REVIEW

of a thesis for awarding the Doctor of Philosophy (PhD) degree
in the professional field 4.2. Chemical Sciences and doctoral program Organic chemistry

Author: **Silvia Hristova Hristova,** PhD student at the Institute of Organic Chemistry with Centre of Phytochemistry –BAS,
Thesis title: Tautomerism as an elemental mechanism for signal transfer in molecular devices,
Supervisor: Prof. DSc Liudmil Antonov
Reviewer: Prof. Boris Lubomirov Shivachev, PhD, IMC-BAS; Member of the Scientific Jury appointed with directors decree РД-09-152/19.06.2020 г. .

The dissertation developed by Silvia Hristova comprises 187 pages contains 79 figures, 15 tables and 37 schemes (not counting the unnumbered schemes of compounds in the text – a total number of 17). In the thesis 193 literature sources are cited. The dissertation format is close to classical template and contains the following chapters: Literature review which ends with the Aim and Tasks of the dissertation, Experimental (experimental) part, Results and discussion part, Conclusions, Contributions and References.

The subject of the dissertation deals with a hot topic in current scientific investigations namely organic molecular switches and electronic components. The investigated compounds and materials are new, and are prepared (synthesized) on the basis of appropriately selected reaction mechanisms and schemes with a view of the subsequent studies and for having desired potential properties. In this sense, the topic is promising, with a potential practical orientation and can serve as a basis for future research work.

The literature review (overview) is presented on 52 pages, and is divided into three subsections. The literature review ends without the author drawing conclusions in an explicit form, but it acts as a basis for determining the Aim of the dissertation and the Tasks that need to be undertaken.

The aim of the dissertation is clearly formulated and is targeted at studying the possible tautomerism and its effect(s) on the switching of nine model systems (organic molecules). To achieve this aim, three main tasks are clearly and precisely formulated: studies of the model systems by absorption UV-Vis spectroscopy and NMR in solution, and an explanation of the observed changes in the model systems undertaken on the basis of the quantum chemical calculations results.

The experimental part covers 10 pages: including a description of the synthesis of compounds 2.1-2.3 and 3.1-3.4 (numbering is according to the thesis), a brief data on their characterization (mostly NMR, mp yield), a description of the equipment used in spectral (UV-Vis, NMR) measurements and X-ray diffraction analysis, as well as brief data on the selected models, basis sets, corrections, approximations, etc. employed n the quantum chemical calculations.

The Results and Discussion section systematizes the data results obtained in the previous two chapter and is divided in two parts: III.1 Molecular Switching in Structurally Modified Sudan I (Compounds 2.x) and III.2 Molecular Rotary Switches (Compounds 3.x). Compounds 2.2-2.3 have been shown to exist as tautomeric mixtures in solution, and the author also shows that the equilibrium can be controlled by protonation / deprotonation of the hydroxyl group. For compound 3.1 the author concludes that the dye exists as a mixture of two isomers of one and only tautomer, which differs from Mahmudov et al. [137]. The quantum chemical calculations predict that the increase in the number of condensed aromatic nuclei e.g. imaginary compounds 3.5 and 3.6 does not significantly affect the studied equilibrium. The authors draw model for the rotary switches "E, E ', Z, Z'" in solutions that use of ^{2}J constants and makes it possible to distinguish each of the isomers, due to the formulation of a unique logical combination of ^{2}J constants.
The conclusions that are made and the indicated Contributions summarize the debate undertaken in the Results and discussion section and thus display that the PhD student Silvia Hristova has successfully dealt with all stages of the scientific work of the dissertation.
I have no general remarks on Silvia Hristova's dissertation, but it will be interesting to see the explanation of the use of the non so trivial determination of the "The exact position of the maxima" using second derivatives (absorption curves).

In conclusion, Silvia Hristova's dissertation deals with an interesting and current problem related to the study of the processes allowing the control of the stability and properties of molecular systems (at t molecular level). The scientific studies are conducted at a high experimental level using modern techniques, and the results are discussed critically and in depth. I believe that the presented dissertation, the accomplished and undertaken scientific work fully meets the volume, methodological level and number of publications in the scientific literature set out in the Statute for the conditions and procedures for the acquisition of scientific degrees in the Law for the development of the academic staff in the republic of Bulgaria" (LDASRB), the "Regulations for the application of the LDASRB" (RALDASRB) and the criteria of the Institute of Organic Chemistry with Centre of Phytochemistry - BAS.

Based on the above, I give my positive assessment and propose the Scientific Jury to award Sylvia Hr. Hristova the educational and scientific degree " Doctor of Philosophy" (PhD) the in professional field 4.2. "Chemical Sciences", doctoral program: Organic Chemistry.

Sofia, 30.07.2020 г.

prof. B. Shivachev, PhD