

OPINION

by Assoc. Prof. Dr. Stanimir Petrov Manolov

Faculty of Chemistry at University of Plovdiv „Paisii Hilendarski“,

on a dissertation for the award of the educational and scientific degree “**Doctor**”

in: field of higher education: **4. Natural Sciences, Mathematics and Informatics**

professional field: **4.2. Chemical Sciences**

doctoral program: **Analytical chemistry**

Author: Dimitar Genchev Stoitsov

Thesis theme: „NMR and vibrational spectra assignment for verification and elucidation of the structures of aromatic organic and metal-organic coordination compounds“

PhD Supervisors:

1. Prof. D.Sc. Plamen Nikolov Penchev – University of Plovdiv “Paisii Hilendarski”, Faculty of Chemistry, Department of Analytical Chemistry and Computer Chemistry.
2. Assoc. Prof. Dr. Marin Neykov Marinov – Agricultural University of Plovdiv, Faculty of Plant Protection and Agroecology, Department of Chemistry, Phytopharmacy, and Ecology and Environmental Protection.

1. General description of the submitted materials

By Order No. RD 22-1706 of 21.07.2025 of the Rector of Plovdiv University “Paisii Hilendarski” (PU), I was appointed as a member of the scientific jury to conduct the procedure for the defense of the dissertation entitled “*NMR and vibrational spectra assignment for verification and elucidation of the structures of aromatic organic and metal-organic coordination compounds*” for the acquisition of the educational and scientific degree “Doctor” in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional field 4.2. Chemical Sciences, doctoral program “Analytical Chemistry”. The author of the dissertation is Dimitar Genchev Stoitsov – a full-time PhD student at the Department of “Analytical Chemistry and Computer Chemistry”, supervised by Prof. D.Sc. Plamen Nikolov Penchev from University of Plovdiv “Paisii Hilendarski” and Assoc. Prof. Dr. Marin Neykov Marinov from the Agricultural University of Plovdiv.

The set of materials submitted by the PhD student Dimitar Stoitsov on electronic media complies with Art. 36 (1) of the Regulations for the Development of the Academic Staff of PU and includes all required documents. The PhD student has provided the dissertation, an abstract, and four publications in specialized journals indexed in the Web of Science and Scopus databases.

Dimitar Stoitsov was enrolled as a full-time PhD student on 01.03.2021, and as of 01.03.2025, he was discharged with the right to defend. During this period, he worked as an assistant at the Faculty of Chemistry of PU 'Paisii Hilendarski'."

2. Relevance of the topic

Research aimed at confirming and elucidating the structures of organic and organometallic compounds is of key importance for the development of modern chemistry. The synthesis of new substances with biological activity or with specific physicochemical properties inevitably requires reliable structural characterization. It is precisely here that spectral methods, and in particular NMR and vibrational spectroscopy (IR and Raman), are established as fundamental approaches to analysis.

The development of highly sensitive instrumentation and advanced methods for one-dimensional and two-dimensional NMR experiments, as well as the availability of computer software for spectral processing and simulation, have significantly expanded the possibilities for obtaining reliable information on molecular structure. Nevertheless, the literature still contains numerous organic and organometallic compounds for which the data are partially correlated, incomplete, or incorrectly interpreted.

The dissertation presents additional vibrational data for representatives of several classes of organic and coordination compounds, including newly synthesized ones. This not only facilitates their correct structural characterization but also contributes to the enrichment of databases used by the scientific community for comparative analysis and spectral prediction.

In the context of contemporary science, where the synthesis of new pharmaceuticals, catalysts, and functional materials is based on in-depth knowledge of molecular structure, the subject of the dissertation is fully relevant and of high practical value

3. Knowing the problem

The author demonstrates in-depth knowledge of the existing problems in the field, noting that the isolated interpretation of only one type of spectra (e.g., solely 1D NMR or only vibrational spectra) is often insufficient for reliable structural determination. The dissertation provides a detailed review of one-dimensional and two-dimensional NMR methods (^1H , ^{13}C , COSY, HSQC, HMBC, NOESY, etc.), as well as vibrational spectroscopy (IR and Raman), clarifying their advantages, limitations, and applicability to different classes of organic and coordination compounds.

The understanding of the problem is further reflected in the critical analysis of existing databases and software tools for spectral simulation and interpretation. The necessity of providing fully assigned NMR data for new or rarely studied structures is emphasized, as such data support not only specific structural characterization but also the development of global reference resources.

The review also summarizes the main classes of compounds included in the dissertation, among them fluorenylspirohydantoins, naphthopyranones, pyrimidine complexes of Au(III) and Cu(II), dispiroimidazolidines, *N*-phenyl-2-(2,2,2-trichloroacetamido)benzamides, and 1H-benzo[*d*]isoquinoline-1,3(2H)-diones. In addition, the application of specialized NMR software for assisting in the confirmation and elucidation of these organic structures is examined, which facilitates interpretation and increases the accuracy of the analysis.

