REVIEW

by Prof. Dr. Todor Minkov Dudev
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of the materials submitted for participation in the competition
to hold the academic position of 'associate professor'
at the **Institute of Organic Chemistry with the Center for Phytochemistry (IOHCF**), **BAS**
by field of higher education
"Chemical Sciences" professional direction 4.2 "Organic Chemistry"

In the competition for 'associate professor, announced in the State Gazette, no. 9 of 9/30.01.2024 and on the website of the IOHTCF, BAS, as a candidate participates **Ch. Assistant Professor Dr. Vera Ventsislavova Deneva** from IOHTCF – BAS.

1.General presentation of the received materials

To participate in the announced competition, only one candidate has submitted application, Ch. Assistant Professor Dr. Vera Ventsislavova Deneva, IOHTCF – BAS. The presented by Ch. Assistant Professor Vera Ventsislavova Deneva, PhD, set of materials is in accordance with the Regulations for the Development of the Academic Staff of the IOHTCF, and meets the criteria of the IOHTCF-BAS for occupying the academic position "associate professor".

The candidate ch. assistant professor Vera Ventsislavova Deneva, Ph.D., has submitted a total of 26 scientific papers. 16 scientific papers that are not part of the Ph.D. dissertation are accepted for review and are counted in the final evaluation along with 11 research projects. 5 scientific papers on the dissertation and 5 scientific papers outside the competition's topic are not reviewed. The distribution of scientific works determined for peer review according to the relevant Q factors is as follows: **Q1 – 12 publications and Q2 – 4 publications.**

2.Brief biographical data of the applicant

Vera Deneva completed her higher education (bachelor) at the Faculty of Chemistry of the University of St. Kliment Ohridski" in 2007, and in 2009, in the same faculty, she received a master's degree in Organic Chemistry. In 2009, she entered a doctoral program at the Institute of Organic Chemistry with the Center for Phytochemistry - BAS, where in 2013, under the supervision of Prof. Lyudmil Antonov, she successfully defended her doctoral dissertation on the topic "Experimental and

theoretical studies of tautomeric systems based on azo-naphthols and their azomethine analogues'. In 2012, she was appointed as an Assistant Professor at IOHTCF-BAS, and in 2017, at the same institute, she rose to the position of Chief Assistant Professor. Throughout her career, Dr. Deneva has published 26 scientific papers in refereed high-impact (mostly Q1 quartile) journals in the field of tautomeric conversions in systems suitable for use as molecular switches and sensors. The results of her research have been reported at 13 national and international scientific conferences. She specialized in Universite de Fribourg, Switzerland (10.2011 – 06.2012). She is the winner of the BAS award "I.E. Geshov" for the youngest scientist under 30 (2011). She was a participant or supervisor in, respectively, 9 and 1 successfully completed national scientific projects under the Scientific Research Fund as well as a participant in two scientific networks on supramolecular chemistry (Suprachem@Balkans.eu and SupraMedChem@Balkans.Net) funded by the Swiss National Science Foundation foundation.

3.General characteristics of the applicant's activity

Evaluation of the candidate's scientific and scientific-applied activity

For the competition, Dr. Deneva presented 16 publications, all printed in international refereed journals, and grouped into indicators group B (6 publications) and D (10 publications). All articles were published between 2017 and 2023 and do not overlap with the works used to obtain the educational and scientific degree "Doctor" (2013). Out of all 16 publications, 12 fall into quartile Q1 and the remaining 4 fall into quartile Q2. The impact factors of the journals where the works are published vary between 1.7 and 6.6, with those with values of 3.3 - 4.6 prevailing. With the exception of one article (No. 6 from group D; two co-authors), all articles are the work of a large group of co-authors (between 6 and 10). Dr. Deneva is first author in 6 of the publications, second author in 5 of them, third in 2 publications, fourth in 2 works and fifth in 1 article. The majority of publications (11) are in collaboration with scientists from abroad. The articles included in the contest have been cited 118 times by independent sources. The candidate's research results have been presented, after 2013, with posters (7) and oral reports (2) at 5 national and 4 international conferences.

Contributions (scientific, scientific-applied, applied)

Dr. Deneva's scientific contributions are aimed at studying and characterizing tautomeric conversions in a number of classes of organic molecules, as well as determining the key factors affecting

tautomeric equilibrium in these systems. Specifically, the candidate's research is focused on the following classes of organic molecules:

Azo dyes (Articles 1 and 5 of Indicator C and 1, 4, 5 and 6 of Indicator D)

