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Review of Doctoral dissertation of M.Sc. Khalil Salem A. M. Sheweshein: "Structural, spectroscopic and electronic properties of chosen pyridine triazoles"

The doctor dissertation is focused on studies of a few derivatives of triazolo-pyridine. Triazole ring systems are known for their biological activities that make them suitable candidates for production of many analgesic, antiviral, antibacterial etc. drugs. They can also be used for developing of fungicides and herbicides as well as optoelectronic materials. In spite of many applications of these systems, their structural, vibrational and electronic properties have not been widely studied. The undertaking of synthesis of two novel triazolo-pyridine derivatives and their characterization by means of various experimental as well as quantum chemical methods are, therefore, fully justified.

The research plan was very rich and the thesis includes:

1) Synthesis of 7-methyl-1H-[1,2,3]triazolo[4,5-c]pyridinium nitrate and 4,6-dimethyl-5H-[1,2,3]triazolo[4,5-c]pyridinine.
2) Characterization of the obtained materials and 6-methyl-1H-[1,2,3]triazolo[4,5-b]pyridine using X-ray diffraction, TGA, DSC, Raman, IR, electron absorption and luminescence methods.
3) Quantum chemical calculations.

The thesis has 80 pages, 21 figures and 12 tables. The number of references is 112 and choice of these references indicates good knowledge of the studied subject by the author. The thesis is composed of 5 chapters, summary of the main achievements, summary of the thesis,

CV, references, list of schemes, figures and tables. In general, I found the structure of the thesis very clear.

In the first chapter, Introduction section, the author presented in very clear way his motivation and information which materials were subject of the thesis. The author also presented short description of heterocyclic compounds and their importance in pharmacology and biological processes. More details were given by the author on chemical properties and applications of pyridine, triazole and triazolopyridine and their derivatives since the thesis focuses on studies and properties of related compounds. At the end of this chapter, vibrational spectroscopy of organic compounds was briefly described. This chapter is well-written and the information presented is necessary for understanding next chapters of the thesis.

In the second chapter "experimental section", the author described experimental methods used for characterization of the obtained materials, i.e., X-ray diffraction, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as well as vibrational (IR and Raman) and optical (electron absorption and emission) spectroscopic methods. This chapter contains also information of quantum chemical calculations. The short description of each method, together with information on type (model) of the instrument used in the measurements, is important for understanding results presented in the subsequent chapters. All important information was enclosed but there are also some unclear descriptions and mistakes. For 7MTPhcNO_3 •H2O sample, information is missing that it was also studied by TGA method. The mass of 4,6M5HTPc(H_2O)$_4$ was given as 7.241 mg. The accuracy is certainly too high. Two types of IR spectrometers are mentioned and it is not clear for me why the samples were not measured using only one of them and which sample was measured with Biorad and which with Nicolet instrument. The statement that the Nicolet instrument has "a HeNe laser as an IR radiation source" is not correct.

In the third chapter, the author discusses results of his studies of 7-methyl-1H-[1,2,3]triazolo[4,5]pyridinium nitrate. This compound was synthesized for the first time and the author gives details of its synthesis, crystal structure, thermal behavior and vibrational properties. In my opinion, the section describing thermal behaviour should be placed just after the synthesis one. X-ray diffraction data were very well described and it was shown that in this crystal organic cation is almost planar. This cation forms medium strength hydrogen bonds with the NO_3^- and H_2O groups. There are also weaker C-H···O bonds. The author also lists optimized and experimental parameters in Table 3.2. Three columns for the optimized parameters are shown: one for 7MTPHc, second for 7MTPHc•H_2O and third for 7MTPc•NO_3.

I miss here a short comment on similarities/differences between the experimental and theoretical data.

