REVIEW

of prof. Denitsa Yancheva Pantaleeva, PhD,

Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,

Regarding: thesis for awarding the Doctor of Philosophy (PhD) degree in scientific area "Natural Sciences, Mathematics and Informatics", professional field 4.2. "Chemical Sciences", doctoral program in Organic Chemistry

Author: *SILVIA HRISTOVA HRISTOVA*

Thesis title: *TAUTOMERISM AS AN ELEMENTAL MECHANISM FOR SIGNAL TRANSFER IN MOLECULAR DEVICES*

Supervisor: *Prof. DSc Liudmil Antonov, Institute of Organic Chemistry with Centre of Phytochemistry, BAS*

1. General description of deposited materials

The author of the doctoral thesis – Silvia Hristova Hristova, is a doctoral student in the regular form of training at the Laboratory of Organic Synthesis And Stereochemistry, IOCCP-BAS, under the supervision of Prof. DSc Liudmil Antonov from the same laboratory.

The set of documents in hard copies deposited by Silvia Hristova **complies** with the internal Rules of Procedure of IOCCP-BAS and satisfies the criteria of BAS for awarding a Doctor of Philosophy (PhD) degree. The doctoral student has deposited CV, doctoral thesis, abstract of the doctoral thesis in Bulgarian and English language, list and hard copies of the publications covering the doctoral thesis materials, lists of citations of the publications, conference presentations, project participations and the corresponding hard copies, as well as a general report on the doctoral training and the awarded credits. The documents are well organized and present clearly the education and scientific work carried out in the doctoral training.

2. Short description of the doctoral student biography

Silvia Hristova has graduated the Faculty of Chemistry and Pharmacy of Sofia University "St. Kliment Ohridski". She has received her Bachelor degree in Chemistry in 2015, and continued her education in a Master degree program in "Current Synthetic Methods and Analysis of Organic Compounds". In 2016 she has graduated as a Master student with an excellent grade. In 2017 S. Hristova has started a doctoral training at IOCCP-BAS, under the supervision of Prof. DSc Liudmil Antonov. In the period 2016-2019, she has been an active member in 8 scientific projects funded by Bulgarian and international funding organizations, which has resulted in a broad publication record – S. Hristova is a co-authors of 12 publications in total, covering the doctoral thesis material and the other scientific activities.

3. Topicality of the thesis and relevance of the planned scientific tasks

The aim of the doctoral studies of Silvia Hristova is elucidation of the possible tautomerism and its effect on the switching action of two groups of compounds: naphthalen-2-ol azo dyes with possible controllable tautomerism of the "proton crane" type, and β-diketone arylhydrazones – in the role of rotary switches. The structure and tautomeric interconversions of the two groups of compounds are characterized by means of experimental techniques (UV and NMR spectroscopies, X-ray diffraction) and quantum-chemical methods. The possible controllable shifting of the tautomeric equilibrium by external stimuli (pH changes, concentration effects) was clarified by molecular spectroscopy.

The study falls within a field of great scientific interest, fuelled by the constantly growing search of new approaches to enhance the performance of the electronic devices and to reduce their components' size. In the context of these technological needs, the development of molecular devices is a promising approach that offers versatile options to tune the desired properties by modification of the molecular structure.

4. Topic presentation by the doctoral student

The literature survey presented within the thesis clearly demonstrates the extensive knowledge of S. Hristova in the topic of the research and her good skills to analize and summarize the literature data. The thesis includes more than 190 literature references, covering the most recent advances in the filed as well – 135 of them are cited in the Literature review section, while the rest are supporting the discussion of the scientific results. The current state-of-the art in the field and the specific focus of the doctoral studies are presented by S. Hristova in a consice and clear manner.

5. Methodology of the study

The methodology of the study relies on appropriate methods and guarantees the accomplishment of the research aims. The analytical methods applied in the study – spectroscopic techniques and X-ray analysis, have provided reliable information on the structure in crystal state and solution, the tautomeric forms of the compounds and the effect of external stimuli. The choice of M06–2X functional and TZVP basis set, applied in the current quantum chemical calculations, is based upon the good performance of this combination reported earlier for structurally related compounds. The high theoretical level has allowed an accurate description of the spectral changes in solution.

6. Characteristics and scientific contributions of the thesis

The doctoral thesis covers 190 pages and includes Introduction, Literature Review, Aim and Scientific Tasks, Results and Discussion, Conclusions, Contributions, and References. The references cited in the thesis are numbers as 193, but actually are even more as in some cases several articles are given within a number. The thesis includes a large number of figures (over 70) and schemes (over 30), along with 15 tables.

