

STATEMENT

by prof. Vassil Borissov Delchev, DSc,
from the Department of Physical chemistry, University of Plovdiv
on the materials for the defence of a doctoral thesis
for the awarding of the academic degree *Doctor of philosophy* (PhD)
in the Institute of general and inorganic chemistry – Bulgarian academy of sciences
(IGIC - BAS)

Field of higher education: 4: Natural sciences, mathematics and informatics
Professional area: 4.2. Chemical sciences
Scientific field: Theoretical chemistry

PhD student (aspirant): Nina Stoyanova - Nankova, IGIC-BAS

Title of the doctoral thesis: „Theoretical investigation on the proton transfer mechanism
in monomeric units of nucleic acids and biologically active
compounds taking into account a specific medium effect”

Scientific supervisor: prof. Venelin Enchev, DSc

Director's order for the constitution of the Scientific jury: **ПД-09-124/12.07.2023 г.**
Decision of the first meeting of the Scientific jury: **to write an academic statement.**

All materials for the defence of the doctoral thesis for the awarding of the academic degree *Doctor of philosophy* to Nina Stoyanova are presented in digital form. The documentation involves: 1) Director's orders for taking her as a PhD student (№ ПД-09-78 / 28.06.2019 г.) and for the finishing of the PhD study (№ ПД-09-92 / 14.06.2022 г.); 2) a certificates/protocols for passed examinations during the PhD study; 3) a standard *Curriculum Vitae*; 4) a diploma for higher education – master only; 5) a list of publications included in the PhD thesis; 6) a list of citations; 7) a list with participations in conferences and other scientific events, awards; 8) a PhD thesis, 9) an abstract (summary) of the PhD thesis in Bulgarian only.

Biographic information

Nina Stoyanova has been born in Sofia, Bulgaria. In the period 2011-2016 she is a bachelor in “Computer chemistry” at the Sofia University. In 2018 she has graduated the same university with a master's level diploma in “Medicinal chemistry”. In 2018 and 2021 she has passed two summer schools. After finishing her bachelor's level Nina Stoyanova has been selected to the position “Chemist” at the Institute of organic chemistry – Bulgarian academy of sciences. Two years later she has been nominated at the position “assistant professor” at the same institute in the “Structural organic analysis” laboratory. In 2019 she has moved at the Institute of general and inorganic chemistry – Bulgarian academy of sciences, at the same position. Since Mai 2023 she works as a “Chemist” in the “Theoretical and computational chemistry” laboratory at the same institute

Nina Stoyanova shows a very good command in English language (level B2). Her personal skills are connected with the different quantum chemical packages and graphical / visualization programs as GAMESS, Gaussian, Origin, MOPAC, Chemcraft, FireFly etc. In the CV file Nina Stoyanova has declared 6 scientific papers with impact factors – five with quartiles Q2 and one with quartile Q1. I can say that the candidate meets the national minimum requirements for the acquisition of the scientific and educational degree "Doctor".

Importance of the theme

The dissertation treats important for science questions on the tautomeric equilibrium in DNA / RNA nucleobases and their derivatives. Special attention is paid to the influence of the

surroundings on the tautomeric equilibria and it is shown that the solvent can drastically change the kinetics and thermodynamics of the processes. These are questions of great importance for the prediction of different properties of the studied systems in solvents (mostly water) and for control of the reactions in order to escape from some negative processes that might occur in the living world (like point mutations etc.).

Publications included in the doctoral thesis

The results from the PhD thesis are published in 3 journals with a deep impact: *Journal of Biomolecular Structure and Dynamics* (Q2), *Photochemistry and Photobiology* (Q1) and *International Journal of Quantum Chemistry* (Q2). The paper in the first journal is cited 5 times in international journals. The total impact factor of the published papers is about 8.5. The results are reported on 7 scientific forums. One prize has been awarded.

Methodology

The studied reactions and interactions in the dissertation are performed by means of quantum chemical methods included in the standard packages of GAMESS-US and GAUSSIAN. Most of the calculations were carried out with functionals of the Density functional theory as well as with the *Møller-Plesset* perturbation theory. The coupled-cluster methods CCSD and CCSD(T) were also applied for some of the calculations. The selected methods are accurate enough for the prediction of the properties of the molecules and investigations of reaction mechanisms.

The surroundings (mostly water) was modeled by two basic approaches: 1) use of the implemented continuum models in the standard quantum chemical packages GAMESS-US and Gaussian; 2) discrete interactions of solvent molecules with the studied systems.

The rate constants of the reactions were estimated by the *Eyring* equation (8) which is wrongly written (the minus sign in front of ΔG^\ddagger is missing). In this aspect a question arises: are the rate constants calculated with eq. (8) or the minus sign is taken into account? Another question is what is the logic of eq. (9) for reversible reactions? It is a simple sum of two rate constants and I cannot understand why it is called observable rate constant!!! I also disagree with the statements in page 38 that "...at high temperature, $k < 1$." Furthermore the transmission coefficient is close to unity for adiabatic reactions, however it should be taken into account for example for tunneling processes etc.

Autoreferat (PhD thesis summary)

The PhD thesis summary in Bulgarian comprises 40 pages and it describes the major points of the dissertation. I did not find an English version of the PhD thesis summary.

CONCLUSION

The provided materials for the current procedure are in agreement with the Law for development of the academic staff in Republic of Bulgaria, the Rules for its application as well as with the minimal national requirements in the professional field. I consider that Nina Stoyanova is a complete scientist in the area of research and she can guide an independent research in the field of computational organic chemistry and the chemistry of reaction mechanisms. All this and the aforementioned facts drive me to give my **positive vote** for the awarding of the academic degree *Doctor of philosophy* (PhD) of Nina Stoyanova - Nankova in the field of higher education: 4: Natural sciences, mathematics and informatics; professional area 4.2. Chemical sciences; scientific field: Theoretical chemistry.

18.05.2021 г.
Plovdiv