The last part of the third chapter is most important since it contains detailed information on vibrational properties of this compound. This section was divided into a few subsections describing vibrations of nitrate anion, organic cation (methyl groups and triazolopyridinium rings) and hydrogen bond vibrations. Regarding nitrate anion vibrations, the assignment given in Table 3.4. is correct but in my opinion it would also be of interest to list calculated modes and assignment also for the 7MTPc•NO_3 cluster (the author shows only the calculated IR and Raman spectra). It is also not clear if calculations were performed for a neutral organic molecule or cation. Nevertheless, calculations of vibrational modes for the organic component are very valuable part of the thesis. The assignment of these modes was discussed in details and especially important data were obtained for lower wavenumber modes, which are much more difficult to assign than modes observed above 1000 cm^{-1}. It is important to add here that the experimental spectra were recorded for the solid state sample and, therefore, some low wavenumber bands should be assigned to the lattice modes. The author also discussed influence of hydrogen bonds on vibrational properties of the organic cation. This is also an important part of the thesis since numerous literature data reporting DFT data neglect this effect treating molecules/cations as isolated objects. Again, I think that it would be useful to add (maybe as a supplement) a table presenting calculated modes for 7MTPHc•H_2O cluster.

The fourth chapter of the thesis describes data obtained for 4,6-dimethyl-5H-[1,2,3]triazolo[4,5-c]pyridine in a new zwitterionic form, in which the proton is transferred from the triazolo to pyridine ring. This compound crystallizes in the triclinic structure, space group *P*-1, and the zwitterions are held in the structure through N-H···O and O-H···N hydrogen bonds. The author calculated molecular electrostatic potential maps. These calculations showed that the zwitterions are strongly polar and interactions between these zwitterions stabilize the crystal structure. The structure is stable to about 150°C, and above this temperature water molecules are lost. The structure of this chapter is similar to that of chapter 3. However, Table 4.4. lists calculated wavenumbers also for clusters containing water molecules. This is very helpful in understanding effect of hydrogen bonds on vibrational properties. In general, assignment of modes is correct and the author clearly identified modes related to water molecules involved in medium strength hydrogen bonds. To facilitate this, the author performed temperature-dependent studies down to 80 K. He observed splitting of a few bands at low temperatures and stated that "this effect can originate in the band narrowing or it can be a result of lowering symmetry of the unit cell from C_i to C_1." Judging from the spectra

and the fact that most pronounced changes are observed for vibrations of water molecules, it seems that the observed changes are not related to a phase transition. Nevertheless, the author should perform DSC measurements below room temperature to better understand this behavior.

The fifth chapter is devoted to spectroscopic properties of two triazolopyridine isomers, [4,5-b] appearing in previously reported 6-methyl-1H-[1,2,3]triazolo[4,5-b]pyridine (6MTPb) and [4,5-c] system appearing in the described above 7-methyl-1H-[1,2,3]triazolo[4,5]pyridinium nitrate. The author identified a number of modes characteristic for skeletal vibrations of separate triazol and pyridine ring as well as modes involving vibrations of both rings. These modes were collected in Table 5.2. and it was shown that the same type vibrational modes my differ for two isomers even by more than 100 cm^{-1}. Thus the author clearly showed that these vibrations can be used as a diagnostic tool for distinguishing between [4,5-b] and [4,5-c] isomers. In contrast to ring vibrations, modes related to the methyl groups show similar wavenumbers for both isomers and cannot be used as a diagnostic tool. The author also showed that the two compounds have different optical properties. The electron absorption bands are observed in the ultraviolet region and have a few components that were attributed to transitions between various electronic levels that were calculated using DFT method. Both compounds show also luminescence with the maxima at 505 nm for 6MTPb and 440 nm for 7-methyl-1H-[1,2,3]triazolo[4,5]pyridinium nitrate.

The last chapter gives a short summary of the thesis and lists the main achievements.

In summary, I found the subject of the thesis interesting. The presented data are of great scientific value and the author has published them in two publications. He is also a first author of one more paper. The results were also presented on one international conference.

In general, the thesis is well written and discussion sound. The presented discussion shows that the author has deep understanding of structural, vibrational and optical properties. The number of typos and errors is small. In my opinion the rich experimental and theoretical data and presented analysis of the obtained results show that the author of the thesis will be able to carry on research on organic and organic-inorganic hybrid materials. I agree with the interpretation of nearly all data by the author and my comments to the author are not critical but I wanted to emphasize that some improvement of presentation could help to better evaluate the obtained results. I regard these comments as suggestions for future work.

The doctor dissertation fulfils criteria of the Polish Law from 2003-03-12 (Dz. U. No 65/03, 595, and later changes) and regulation of the Minister from 2004-01-15 (Dz.U. No 15/04, 128 with later changes).

I recommend, therefore, acceptance of the dissertation and allow M.Sc. Khalil Salem A. M. Sheweshein to defend his thesis.