The Literature review section presents a detailed survey on the tautomerism and the factors affecting the tautomeric equilibria, the applicability of the molecular spectroscopy in the study of these phenomena, and different types of molecular switches. The survey covers a wide variety of studies in the field, including such performed by the scientific group of the supervisor.

In order to accomplish the aim and the tasks, the doctoral student has focused on two groups of compounds: naphthalen-2-ol azo dyes and β-diketone arylhydrazones. The study of the first

group of compounds has clarified the role of the additional unconjugated functional group on the tautomeric equilibrium. The study on the second group of compounds – derivatives of 2-(2-(2-hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-dione, has explored the propensity of the compounds to conformational, tautomeric and ionic conversions in nonpolar and polar solvents, as well as the effect of the solvent, temperature, concentration, and the presence of water of base. The effect of a larger number of fused rings in the stator was studies as well, even though with a relatively small number of model compounds.

The original research results are systematically presented in the thesis supported by a set of figures, schemes and tables. The discussion of the results is detailed and follows a good scientific level. A critical approach to the interpretation of experimental data, provided by other authors in earlier studies, has been demonstrated by the doctoral student and has resulted in additional characterization and revision of the existing interpretation.

7. Contribution and significance of the research results for the science and practice

The doctoral thesis of S. Hristova provides contributions of scientific significance (development of an approach for stimulated proton transfer by introducing an unconjugated functional group into the molecule; complementation and revision of the existing interpretation of scientific data) as well as contribution of practical meaning (development of an approach for discrimination between the isomers of β-diketone arylhydrazones in solution based on ^{2}J constants).

8. Преценка на публикациите по дисертационния труд

The doctoral studies are supported by publication of 4 scientific papers in international renewed journals with high impact factors. In all publications and conference presentations S. Hristova is the leading author which testifies her leading role in the studies.

9. Personal involvement of the doctoral student in the studies

The predominant role of S. Hristova in the accomplishment the planned scientific tasks and the aim of the study are well demonstrated by her doctoral thesis and the respective publications. In the course of her doctoral studies, she has acquired an extensive knowledge in the field of organic materials for development of molecular devices and advanced skills in the application of modern analytical and computational methods.

10. Summery (abstract) of the thesis

The summery (abstract) in Bulgarian and English language reflect precisely the content, the conclusions and the contributions of the doctoral thesis.

11. Remarks and recommendations

In my opinion, the graphical materials (figures and schemes) in Result and Discussion section could be presented in some condensed form – the large number of figures and schemes hampers to some extend the reading. Part of the included figures might be designed as subsections of a joint figure or by some other summarized way of presentation.

The interpretation of the experimental data in solution and the assignment of the observed absorption maxima to the possible isomeric, tautomeric and ionic forms, predicted by quantum chemical calculations, might be successfully complemented by other spectral methods capable of providing conclusions on the structural changes, such as IR spectroscopy in solution.

12. Personal impressions of the doctoral student

My personal impressions of Silvia Hristova, acquired during her presentations at the Scientific Colloquium "Functional materials, computational modeling and technologies" of IOCCP-BAS and the discussion following these presentations, are excellent. To my opinion, S. Hristova is a well-trained young researcher with developed skills of personal initiative and thoroughness in the scientific research.

13. Recommendations for future application of the scientific results and contributions of the doctoral thesis

Having in mind the topicality of the research area and the promising results obtained within the doctoral studies, I can recommend to broaden the elucidation of the molecular rotors with the synthesis and study of new β-diketone arylhydrazones with other electron acceptor groups in the structure.

CONCLUSION

The doctoral thesis ***provides results of scientific and practical importance which are original contributions to the science*** and **comply with all** criteria for awarding a PhD degree specified in the Law for the development of the academic staff in the republic of Bulgaria (LDASRB), the National regulations for the application of the LDASRB (RALDASRB) and the corresponding Regulations of BAS. The presented materials and the results from the doctoral studies **fully** satisfy the specific internal Rules of Procedure of IOCCP-BAS.

The doctoral thesis demonstrates that the doctoral student Silvia Hristova **has acquired** extensive theoretical knowledge and professional skills in the scientific specialty "Organic Chemistry", and **confirms** her ability to conduct independently a scientific research.

Based on the above, I give my ***positive assessment*** of the studies presented by the reviewed thesis, abstract, scientific results and contributions, and ***suggest to the Scientific Jury to award Sylvia Hristova the educational and scientific degree "Doctor of Philosophy" (PhD)*** in scientific area "Natural Sciences, Mathematics and Informatics", professional field 4.2. "Chemical Sciences", doctoral program in Organic Chemistry.

10.08.2020.

Reviewer: Деница Панталеева, СОА, ИОХЦФ-БАН, София, България

Prof. Denitsa Pantaleeva, PhD