By combined use of UV/VIS and NMR spectroscopy, quantum chemical calculations and crystallographic analysis, the effect on the behavior of the tautomeric proton of structural modifications in azonaphthol dyes as well as complexation with alkaline earth cations has been revealed. The role of tautomerism as the main switching mechanism in the selective complexation with the ligand 4-(phenyldiazenyl)naphthalen-1-ol as a tautomeric fragment and an amide group as an antenna for binding to metal ions was evaluated. Based on the conducted research, a system was developed in which complexation with metal ions completely shifts the tautomeric equilibrium to the keto-tautomer and significantly increases the stability of the formed complex. A theoretical design of tautomeric optical sensors, based on the same ligand, for the detection of alkaline earth cations is proposed. In Group B publication 5, two new 4-OH coumarin-based rotary switches containing fixed carbonyl groups in the rotor are analyzed using molecular spectroscopy and quantum chemical calculations. Protonation is shown to be the driving force for E/Z switching, and the possible mechanism of the process is also proposed. Group C publication 1 reveals the key role of water and convincingly proposes a new (supported by both theoretical and experimental data) tautomerization mechanism of ethyl-2-(2-(quinolin-8-yl)hydrazono)-2-(pyridine) -2-yl)acetate: proton transfer from the Z- to the E-form of the switch is accomplished by chains/wires of water molecules, which is accompanied by a significant lowering of the activation energy of the tautomeric conversion.

Shiff bases (Articles 2, 3 and 6 of Indicator C)

The tautomeric equilibria (using UV-VIS and fluorescence spectroscopy, crystallography and quantum chemical calculations) of two 4-substituted phthalimide 2-hydroxyl Schiff bases with different 2-hydroxyaryl moieties have been investigated. Tautomerism has been observed for the compound with the naphthyl moiety (solvent dependent), while none has been reported for the phenyl analogue. Publication 3(C) sheds light on the tautomerization of two newly synthesized Schiff bases derived from 7-hydroxyquinoline. Upon irradiation, both compounds exhibit rotation about a specific bond, resulting from intramolecular excited-state proton transfer, making them suitable candidates for use as bistable switches. The process of intramolecular rotation stops when the system is protonated. The combined use of spectral and quantum chemical methods revealed the mechanism of tautomeric conversion in two other molecular switches, N-(benzo[d]thiazol-2-yl) picolinamide and N-(benzo[d]thiazol-2-yl) isonicotinamide. The obtained results elucidate the photophysics and proton

transfer dynamics of these systems, which reveals their potential applications as optoelectronic devices.

Tautomer Equilibria in Other Organic Systems (Publications 4 of Indicator B and 1, 8, 9, 10 of Indicator D)

In a series of publications, in-depth analyses of tautomeric processes have been performed on 10-hydroxybenzo[h]quinoline and its structurally modified compounds (Publication 1(D)), a rotor switch synthesized with a pyridyl ring and a carboxyl group as mobile substituents (Article 4(B)), pinene-bipyridine and pinene-phenanthroline derivatives (Article 8(D)), favipiravir (Article 9(D)) and a group of compounds with a 1,3,5-triazine nucleus (Article 10(D)) . The mechanism of proton transfer in these systems has been elucidated. The key factors influencing the tautomeric equilibrium have been determined.

Other topics (publications 3 and 7 of indicator D).

Publications 3(D) and 7(D) are devoted to the use of near-infrared and Raman spectroscopy for the quantitative determination of active components of pharmacological interest in natural products, as well as the quality of Bulgarian wines. The articles offer reliable and innovative approaches to perform relevant analyses.

4. Assessment of the candidate's personal contribution

Dr. Deneva has made a significant contribution and has been the driving force in the development and shaping of the majority of the publications included in the competition. The fact that, in the articles with a large number of co-authors, she is the first author in 6 and the second author in 5 of them is indicative.

5. Critical remarks and recommendations

Dependencies regarding the behavior of the tautomers of the studied systems in different environments and chemical environments have been convincingly deduced. To what extent are the results of the conducted research applicable in practice and have steps been taken to patent the obtained results?

Conclusion

The publications and habilitation thesis submitted by the candidate are on the topic of the competition and represent original scientific developments with significant contributions in the field of tautomeric transformations in organic systems and molecular rotors and switches. The attached materials give me reason to believe that the candidate is an established scientist in his field with deep knowledge and practical skills in the field of molecular spectroscopy and theoretical chemistry. Demonstrates excellent mastery of a set of experimental and computational approaches, which allows her to study at a high scientific level (state-of-the-art) complex molecular systems with non-trivial behavior and physico-chemical characteristics. The obtained results are of an innovative nature (proof is the series of publications in high-impact journals) and can be classified as novelties in scientific research. The candidate demonstrates maturity, creative thinking and the ability to select and successfully solve tasks with a high impact for science and practice.

In conclusion, as a result of the above, I am convinced that with her scientific and research activity, Ch. Assist. Prof. Dr. Vera Ventsislavova Deneva fully meets all the requirements of the Law on holding the academic position “Associate Professor". I offer Ch. Assist. Prof. Dr. **Vera Ventsislavova Deneva**, to be elected Associate Professor in professional direction 4.2 Chemical Sciences (Organic Chemistry) at the Institute of Organic Chemistry with the Center for Phytochemistry (IOHTC), BAS.

21.05.2024 Reviewer: 

(Prof. Todor Dudev)