The use of 157 literature sources, 36% of which are from the last 10 years, demonstrates the good level of literature awareness of PhD student Stoitsov

4. Research methodology

The research methodology has been developed with a high degree of precision and clarity, providing a detailed description of the instrumentation used, the working conditions, and the techniques applied for the registration of spectral data. Dimitar Stoitsov ensured the reproducibility and reliability of the results through strictly defined parameters for the measurement of IR, Raman, and NMR spectra, as well as by applying standardized procedures and appropriate internal and external standards.

The inclusion of various methods—FT-IR, ATR, Raman, 1D and 2D NMR, solid-state CP-MAS techniques, and atomic spectral analyses—demonstrates a comprehensive and interdisciplinary approach to the studied compounds and their complexes. This wide range of experimental methods provides high analytical value to the dissertation and guarantees the objectivity and validity of the obtained results.

5. Characteristics and Evaluation of the Dissertation and Its Contributions

The dissertation has been prepared at a high scientific level, with a volume of 144 pages, and includes the following main sections: Introduction (8 pages), Section 1: Literature Review (31 pages), Section 2: Materials and Methods (3 pages), Section 3: Results from Spectral Correlations (75 pages), Conclusion (2 pages), Scientific and Applied Contributions (1 page), List of Publications on the Topic (1 page), and References (11 pages).

The main contributions of the dissertation can be summarized as follows:

1. Contribution to the enrichment of scientific literature through the provision of fully assigned NMR data and partially assigned vibrational spectral data for various classes of organic compounds;
2. Correction of inaccuracies in previously published and assigned NMR data for four organic structures included in the dissertation;
3. Contribution to the enrichment of the NMRShiftDB database through the introduction of the structures of fluorenylspirohydantoins and naphthopyranones, as well as part of the assigned ¹H and ¹³C NMR data for them.

6. Assessment of the Publications and the PhD Student's Personal Contribution

The list of scientific publications by Dimitar Stoitsov related to the dissertation includes a total of four articles. Of these, three are refereed and indexed in the *Web of Science* and *Scopus* databases, while one publication is indexed only in *Scopus*. Two of the publications appear in journals with quartile **Q2** – *Applied Sciences* (IF = 2.5) and *Crystals* (IF = 2.4), while the remaining two are in journals with quartile **Q4** – *Molbank* (IF = 0.4) and *Bulgarian Chemical Communications* (without an impact factor).

The individual contribution of Dimitar Stoitsov is clearly traceable: in two of the publications he is listed as first author, and in the other two as second author. This indicates his substantial involvement in both the preparation and the composition of the works. The publications were produced in 2024 and reflect the content and scientific contribution of the dissertation. At present, no independent citations of the publications have been recorded, which is understandable given their relative novelty and recent publication.

The publication activity of the PhD student fully complies with the regulatory requirements for obtaining the educational and scientific degree of “Doctor”. The minimum national criteria, as well as the minimum requirements outlined in the Regulations of Plovdiv University for the Development of the Academic Staff (RAS), are not only met but significantly exceeded. The PhD student has presented four publications in refereed and indexed journals with quartiles **Q2** and **Q4** (62 points, compared to the required 30).

7. Abstract (Short thesis)

The shortened version of the PhD thesis (34 pages) is fully consistent with the content of the dissertation and represents a synthesized version reflecting its essence. It presents the obtained results in a complete and reliable manner, along with their analytical review. The abstract has also been prepared in English in a corresponding volume (34 pages).

8. Recommendations for future use of the dissertation contributions and results

The presented dissertation contains a sufficiently extensive and scientifically substantiated research material, developed in full accordance with established academic standards and requirements for this type of work. I find no grounds for critical remarks or significant recommendations regarding the conducted research and the manner in which the results are presented. The scientific contribution is indisputable, and the exposition demonstrates a high degree of competence and methodological rigor. I recommend that the PhD student continue to develop his research activities in the field with the same determination, consistency, and professionalism.

CONCLUSION

The dissertation contains scientific and applied-scientific results that constitute an original contribution to science. In terms of its volume and the number of publications produced, it fully meets all the requirements of the Law on the Development of the Academic Staff in the Republic of

Bulgaria (LDASRB), the Regulations for the Implementation of LDASRB, and the Regulations of University of Plovdiv “Paisii Hilendarski”.

The research convincingly demonstrates that PhD student Dimitar Genchev Stoitsov possesses in-depth theoretical knowledge and the necessary professional competence within the framework of the doctoral program “Analytical Chemistry”. The work showcases his ability to conduct independent and methodologically sound scientific research, which is indicative of his development as a mature researcher.

For the reasons stated above, I confidently give my **positive** evaluation of the conducted research and **recommend to the esteemed scientific jury to award the educational and scientific degree of “Doctor”** to Dimitar Genchev Stoitsov in the field of higher education: 4. Natural Sciences, Mathematics and Informatics, professional field 4.2. Chemical Sciences, doctoral program “Analytical Chemistry”.

25.09.2025

Reviewer:

(signature)

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Assoc. Prof. Stanimir Manolov, PhD