R E V I E W

by Prof. Todor Minkov Dudev, D.Sc.

Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski",

member of the Scientific Jury appointed by order RD-09-152/19.06.2020

of

the Ph.D. thesis of a full-time doctoral student

Silvia Hristova Hristova

presented for awarding a Doctor degree in the Professional area

4.2. "Chemical Sciences", Specialty "Organic Chemistry"

Thesis title: **Tautomerism as an elementary mechanism for signal transmission in molecular devices**

Supervisor: Prof. Liudmil Antonov, D.Sc.

Silvia Hristova Hristova obtained her both B.Sc. (in "Chemistry", 2015) and M.Sc. (in "Modern methods of synthesis and analysis of organic compounds", 2016) degrees from the Faculty of Chemistry and Pharmacy, Sofia University. Since 2017 she has been a full-time doctoral student at the Institute of Organic Chemistry with Centre of Phytochemistry, BAS. During her doctoral studies she has carried out a three-month specialization at the University of Friburg, Switzerland. Silvia Hristova has co-authored 12 articles, published in peer-reviewed scientific journals.

Doctoral thesis is well written/formatted and clearly and convincingly describes the scientific achievements of the candidate. It contains 190 pages, 79 figures, 15 tables, 37 schemes, 193 literature sources and 3 appendices. It is based on 4 published, within the period 2017-2020, papers (2 articles in Dyes and Pigments; IF = 3.76; quartile Q1, one in Journal of Molecular Liquids, IF = 4.51 quartile Q1, and one in Chemistry). These have been already cited 5 times in the scientific literature. Results from doctoral studies of Silvia Hristova have been presented at 15 scientific forums in the form of oral (5 participations) and poster (10 participations) presentations. The abstract of the thesis provided correctly reflects the basic results and scientific achievements of the candidate.

Thesis is structured as follows:

- Introduction (2 pages)
- Literature survey (49 pages). The basic physico-chemical characteristics of different type of molecular devises, based on tautomeric transformations, are presented
- Aims and tasks of the dissertation (2 pages)
- Experimental part (11 pages). It includes the procedures involved in synthesizing and characterizing the compounds under study, spectroscopic measurements, X-ray crystallographic determinations, and quantum-chemical calculations.
- Results and discussion (100 pages)
- Conclusions (2 pages)
- Contributions (1 page)
- Appendices (4 pages)
- Literature cited (24 pages)

Relevance of the conducted research: The topic of the presented dissertation is especially timely given the increased demand for new molecular electronic components, which, based on chemical transformations, can be used as structural elements (wires, switches, logic elements, capacitors) in working hardware devices. The dissertation focuses on studying molecules with pronounced tautomerism, which can play the role of rotary switches and molecular cranes.

Results: Part of the dissertation is dedicated to studying the tautomeric equilibrium in a group of azo dyes. This is a wide class of organic compounds that are highly stable and find application in a number of areas of everyday life and technology. They have a well-defined enol-azo / keto-hydrazo tautomerism. However, their potential for use in molecular electronics is poorly understood. To shed light on this problem, the candidate has selected a series of representatives of this group of azo dyes (two of which have been synthesized and characterized for the first time) and has conducted detailed research on the processes of their teutomerization. Through the combined use of experimental (electron absorption spectroscopy and X-ray diffraction analysis) and theoretical (quantum chemical calculations) methods, the main factors governing the tautomeric equilibrium in these systems have been derived. These are internal (introduction of a substituent that is able to form an additional intramolecular hydrogen bond and which transmits the effect of external stimuli on the tautomeric residue) and external (solvent polarity and medium pH). The presented results convincingly show that the variation

of these parameters allows for controlled manipulation of the tautomeric equilibrium in solution. It has been found that one of the newly synthesized compounds (2.3 according to the nomenclature of the dissertation) is suitable for use as a tautomeric switch.

A large part of the dissertation is given to studies of tautomerization in molecules with potential application as molecular rotor switches. Attention has been focused on the rotary switch 2- (2- (2-hydroxy-4-nitrophenyl) hydrazono) -1-phenylbutane-1,3-dione (compound 3.1 in the dissertation) and its derivatives. Through the combined use of state-of-the-art experimental and theoretical methods, an extremely detailed and in-depth analysis of the tautomerization processes in these systems and the factors on which they depend has been conducted. Based on the results of performed research, the dominant model for tautomeric conversions of compound 3.1 has been refuted and a new one has been proposed, which has been already recognized by the international scientific community. The influence of a number of factors (solvent properties, temperature, concentration, presence of water, basic agent, number of condensed aromatic cores in the stator) on the stabilization of the specific tautomeric forms of the compounds from the target group was evaluated. Conclusions are made regarding the applicability of some of the studied objects as rotary switches.

Contributions to the dissertation:

• The role of stimulated proton transfer on the tautomeric equilibrium in azo dyes has been established by introducing into the molecule an unconjugated functional group, playing the role of an "antenna" for transmitting the effect of external stimuli on the tautomeric subunit.

• The existing paradigm in the literature on the processes of tautomerization in the group of studied molecular rotors is refuted and a new model is proposed, based on the combined application of state-of-the-art theoretical and experimental approaches.

• The key determinants and levers for controlling the tautomerization processes in the studied objects have been identified.

Conclusion: The Ph.D. thesis of doctoral student Silvia Hristova is a comprehensive, in-depth, well-planned and well-executed research. The topic is relevant and the research will find a wide response among the scientific community. The work is written clearly and in a logical sequence. With the exception of some minor inaccuracies of a technical nature, I have no general remarks on the work. The doctoral student is a young researcher with knowledge and skills for independent research. She has skillfully selected and applied modern approaches

/ techniques for solving the set tasks. She has done a lot of research work at a very high scientific level. The achieved results can be referred to the category of novelties in scientific research. They provide a basis for further studies of tautomerization processes in systems with potential for application in molecular electronics.

The dissertation and the attached author's abstract of doctoral student Silvia Hristova correspond in volume and quality to the Law for development of the academic staff in the Republic of Bulgaria. The above gives me a reason to assess very highly the dissertation and to convincingly propose to the esteemed scientific jury to award Silvia Hristova Hristova the educational and scientific degree "Doctor" in the professional area 4.2. Chemical sciences (Organic chemistry).

27.07.2020

prof. Todor Dudev