temperature and water molecules still exist in its structure up to the temperature.

- The studied material contains the triazolopyridine skeleton that appears in a wide class of pharmaceuticals. Its IR and Raman studies allowed us to distinquish the characteristic pattern of the bands that can be used as a diagnostic tool for identification of this double ring system in different pharmaceuticals. These include the bands observed at: 1275 cm^{-1} corresponding to in-plane asymmetric stretching $\nu(\Phi)$ vibration; 777 cm^{-1} assigned to the in-plane symmetric $\nu_s(\Phi)$ vibration; 547-549 cm^{-1} described as wagging $\gamma(\Phi)$ vibration.

3. The crystal, molecular and physicochemical properties of 7-methyl-1H-[1,2,3]triazolo[4,5-c]pyridinium nitrate and 6-methyl-1H-[1,2,3]triazolo[4,5-b]pyridine have been compared. The compounds contain triazolo[4,5-c]- and triazolo[4,5-b]-pyridine skeletons in their structure. Their IR, Raman, UV-Vis and luminescence spectra have been measured and analyzed on the basis of DFT quantum chemical calculations. The differences in their spectral properties have been used for recognition of the materials containing isomeric triazolo[4,5-b]- and [4,5-c]-pyridinium forms. The following general statements were derived from the studies of these materials:

- The optical parameters differentiate the studied isomeric molecules 6MTPb and 7MTPHc.
- IR, Raman and UV-Vis spectra show a characteristic pattern of the bands that can be used as a diagnostic tool for identification of double ring systems in different triazolopyridine derivatives containing the [4,5-b] and [4,5-c] isomeric skeletons.
- The HOMO-LUMO transitions are clearly different for the studied isomeric forms. The calculated and observed values are 240 nm (41,670 cm^{-1}) and 237 nm (42,195 cm^{-1}) for 6MTPb and 229 nm (43,670 cm^{-1}) and 224 nm (44,670 cm^{-1}) for 7MTPHc molecules, respectively.
- The Stokes shift calculated from the wavelengths of the bands observed in the absorption spectra equals to 7,190 cm^{-1} for 6MTPb and 8,435 cm^{-1} for 7MTPHc isomers.

The general achievement of the results presented in the dissertation shows that vibrational spectroscopy is an excellent method for discrimination of different type triazolopyridines and their isomers what may has the application in the studies of the materials and pharmaceuticals containing such structural units.